Abstract

Accurate knowledge of aerosol size and composition is important for the understanding of their effects on both the atmosphere and the health of those who inhale them. Ultrafine aerosols (0.25 nm to 10 nm radius) and small clusters (2 molecules to 0.25 nm radius) can only be detected down to radii of a few nanometers and no chemical information is provided. A photoion spectrometer was previously built and is used to dope clusters and ultrafine aerosols with Na atoms. The subsequent Na-cluster complexes are then ionized by a UV laser. This technique is currently believed to be the softest ionization method available. Calculations were done to predict the efficiency of this system because a direct comparison with other systems cannot be made over the complete size range. These calculations include, the probability of a particle colliding with a Na atom in the oven, the average lifetime of Na-cluster complexes and their photoionization efficiency. Calculations in this thesis focus on the collision probability and include predictions as to the most efficient temperature of the Na oven for Na pick up. The temperature of the Na oven was also found to experimentally agree with the calculations, because the vapor pressure of Na plays a significant role in the collision probability. Characterization of the sodium doping technique was done through experiments comparing direct XUV ionization with UV ionization of small Na doped clusters. The fragmentation of acetic acid clusters was characterized for the monomer and oligomers up to the tetramer. It was found that up to two acetic acid molecules evaporated from the clusters. The Na doping technique also reveals a significant difference in the size distribution as seen by UV and XUV laser ionization for large dimethyl ether and acetic acid clusters, and a smaller yet
visible difference for large water clusters. Different UV wavelengths were also investigated including wavelengths above and below the ionization energy of a lone Na atom. The Na doping technique was found to be a softer technique than direct ionization with XUV light, because no fragmentation of molecules occurred and evaporation was minimized.
Preface

Portions of Chapter 3 and Section 4.1.1 were published in P. W. Forysinski, P. Zielke, D. Luckhaus, J. Corbett, and R. Signorell, “Photoionization of small sodium-doped acetic acid clusters” The Journal of Chemical Physics 134, 094314 (2011) [1]. My contribution to this publication was calculations of Na collision probabilities and, with Piotr Forysinski and Dr. Philipp Zielke, the collection and analysis of data. Dr. David Luckhaus calculated average lifetimes of the Na-cluster complexes. Piotr Forysinski and Dr. Ruth Signorell wrote the manuscript.

Portions of Section 3.1.3 and Chapter 4, excluding Section 4.1.1, are published in B. L. Yoder, J. H. Litman, P. W. Forysinski, J. L. Corbett, and R. Signorell, “Sizer for Neutral Weakly Bound Ultrafine Aerosol Particles Based on Sodium Doping and Mass Spectrometric Detection” Journal of Physical Chemistry Letters 2, 2623-2628 (2011) [2]. My contributions included the calculation of Na collision probabilities and data collection. Dr. Bruce Yoder, Piotr Forysinski, Jessica Litman and I collected the data. Dr. Ruth Signorell designed the research and wrote the manuscript.
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Dedication

To Mom, Dad and Andrew, your support made this possible.

Phil 4:13
Chapter 1 Introduction

1.1 Motivation

Aerosols play many significant roles in Earth’s atmosphere including cloud formation, smog and counteracting global warming [3]. They affect human health as well, because ultrafine aerosols are able to penetrate deeper into the lungs than larger aerosols [4]. Accurate detection of aerosol size and composition is important in furthering the understanding of both chemical processes in the atmosphere and side effects on the health of those exposed to them. The current understanding of aerosols and the processes involved in nucleation (i.e. the formation of aerosols from the gas phase) is limited by the detection limits of analytical instrumentation. In order to be able to achieve better understanding in these areas, reliable size detection of aerosols will need to be extended down in size to ultrafine aerosol particles (0.25 nm to 10 nm radius) and clusters (2 molecules to 0.25 nm radius). In addition to this, knowledge of their chemical makeup will be needed. If both of these goals can be accomplished, it may lead to studies able to further the current understanding of the role of aerosols in the environment [5].

Knowledge of the size of aerosol particles is important for several reasons. Different sizes affect light scattering differently, and vary in their contributions to preventing global warming [4,6]. Particle size also has a great effect on whether or not it is deposited into one’s respiratory tract. In addition to this, being able to detect a wide range of cluster sizes, including those down to a few molecules is important for studying nucleation [5,7,8]. For example, Kulmala et al. used a variety of techniques and were able to infer that there were neutral particles which they were unable to measure directly, that had contributed to the formation of larger aerosols which they were able to measure [8].

The composition of aerosol particles is an important piece of information that can lead to a deeper understanding of their effects in the atmosphere. In addition to this, if the chemical composition of aerosol particles is known, it may be possible to detect key molecules in the nucleation process and further the understanding of their contribution to the nucleation process [8].
There are many different techniques which have been developed in order to detect aerosols [6,8–13]. Instruments that can in principle measure the size of volatile clusters and ultrafine aerosols include elastic scattering, Rayleigh scattering, infrared spectroscopy, core-level photoelectron spectroscopy, electron and neutron diffraction, scanning mobility particle sizers (SMPS) and mass spectrometry (MS) [8,10,14–36]. Aerosols with \( r \geq 100 \) nm can be easily detected through these methods and many research groups are working to extend lower detection limits [10,11,27,28]. It is the ultrafine aerosols with sizes with radii below 20 nm which prove to be much more difficult to measure, which is particularly true for weakly bound aerosols. All of the aforementioned detection methods, except SMPS and MS, yield only average cluster size or need large scale facilities. Because of this, only SMPS and MS are discussed.

SMPS and condensation particle counters (CPC) are able to give two pieces of information on the particles that they analyze. The first is the particles size and the second is the concentration of particles. These systems measure so-called particle number size concentrations. In the SMPS, the particles are separated according to their mass by a differential mobility analyzer. After this, a CPC is used to determine the number of the particles [37]. CPC is able to detect aerosols by condensing a vapor such as butanol onto the particles to increase their size to the point where they can be detected via light scattering [37,38]. Commercial CPCs can detect particles with a diameter as small as 2.5 nm [39]. However, because it uses condensation to increase the particle diameter, it is unable to yield further information on the chemical makeup of the particle. The major disadvantage of the SMPS/CPC system is that it is limited to non-volatile aerosols. Weakly-bound systems simply evaporate during the detection.

Mass spectrometry is, in principle, able to provide information on particle size and, through the exact mass, a chemical composition. “The ideal aerosol mass spectrometer should be capable of determining the size of an individual aerosol particle, and provide a quantitative measure of each of its molecular constituents in real time” [4]. Nash et al. explained that this is a particularly difficult achievement since an accurate size distribution is needed as well as knowing whether it is a homogenous mixture of heterogeneous particles or if it is heterogeneous mixture of homogenous particles [4]. One of the main difficulties with mass spectrometers is the harsh conditions caused by ionization. Ionization techniques may cause changes to clusters, either
changing the size distribution (through evaporation) or original molecular composition (through chemical reactions within the cluster).

Common techniques used to ionize weakly-bound large clusters include electron ionization (EI), resonance enhanced multi-photon ionization (REMPI), and pulsed laser ionization using extreme ultraviolet (XUV) [4,18,31,40,41]. Electron ionization is a commonly used technique. However it is usually a very harsh technique because high energies (typically ~ 70 eV) are often used [41]. An alternative to this is REMPI; however this does not necessarily ionize different types of clusters with equal efficiency, may have multi-photon processes contributing to fragmentation, and is not broadly applicable to clusters [4,18]. Another alternative is single photon ionization. The XUV used for this must be at or near the ionization energy (IE) of a cluster to reduce the chance of fragmentation by limiting the excess energy put into the cluster. XUV can be produced by 4-wave mixing and tuned to be close to the IE of a cluster. Even though this is a much softer ionization technique than EI, it can still cause a significant of fragmentation because bonds may be broken once ionization occurs. If this happens, excess energy may be available to evaporate additional molecules from the cluster.

There are two major problems with these ionization techniques if applied to weakly-bound clusters. The first is that the chemical composition of the original cluster is lost if any chemical changes occur after ionization. The second is that the cluster distribution will be misrepresented due to evaporation. These challenges in cluster detection could be addressed by the addition of a sodium atom to each cluster (termed sodium doping). This allows ionization to occur with a (single) less energetic photon, which lies in the ultraviolet range (UV). Side reactions should be prevented because the IE of Na is much lower than the IE of the other atoms or molecules within the cluster. Less excess energy should be present, thus preventing large portions of the cluster from evaporating. There is still some evaporation of monomer units from the cluster, but, this should be negligible for all but the smallest clusters (i.e. n ≤ 10), in comparison to the overall cluster size.

A photoion spectrometer with a sodium oven was built previously in this group. This was designed to provide both chemical information and an accurate size distribution from an
individual molecule up to 10 nm. A Na oven was included in the experimental setup in order to add a single sodium atom to each cluster. The molecular beam was passed through the Na oven in order for each cluster to pick up a single Na atom. Subsequent UV ionization should be softer than other “soft” ionization techniques.

1.2 State of the Field

It has been shown in the literature that the sodium doping technique is effective for the study of electron solvation. The doping of clusters has been utilized in research groups such as the Buck group [18,25,31,42–59]. The Buck and Hertel groups have used this to study solvation by studying very small clusters to increasingly large clusters. This has led to information on the IE of Na doped clusters as well as research regarding the vibrational modes of these clusters ([42,44,60]). MS and IR spectroscopy were employed and theoretical studies were used to compliment them [43,45,49,51,55,57]. The IE of doped clusters have been found for NH₃, H₂O and MeOH as a function of size. It was found that the ionization energy decreased as the cluster size increased [43,49,51,55,57]. This shows that there is potential for further reduction of excess energy after ionization by using a laser with an energy which is lower than the IE of a single Na atom.

Evaporation was found to be a problem when noble gas clusters were ionized with electron ionization. It was found by the Buck group, for example, that for Xe₁₀₂₈₀ up to 8560 Xe atoms could evaporate from it [18,31]. This has significant implications for the detection of clusters because only 1/5th of the cluster would have been detected. Evaporation must be minimized to produce an accurate size distribution. In addition to evaporation of molecules from a cluster, chemical reactions are likely to occur at the site of the localized charges [18]. Many clusters are known to fragment in specific patterns. Fragmentation can be seen in H-bonded systems often appearing as protonated molecules within a cluster [18,41]. This could be seen in research from our own group with acetic acid [1,61].

Vaporization of sodium for doping can be accomplished either through laser ablation [54,62] or by melting sodium metal in a Na oven to produce the desired vapor pressure. The Na can then be added to the clusters through crossed beam experiments [63–65], or by passing molecular beams
through the Na oven [46,51]. Research has been carried out, not only with sodium but with a variety of different metals from the alkali group [51–54]. Sodium was chosen for use in the oven because it has both a low IE, 5.14 eV, and melting point, 371 K, [66]. This approach was employed in the current work. It was originally designed by Scoles [67] and has been utilized by the Buck group [18,43,46], as well as in this group [1].

Electron ionization, multi photon and single photon ionization techniques have been used to ionize clusters in molecular beams. The Buck group has done both experimental and theoretical research into the fragmentation of clusters. It was found that EI produced strong fragmentation compared to the Na doping technique [18]. Using REMPI to ionize clusters also led to fragmentation. In addition to this, REMPI was not found to be an ideal ionization technique due to the rapid decay of the excited states [18]. In order to prevent the excited states from decaying before the cluster can be ionized, single photons were used to ionize the clusters [18].

Evaporation may still occur with doped clusters. For example, the IE of the bulk very large ammonia clusters doped with Na is 3.2 eV [55]. Excess energy of ~ 1 eV (or less) from single photon ionization with UV laser radiation may potentially cause fragmentation (in the form of evaporation) because this is comparable to the binding energy between Na and NH$_3$ [55]. While this potential to fragment still exists, it should not be as problematic as 25 eV or more used in electron ionization experiments [18] (see Section 4.1.1).

1.3 Overview of Thesis

It is the purpose of this Master’s thesis to show that the Na doping technique allows the TOF-MS to detect weakly-bound molecular aggregates from small cluster (dimer, trimer, etc.) up to ultrafine aerosol particles (with sizes of about 10 nm).

This is accomplished through a combination of experiments and calculations. Calculations at each stage of the molecular beam’s path to the multichannel plate detector (MCP) are required to achieve a qualitative understanding of the behavior of the sizer (Chapter 3). The steps include the following: collisions with sodium inside the Na oven (Na capture, see Section 3.1), decay time of the Na-cluster complex (see Section 3.2), photoionization of the clusters-complexes (see Section
3.3), fragmentation after photoionization, and ion detection efficiency at the MCP. The calculations presented in this thesis focus on the collision cross sections of four different types of clusters. These are ammonia, water, carbon dioxide and acetic acid. The molecules were chosen because they span a variety of molecular properties. They represent both volatile and semi-volatile clusters, and are held together by forces of varying strength, from Van der Waals forces to hydrogen-bonding. The uncertainties of these calculations are also presented, and the effects of choosing the vapor pressure of Na by varying the oven temperature are discussed.

Two different models were used for the collision cross section calculations, the hard sphere (HS) model (using the geometric cross section) and the Langevin (L) model which incorporates long range intermolecular interactions into the cross section. This was done because single molecules interact with other atoms or molecules through long range interactions. Large clusters and aerosol particles, on the other hand, interact with other clusters, atoms or molecules on a level that can be described (sufficiently) accurately through their geometric size. By modeling cross sections with both these methods, it can be seen more accurately above what size intermolecular interactions can be ignored and the simpler HS model can be employed successfully.

In addition to calculations, experiments were performed on a variety of clusters including acetic acid, ammonia, water and dimethyl ether. The variety of neutral clusters which can be detected is also shown to include both volatile and semi-volatile clusters. The fragmentation process of small doped acetic acid clusters is investigated (see Section 4.1.1). The fragmentation processes of larger clusters were not studied because too many species are present in the spectra. However, it is shown through investigating large clusters, that the Na doped clusters can be detected, and cause less fragmentation than even the softest ionization methods (i.e. XUV single photon ionization); and the size range of cluster detection is demonstrated in the case of ammonia clusters (see Section 4.1.2). The effects of different experimental temperatures for the Na oven are also investigated (see Section 4.3).
Chapter 2 Experimental

A home-built ion mass spectrometer with a tunable laser light source (800 nm to 67.5 nm) equipped with a sodium oven was employed in the studies presented in this thesis. It has been previously used to study the ionization energies and vibrational dynamics of CH$_2$F$_2$ [13,18,19,42–45,48,50,68–73] and acetic acid [1,61]. It was also used in the experimental work to ionize both doped (using UV) and undoped (using XUV) clusters in order to characterize the Na-doping technique. The optical set up in these studies was able to produce laser radiation with wavelengths that could ionize clusters with minimal excess energy to prevent fragmentation. The range of wavelengths necessary to ionize many different cluster types would have been cumbersome, because only a few types of molecules could be ionized at a time without fragmentation and chemical reactions occurring once ionized. In order to look at a variety of molecules with a single wavelength, a Na oven was added to dope clusters with a single Na atom. This was expected to reduce fragmentation of the clusters to the point where it was negligible [19] as well as prevent chemical reactions as the molecules themselves would no longer be ionized, thus allowing the whole doped cluster to be detected by the MS.

The Na atom reduces the ionization energy of the cluster and should allow for ionization with photo-energies in a relatively narrow range just below 5 eV. To produce photons near the IE of the doped clusters, a UV laser at 266 nm was used (See Section 2.2.2). A tunable dye laser was also used to provide flexibility in the energy used for ionization (See Section 2.2.2), as some clusters may still have a higher IE than 4.7 eV (266 nm). Tunable extreme ultraviolet (XUV) light was used for direct ionization of undoped clusters for comparison (See Section 2.2.1).

2.1 Ion Mass Spectrometer with Sodium Oven

The molecular beam machine used in the experiments consisted of a series of three differentially pumped vacuum chambers, as shown in Figure 2.1. These are the sample injection chamber, the Na oven chamber and the TOF chamber. Two additional vacuum chambers necessary for XUV-light generation are attached to these. The 4-wave mixing chamber and the grating chamber are further described in Section 2.2.
Clusters were made by pulsed supersonic expansion of sample gases into the sample injection chamber, shown in Figure 2.1. The cylinder containing the gas (or sample cylinder, see Section 2.3) was attached to the sample nozzle. Clusters were made from the supersonic expansion of sample gas(es) by pulsing a temperature controlled nozzle (General Valve, Series 9) at a 10 Hz repetition rate with a 400 - 700 µs opening time. The nozzle orifice used in the experiments was typically 250 µm in diameter (various sizes from 100 µm to 1000 µm were also available and used on occasion). Teflon or Kapton poppets (Parker Hannifin Corporation) were used. Both materials were chosen for their chemical inertness. Kapton was used because it was more stable at low temperatures. The nozzle was cooled by a Lauda Proline RP 1290 chiller using octamethyltrisiloxane (ABRC) for the bath liquid, which are efficient down to 193 K. Cooling
the nozzle allowed various degrees of saturation of the gases to be used in forming clusters. The degree of saturation was further controlled by changing the sample backing pressure which was controlled through regulators on the gas and sample cylinders.

After exiting the nozzle, the molecular beam passes through a 1mm skimmer (Beam Dynamics, Model 2) before entering the Na oven. Inside the Na oven, the molecular beam passes through Na vapor and individual clusters pick up a single Na atom. The Na oven is similar in design to those in references [1,14,72,74–85]. The path length through the Na oven is 44 mm. The Na oven is heated by heating coils at the bottom and the top of the oven as shown in Figure 2.2. The bottom contains Na metal and is typically heated to between 473 K and 498 K (See Section 3.1.3 and 4.3 for further details). This temperature melts the Na metal (mp = 371 K [77]), and its vapor pressure is sufficient to allow clusters to be doped with a single Na atom. A negligible number of clusters are double doped. The top is typically heated to 413 K keeping Na in the liquid state in order to return to the reservoir in the bottom of the oven and minimize Na sticking on the wall of the oven.

Figure 2.2 The sodium oven contains Na in the bottom and is heated by coils to 498 K. There are coils on the top as well which are heated to 413 K, in order to prevent Na from solidifying on the top of the oven.
After picking up Na, the clusters in the molecular beam are photoionized by the laser. This takes place 80 mm downstream from the Na oven, in the extraction region of the linear TOF-MS. See Section 2.2 for further details on UV and XUV light used for photoionization. Once ionized, the clusters are extracted in a Wiley-McLaren type arrangement using a DC voltage either at 1.5kV (initial experiments) or at 4.5 kV (later experiments). Three metal plates are separately charged to accelerate the ions. A Wiley-McLaren set up limited to a total extraction voltage of 1.5 kV was employed, but could be configured to a single uniform field extraction which allowed the use of higher voltages (up to 4.5 kV).

The ionized clustered are detected by two micro channel plates (MCP) stacked in chevron configuration (Photonis). The potential difference between the front and back MCPs was 2500 V, unless otherwise specified. The front MCP was set to -2500 V in order to detect positive ions and the back of the MCP was ground (0 V). The anode was set to -200 V, and the signal was collected by a 500 MHz oscilloscope (LeCroy Waverunner).

The timing of the experiment was controlled by 2 four channel delay / pulse generators (Stanford Research Systems Inc., Model DG535). The timing scheme for adjusting the positions within the molecular beam which is to be probe is shown in Figure 2.3. The nozzle was opened at a delay (Figure 2.3 a) which was adjusted according to the position in the molecular expansion which was to be probed. This allowed cluster sizes to be capped at a particular maximum cluster size or maximized as necessary (Figure 2.3 c-e). After a further delay the q-switch was triggered. This sent the laser pulse into the molecular beam. Figure 2.3 c-e illustrates the effect of adjusting the nozzle delay of the laser pulse relative to t = 0. Longer delays for the nozzle (Figure 2.3 c) corresponded to ionizing clusters closer to the beginning of the expansion because the q-switch delay was fixed relative to t = 0. Shortening the nozzle delay resulted in probing the molecular beam closer to the middle (Figure 2.3 d) or end (Figure 2.3 e) of the expansion. At shorter delays the molecular beam will travel further before the laser pulse is fired, allowing the end of the expansion to be sampled.
Figure 2.3 Timing delay scheme for the opening of the nozzle and the firing of the laser. a: neither nozzle nor laser has fired. B: the nozzle opens and the molecular expansion occurs. c-e: then the q-switch on the laser is triggered and the laser pulse ionizes the molecular beam. Where in the molecular expansion will be probed depends on the delay time for the nozzle opening: c: long delay, d: medium delay and e: short delay.

The sample chamber, Na-oven chamber and TOF chamber as well as the 4-wave mixing chamber and the grating chamber are kept under high vacuum. The vacuum chambers are pumped by turbomolecular vacuum pumps which are backed by either by a scroll vacuum pump (Anest Iwata ISP500) or a dry compressing vacuum pump (Pfeiffer OnTool DryPump). The 4-wave mixing chamber is pumped by a Pfeiffer 521 turbomolecular vacuum pump and had a background pressure of $1 \times 10^{-7}$ mbar and a working pressure of $1 \times 10^{-4}$ mbar when the noble gas nozzle was operating. The grating chamber was pumped with a Leybold TW300 turbomolecular vacuum pump and has a background pressure of $2 \times 10^{-8}$ mbar and a working pressure of $3 \times 10^{-7}$ mbar. The sample injection chamber is pumped with a Pfeiffer 2301 turbomolecular vacuum pump to a background pressure of $8 \times 10^{-7}$ mbar. This increased in pressure ranging from $3 \times 10^{-6}$ mbar to $1 \times 10^{-3}$ mbar when the injection nozzle is turned on, and is dependent upon the gas sample used, backing pressure of the gas sample, nozzle diameter and the nozzle temperature. The Na oven is pumped by a Pfeiffer 1201 turbomolecular vacuum pump and the background pressure is $5 \times 10^{-8}$ when the oven was off, and about $6 \times 10^{-8}$ mbar when the Na oven and sample nozzle are on. The TOF chamber is pumped by a Pfeiffer 521 turbomolecular pump had a background pressure of $1 \times 10^{-8}$ mbar and a pressure of $3 \times 10^{-8}$ mbar when the sample nozzle is on.
2.2 Photoionization

2.2.1 Extreme Ultraviolet Photoionization

To compare the Na-doping method with direct ionization methods, extreme ultraviolet light (XUV) with energy sufficient to ionize undoped clusters was used. For small acetic acid clusters up to the octamer \([85]\), XUV light was used to probe the original cluster distribution in the molecular beam. This was possible for small acetic acid clusters because UV fragmentation patterns of these cluster are known \([81,85]\). For the large clusters/ultrafine aerosol particles in Section 4.1.2, XUV light is used for direct ionization of undoped clusters, which allows a comparison to be made between the Na-doping method and direct XUV ionization. Undoped clusters generally need to be ionized with a laser capable of producing XUV wavelengths of 136 nm (9 eV) or more. To ensure that all clusters were ionized, 74.2 nm was used, which is 16.7 eV, \(\sim 6\) eV higher than the IE of acetic acid.

Tunable XUV light with energies up to 17 eV was produced through 2-photon resonance-enhanced 4-wave mixing of light from two dye lasers (both Sirah Cobra Stretch SL) in a rare gas jet, according to Equation 2.1.

\[
2\nu_1 \pm \nu_2 = \nu_{\text{XUV}}
\]  

(2.1)

Both dye lasers (laser 1 and laser 2) were pumped by a Nd:YAG laser and a beam splitter was used to split the 532 nm light into each dye laser, as shown in. Dye laser 1 is kept at a constant wavelength which is then frequency tripled \((\nu_1')\) using a second harmonic generation crystal (SHG) and a third harmonic generation crystal (THG), as shown in Figure 2.4. For example, light of 666 nm wavelength was produced by using 100 mg L\(^{-1}\) DCM (Exciton) in dimethyl sulfoxide (Fisher Scientific, ACS) in the dye laser. This was then frequency doubled using a SHG crystal (Inrad, BBO) to produce 333 nm. A THG crystal (Inrad, BBO) then combines one photon of 666 nm and one of 333 nm to produce \(\nu_1 = 222\) nm. Before entering the 4-wave mixing chamber, the light passes through two harmonic separators (CVI Melles Griot) that reflect the 222 nm and allow the other wavelengths to pass through into beam blocks. The \(\nu_2\) light was produced by the second dye laser, dye laser 2, by frequency doubling in a SHG crystal.
\( \nu_1 \) and \( \nu_2 \) were then overlaid using one of the harmonic separators (dichroic mirrors) and focused onto a Xe gas beam (Spectra Gasses Inc.) in the 4-wave mixing chamber. The two \( \nu_1 \) photons match the 89860.038 cm\(^{-1}\) two-photon resonance in Xe (111 nm). Several 4-wave mixing processes generating XUV are possible in the xenon expansion, as illustrated in Figure 2.5. \( \nu_1 \) could also be used instead of \( \nu_2 \) light to produce \( \nu_{XUV} = 3\nu_1 = 74.2 \text{ nm} \) which is not tunable. A toroidal diffraction grating (Horiba Jobin-Yvon) was used to separate different XUV wavelengths. It can be rotated such that only the desired wavelength enters the TOF chamber (through a pinhole) into the extractor to photoionize clusters. Table 2.1 shows the resonances available to be used the 4-wave mixing process from both Xe and Kr and the range of XUV wavelengths which can be produced. Because the lasers were tunable, the wavelength could be adjusted to produces the \( \nu_1 \) wavelength necessary for the desired resonance, in either Xe or Kr. Typically, the upper Xe or lower Kr resonances were used in the experiments.

<table>
<thead>
<tr>
<th>2-photon resonance /cm(^{-1})</th>
<th>( 2\nu_1 + \nu_2 )</th>
<th>( 2\nu_1 - \nu_2 )</th>
<th>( 3\nu_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr 98855.071</td>
<td>69.3 - 89.8 nm</td>
<td>115.8 - 187.3 nm</td>
<td>67.5 nm</td>
</tr>
<tr>
<td>144310 - 111355 cm(^{-1})</td>
<td>86356 - 53401 cm(^{-1})</td>
<td>148283 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>17.9 - 13.8 eV</td>
<td>6.6 - 10.7 eV</td>
<td>18.4 eV</td>
<td></td>
</tr>
<tr>
<td>14092.862</td>
<td>71.7 - 93.8 nm</td>
<td>122.6 - 205.6 nm</td>
<td>70.9 nm</td>
</tr>
<tr>
<td>139547 - 106593 cm(^{-1})</td>
<td>81593 - 48638 cm(^{-1})</td>
<td>141139 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>17.3 - 13.2 eV</td>
<td>6.0 - 10.1 eV</td>
<td>17.5 eV</td>
<td></td>
</tr>
<tr>
<td>Xe 89860.038</td>
<td>73.9 - 97.7 nm</td>
<td>129.3 - 225.2 nm</td>
<td>74.2 nm</td>
</tr>
<tr>
<td>135315 - 102360 cm(^{-1})</td>
<td>77360 - 44405 cm(^{-1})</td>
<td>134790 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>16.8 - 12.7 eV</td>
<td>5.5 - 9.6 eV</td>
<td>16.7 eV</td>
<td></td>
</tr>
<tr>
<td>Xe 80118.974</td>
<td>79.6 - 108.0 nm</td>
<td>147.9 - 288.5 nm</td>
<td>83.2 nm</td>
</tr>
<tr>
<td>125574 - 92619 cm(^{-1})</td>
<td>67619 - 34664 cm(^{-1})</td>
<td>120179 cm(^{-1})</td>
<td></td>
</tr>
<tr>
<td>15.6 - 11.5 eV</td>
<td>4.3 - 8.4 eV</td>
<td>14.9 eV</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1 2-Photon resonances which can be used to generate XUV light using Kr or Xe. The higher energy Xe and lower energy Kr resonances were used to generate XUV for the experiments in this work.

The laser light enters through the side of the TOF chamber, passes through the molecular beam before hitting the electron multiplier tube (Hamamatsu, R5150-10) used as an XUV detector.
The detector is turned off when collecting spectra to prevent damage to the detector and to prevent electron ionization caused by electrons that could be formed on the detector surface. However, this detector allows the relative intensity of the XUV light to be known before running an experiment.

![Laser Scheme Diagram](image)

Figure 2.4 Laser Scheme. Nd:YAG pump laser produces 1064 nm light which is doubled to 532 nm, this passes through a beam splitter and powers dye laser 1 and dye laser 2. The light from laser 1 was tripled to match the resonance in a rare gas before being directed into the 4-wave mixing chamber ($\nu_1$). The light from laser 2 was doubled before entering the 4-wave mixing chamber. The diffraction grating could be rotated to select from one of the following processes: $3\nu_1$, $2\nu_1 + \nu_2$, $2\nu_1 - \nu_2$ or $\nu_2$.

![2-photon resonance Diagram](image)

Figure 2.5 2-photon resonance enhanced 4-wave mixing (difference frequency mixing and sum frequency mixing).
2.2.2 Ultraviolet Photoionization

Minimal fragmentation of clusters is achieved by doping them with a single Na atom and subsequently ionizing the Na atom with a UV photon. A lone Na atom ionizes at 5.14 eV, thus a laser with a wavelength equal or greater than 241 nm (5.14 eV) should be sufficient for all clusters to be ionized [85].

A pulsed Nd:YAG laser (Quantel ultra 50) with the wavelength at the 4th harmonic, 266 nm (4.66 eV), was used to ionize Na-doped clusters. It typically had a power of ~8.0mJ/pulse with the pulse width ~10 ns and repetition rate of 10 Hz. This light was directed through the bottom of the TOF chamber, into the extractor and passed through the molecular beam before exiting the chamber though a window at the top of the chamber. The laser does not hit any metal within the chamber, which could lead to generation of electrons and consequently to electron ionization.

A tunable dye laser (Sirah Cobra Stretch SL) was used in addition to the Quantel. This was done because the Quantel laser produces laser radiation with a fixed energy of 4.66 eV (266 nm) which is lower than the 5.14 eV (241 nm) necessary to ionize a bare Na atom. It is possible that some clusters have an IE between 266 nm and 241 nm. With the tunable laser, this energy range can be accessed, ionizing clusters which could not be with the Quantel laser, because of the greater flexibility in the tunable laser wavelength. The tunable dye laser was pumped by the frequency doubled light from a Nd:YAG laser (Continuum PR 9010). The laser radiation at 532 nm was typically used at intensities of ~100 mJ / pulse after a 50/50 unpolarized beam splitter. For the acetic acid experiments, the dye used in the dye laser was 160 mg L\(^{-1}\) Pyrromethene 597 (Exciton) in methanol (Fisher Scientific, HPLC grade). It lased between 566 nm and 611 nm with a peak at 582 in ethanol [86]. The lasing wavelength range should be the similar in methanol (with a small red shift). The dye laser output was frequency doubled to typically between 288 nm and 301 nm for the acetic acid experiments. This laser light then passes through the 4-wave mixing chamber and the grating chamber (grating is set to its 0\(^{th}\) order to act as simple reflector) where it is directed into the extractor. When operating the setup for the use of tunable UV light, the noble gas nozzle is turned off.
2.3 Gas Samples

Several different gases were used to form weakly-bound clusters and ultrafine aerosols. Neat dimethyl ether (Praxair, 2.5) was used at backing pressures up to 5 bar absolute, its vapor pressure at room temperature. Neat anhydrous NH₃ (Praxair, 4.5) was used from the compressed gas cylinder, using a regulator (Matheson) for backing pressures 1 bar abs. and above. To form clusters with a lower NH₃ pressure but maintaining a high backing pressure, 0.5 bar NH₃ was also mixed with 9.5 bar He (Praxair, 5.0) in a sample cylinder (Swagelok, 2.25L). The mixture was allowed several hours up to several days to equilibrate.

Acetic Acid and ether gas samples were prepared from liquid samples. Acetic acid (glacial, Fisher Scientific) was poured into a gas cylinder (Hoke, 4L) using an inert atmosphere to prevent the inclusion of moisture from air. Water vapor was removed by adding CaSO₄ (drying agent) to the liquid. The cylinder was then filled with 1 to 3 bar abs He (Praxair, 5.0). The same procedure was used to diethyl ether (Fisher Scientific, ACS).
Chapter 3 Calculations of collision cross sections, Na-cluster complex lifetimes and ionization efficiencies

In order to construct a particle sizer capable of quantitative measurements, it has to be known what fraction of clusters in a sample is being detected. This requires knowledge of the extent which clusters pick up Na atoms, what the average lifetime of the Na-cluster complexes are, to what extent the complexes fragment, what the ionization efficiency is and how efficient the detection is.

3.1 Collision Cross Sections

3.1.1 Theory

Calculations are needed to estimate the probability of Na-cluster complexes forming in the sodium oven as a function of cluster size (and composition). Collision theory was used to calculate the collision cross section, the rate constant, $k$, and the collision probability. The collision cross section was calculated in two ways. The first was using the hard sphere (HS) model to calculate the hard sphere collision cross section. This is simply the geometric cross section of the cluster. The second was using the Langevin (L) model including both induction and dispersion forces to calculate the Langevin cross section, $\sigma_L$. The interaction of large clusters with Na atoms is expected to be determined mainly by geometric size. On the other hand, interactions of small clusters with Na are driven by long range interactions. Using the two different models will show which has the greatest influence on the clusters behavior at each size. If one is much larger than the other, using it will also allow a more accurate estimate of the Na pick up.

The collision cross sections were calculated using Equation 3.1.

\[ \sigma = \pi b^2 \]  

(3.1)

The $\sigma_{HS}$ was calculated using $b_{HS} = r_{cluster} + r_{Na}$ which was calculated using the Van der Waals radius of the Na atom and the radius of the cluster. The L model was employed since the HS
model ignores intermolecular interactions. In particular, cross sections of the smallest clusters (monomers, dimers, trimers, etc) may not be well described by a simple HS model. In this case, the effect of long range molecular interactions may provide a better description. The $\sigma_L$ was calculated using Equation 3.1 in which the largest impact parameter of a cluster, $b_L$ was used. This was calculated using equations 3.2.

$$b_L^2 = \left( \frac{C}{E} \right)^{\frac{2}{s}} \left( \frac{s}{2} \left( \frac{s-2}{2} \right) \right)^{\frac{2-s}{s}}$$

(3.2)

E is the collision energy, $s = 6$ (the distance exponent of potential energy, see Equations 3.3 and 3.4) for induction and dispersion interactions, and $C = UR^s$. $R$ is the distance between the cluster center of mass and the Na atom and $U$ is the potential energy. $U$ was calculated as $U = U_{ind} + U_{disp}$, using Equation 3.3 to calculate the contribution from induction and Equation 3.4 to calculate the contribution from dispersion [84]. Equation 3.3 is simplified by the fact that Na has no dipole, and if the cluster also has no dipole, then $U_{ind} = 0$. $\alpha$ is polarizability, $\mu$ is dipole moment, $IE$ is the ionization energy, $f_o$ is the permittivity of free space and $\phi$ is the relative orientation between Na and the cluster which is traveling along the beam path through the Na oven.

$$U_{ind} = -\frac{C_{ind}}{R^6} = -\frac{1}{4\pi f_o} \frac{\mu_{cluster}^2 \alpha_{Na} + \mu_{Na}^2 \alpha_{cluster}}{R^6}$$

(3.3)

$$U_{disp} = -\frac{C_{disp}}{R^6} = -\frac{3}{2} \frac{IE_{cluster} IE_{Na} \alpha_{cluster} \alpha_{Na}}{IE_{cluster} + IE_{Na}} \frac{\alpha_{cluster} \alpha_{Na}}{R^6}$$

(3.4)

As the velocity of the clusters and the Na atoms have an effect on the probability that they will pick up a Na atom, the velocity of the clusters in the molecular beam, $v_{cluster}$, and the thermal velocity of the Na, $v_{Na}$, were used to calculate the average cross sections, $\langle \sigma \rangle$ (Equation 3.5). The molecular beam is assumed to have a uniform velocity of 1000 m/s. $v_{Na}$ is calculated using the Maxwell-Boltzmann distribution shown in Equation 3.6, which is the thermal velocity
distribution of the Na atoms which is integrated in Equations 3.5 and 3.8. The calculations were done assuming that the Na oven was at 498 K, unless otherwise specified. $v_{\text{rel}}$ is then calculated by Equation 3.7.

$$
\langle \sigma \rangle = \frac{\int \sigma v_{\text{rel}} f(v) \sin \theta \, dv \, d\theta \, d\phi}{\int v_{\text{rel}} f(v) \sin \theta \, dv \, d\theta \, d\phi} \quad (3.5)
$$

$$
f(v) \, dv = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{1.5} v^2 e^{-\frac{mv^2}{2k_B T}} \, dv \quad (3.6)
$$

$$
v_{\text{rel}} = \sqrt{v_{\text{Na}}^2 + v_{\text{cluster}}^2 - 2v_{\text{Na}} v_{\text{cluster}} \cos \theta} \quad (3.7)
$$

The calculation for the collision rate constant, $k$, is shown in Equation 3.8. This is the rate constant for the clusters of a given size in the molecular beam picking up a Na atom as they pass through the Na oven. This is integrated from 0 m/s to 5000 m/s using the Maxwell-Boltzmann distribution shown in Equation 3.6.

$$
k = \int v_{\text{rel}} f(v) x^2 \sin \theta \, dv \, d\theta \, d\phi \quad (3.8)
$$

$k$ is then used in a pseudo first order rate equation, shown in Equation 3.9. This was done because it is assumed that the concentration of Na atoms in the oven was replenished faster than the molecular beam depletes it due to its thermal velocity at the vapor pressure of a 498 K oven. The rate calculated in Equation 3.9 is subsequently used to calculate the probability, $p$, of clusters picking up a Na atom using Equation 3.10, where $t$ is time and $N$ is the initial number of undoped clusters in the beam. This is integrated over the 44 µs travel time (oven path length is 44 mm and beam velocity is assumed to be 1000 m/s), that the clusters have through the Na oven.

$$
r = k [Na] [X]_0 \quad (3.9)
$$
\[ p = \frac{\int_{0}^{4\mu} r\, dt}{N} \times 100\% \quad (3.10) \]

### 3.1.2 Collision Cross Section Results

Four test molecules were chosen for the collision cross section and Na collision probability calculations. NH$_3$, H$_2$O and CO$_2$ were chosen because many studies including clusters of these species exist in the literature [13,18,19,42–45,48,50,68–73]. Acetic acid (AA) was chosen because it had been studied experimentally in our lab [1,61]. In addition to this, these clusters provide a wide range of chemical properties and will be able to show whether Na pick-up is dependent upon the chemical properties of the clusters. Table 3.1 summarizes the data used to calculate the L cross sections as well as the densities used to calculate the number of molecules per cluster (n) in the HS model. The densities at the melting points were chosen to estimate the cluster sizes for each molecule, except in the case of CO$_2$ which had estimated values for n in the literature corresponding to the radius [19]. For simplicity of calculations, points, not tensors, were used for dipoles and polarizabilities. Weaker interactions such as quadrupole-quadrupole interactions were not taken into account because their effect should be minimal. Whenever possible, experimental values were used in the calculations. When this was not possible, theoretical values were used. When neither experimental nor theoretical values were available, they were estimated. For example, when ionization energies of large clusters were not known, the IE was used from the largest known cluster. Polarizabilities were estimated using Equation 3.11 when only the polarizability of the monomer, $\alpha_1$, was known. More experimental work is available in the literature on the polarizability of water clusters [74,86]. Because of this more accurate estimates could be made and the uncertainty in the calculations due to polarizability could be investigated (see Section 3.1.3).

\[ \alpha_{x,n} = \alpha_1 n \quad (3.11) \]
## Table 3.1 Data used in collision cross section calculations for NH₃, H₂O, Acetic Acid and CO₂. Langevin model used mass, ionization energy, dipole and polarizability volume and hard sphere model used density \([1,14,72,74–85]\).

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Cluster Size</th>
<th>Mass (amu)</th>
<th>IE (eV)</th>
<th>(\mu^*) (D)</th>
<th>(\alpha^*) (A³)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>1</td>
<td>17</td>
<td>10.67</td>
<td>1.4718</td>
<td>2.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>34</td>
<td>10.2</td>
<td>2.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>51</td>
<td>10.19</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>liquid</td>
<td></td>
<td>9.74</td>
<td>2.05</td>
<td></td>
<td>0.733</td>
</tr>
<tr>
<td>H₂O</td>
<td>1</td>
<td>18</td>
<td>12.62</td>
<td>1.8546</td>
<td>1.48</td>
<td>2.87</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>36</td>
<td>11.76</td>
<td>2.7654</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>54</td>
<td>11.15</td>
<td>1.2804</td>
<td>1</td>
<td>0.917</td>
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<tr>
<td></td>
<td>liquid</td>
<td></td>
<td>9.9</td>
<td>2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>solid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>1</td>
<td>60</td>
<td>10.65</td>
<td>1.6741</td>
<td>4.74</td>
<td>9.78</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>120</td>
<td>9.53</td>
<td>0</td>
<td>14.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>180</td>
<td>9.53</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>liquid</td>
<td></td>
<td>9.53</td>
<td>1.9</td>
<td></td>
<td>1.045</td>
</tr>
<tr>
<td>CO₂</td>
<td>1</td>
<td>44</td>
<td>13.77</td>
<td>0</td>
<td>0</td>
<td>2.63</td>
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<td></td>
<td>2</td>
<td>88</td>
<td>13.32</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>132</td>
<td>13.24</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Dipole and polarizability volume were estimated using points rather than tensors for simplicity of calculations.

*Densities are taken for the liquids and solids at the respective substances’ freezing points. [85]*

†Calculated by other members of this group, [1].

‡Assumed to be this value for simplicity (of calculations).
molecules or more is determined by their geometric size. The orientation of the molecules within a cluster can have a large effect on the properties of clusters of different sizes [77]. This difference not only affects the physical radius of the cluster but also affects the dipole of the cluster. For example, (NH₃)₂ has a larger dipole than NH₃, whereas (NH₃)₃ has no dipole due to the orientation of the NH₃ molecules. The NH₃ trimer has a slightly lower L cross section, 113.13 Å², than the CO₂ trimer without dipole, 114.59 Å². This shows that differences in polarizability, mass and IE have relatively little effect on the cross section. In general, it was found that polarizability determined the cross section. CO₂, being a larger molecule but still having a similar polarizability to that of the other clusters, has its HS cross section become larger than its L cross section at a smaller cluster size. The AA monomer is larger than CO₂ monomer and also has a dipole which increases its cross section. However, the acetic acid dimer HS collision cross section is greater than its L collision cross section. It has no dipole but a greater polarizability than the other species, thus due to the size of the cluster that causes this. However, for AA, the HS cross sections are high estimates of the approximate values as \( r_{\text{molecule}} \) used to calculate \( r_{\text{cluster}} \) was the \( \frac{1}{2} \) length of the molecule because AA is an elongated molecule. While estimates at this size also influence the NH₃, H₂O and CO₂, cross sections, the uncertainty is greatest in acetic acid as it is the least spherical of the molecules investigated. All of these four molecules switch from having larger \( \sigma_L \) to having larger \( \sigma_{\text{HS}} \) before \( r_{\text{cluster}} \approx 0.5 \) nm.

<table>
<thead>
<tr>
<th>Test Molecule</th>
<th>Cluster size</th>
<th>HS Cross Section / Å²</th>
<th>L Cross Section / Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>1</td>
<td>54.20</td>
<td>96.11</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>67.73</td>
<td>109.42</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>78.12</td>
<td>113.13</td>
</tr>
<tr>
<td>H₂O</td>
<td>1</td>
<td>53.05</td>
<td>88.07</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>66.11</td>
<td>98.87</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>76.13</td>
<td>99.62</td>
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<tr>
<td>CO₂</td>
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<td>77.07</td>
<td>86.95</td>
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<td></td>
<td>2</td>
<td>100.30</td>
<td>102.57</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>118.42</td>
<td>114.59</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>1</td>
<td>94.00</td>
<td>102.21</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>124.76</td>
<td>119.51</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>148.93</td>
<td>136.12</td>
</tr>
</tbody>
</table>

Table 3.2 HS and L cross sections of monomers, dimers and trimers of H₂O, NH₃, CO₂ and acetic acid.
Using the calculated cross sections in Figure 3.1, the rate constants, $k$, were calculated for NH$_3$, H$_2$O, CO$_2$ and acetic acid as a function of cluster size. The rate constants for (NH$_3$)$_n$ are shown in Figure 3.2. As the cluster size increases, the HS cross section becomes increasingly larger than the L cross section (Figure 3.1). Following this pattern, the rate constant of the HS model increases to $>3\times10^{-14}$ m$^3$/s by $n = 1500$ where as the L rate constant is about $1\times10^{-14}$ m$^3$/s at this size. The effect that this has on the collision probability is shown in Figure 3.3 where it can be seen that while the probability for $n < 6$ is determined by intermolecular interactions, the probability for clusters larger than this is determined by their geometric size. Figure 3.3 also illustrates that at an oven temperature of 498 K, 100% collision probability is reached quickly.
Figure 3.2 Rate constants, $k$, for NH$_3$, H$_2$O, acetic acid and CO$_2$ clusters with $r \leq 3.0$ nm. The solid line is the HS model and the dashed line is the L model.
Figure 3.3 Probability of Na pick up by clusters with $r \leq 3.0$ nm. The solid lines with solid squares show the probability resulting from HS cross sections and the dashed lines with empty circles show the probability resulting from L cross section calculations.

It is found by looking at individual cluster sizes when the Na oven is set to 498 K, that the very small clusters, i.e. monomers and dimers, will likely only have a probability of 45% to 60% of picking up Na. The greatest difference between the two models for NH$_3$, at this temperature, is in the monomer; the HS model predicts a probability of 33.5% but the L model predicts a probability of 51.5% of clusters picking up Na. Very similar collision probabilities were found for H$_2$O, CO$_2$ and AA. For clusters 0.5 nm < $r$ < 1.5 nm, the HS model predicts a higher pick up probability than the L model. The differences between the L and HS models range from about 15% to 5%. For a 1.0 nm NH$_3$ cluster, the HS model predicts 97.2% probability of Na pick up, where as the L model predicts 87.3% probability. Likewise, for H$_2$O, AA and CO$_2$ clusters of the same radius, the HS model predicted a 97.2% probability of Na pick up, but the L model predicted 85.5% for H$_2$O, 94.5% for acetic acid and 92.8% for CO$_2$. The HS and L models are
in closer agreement for the probability of Na pick up for acetic acid and CO$_2$ clusters picking up Na atoms than for the NH$_3$ and H$_2$O clusters.

These calculations have shown that the collisions between Na and clusters are, in general, dependent upon the geometric size of the cluster, not its chemical properties. The greater cross section for a given cluster size, whether HS or L, corresponds to a greater Na pick up probability being predicted by that model. At small cluster sizes, i.e. <0.5 nm, L cross sections are larger than the HS cross sections because the intermolecular forces extend the cross section beyond that of the physical radius of the molecules. The cross section for larger clusters is dominated by their geometric size (hard sphere). The calculated collision probability of Na should be sufficient to correct the measured size distribution for the size dependant pick-up efficiency.

3.1.3 Sodium Oven Temperature Effects on Sodium Collision Probability

At very high concentrations of Na, double doping becomes possible. This is undesirable because it makes the mass spectra more complicated. The initial collision calculations were done assuming that the Na oven temperature was 498 K and that the Na concentration was at the corresponding vapor pressure. Increasing this will not only increase the thermal velocity of Na but will increase its vapor pressure. The effect of the higher concentration of sodium was tested experimentally, and is discussed in Chapter 4 (see Section 4.2.1). In order to prevent double doping, a temperature of 498 K or lower is needed.

Whether or not an oven temperatures lower than 498 K would have sufficient vapor pressure to dope the clusters efficiency was investigated. Na capture probability calculations were done at 498, 473 and 448 K. Figure 3.4 shows the effect that decreasing the oven temperature may have on the probability Na collisions, taking into consideration the vapor pressure of Na at the aforementioned temperatures. The collision probability decreased significantly because fewer Na atoms were available to collide with the clusters. The probability that monomers were doped dropped to less than 20 % when the temperature was decreased to 473 K and to less than 10 % at 448 K. The vapor pressure of Na changed from having $1.2 \times 10^{19}$ atoms/m$^3$ at 498 K to having $8.32 \times 10^{17}$ atoms/m$^3$ at 448 K as calculated from the CRC handbook [85].
Figure 3.4 Change in probability of Na pick up in NH₃, H₂O, CO₂ and AA clusters as a function of temperature which changes the Na vapor pressure. Squares are 498 K, triangles are 473 K and circles are 448 K.

For the smallest clusters, the L model predicts a greater number of collisions and the HS model dominates at larger clusters. Figure 3.5 compares the L and HS collision probabilities at 448 K, 473 K and 498 K. It can be seen that the HS model predicts a much higher Na collision probability than the L model for NH₃ particularly at 448 K, as the HS cross section becomes increasingly larger than the L cross section. At higher temperatures, the difference is negligible as the probability is, or is nearly, 100 %. The predominant collision probabilities at each temperature were combined for comparison of the effect Na concentration has in Figure 3.4. This shows more clearly that as the Na concentration is lowered, the probability of a cluster colliding with Na has decreases from 45 % at 498 K, to 4 % at 448 K. All clusters should collide with Na at r ≥ 1.5 nm at 498 K, at r ≥ 3 nm at 473 K and at r ≥ 6 nm at 448 K. This indicates that it is important to have the Na oven between 473 K and 498 K for experiments.
Figure 3.5 Collision probability between Na and NH$_3$ clusters. a: HS (squares) vs L (circles) models at $T_{oven} = 498$ K from $r < 2$ nm (inset $r < 10$ nm), b: HS (squares) vs L (circles) models at $T_{oven} = 473$ K from $r < 2$ nm (inset $r < 10$ nm), c: HS (squares) vs L (circles) models at $T_{oven} = 448$ K from $r < 2$ nm (inset $r < 10$ nm).

3.1.4 Collision Cross Section Uncertainty Evaluation

Uncertainties were investigated for the collision cross section calculations. The uncertainty in the L calculations for the smallest clusters (monomers, dimers and trimers), were contributed to by uncertainties in the IE, dipole moment and polarizability. Because it was found that polarizability was the largest contributor to the uncertainty of the L calculations, it was also investigated in the larger clusters. In addition to this, the uncertainty in the HS cross section calculations was calculated due to the density of the clusters. These were investigated in order to see if there would be a significant impact upon the collision probability.
Uncertainties in cross sections due to variations in ionization energies, dipole moments and polarizabilities were investigated for the smallest clusters (monomers, dimers and trimers). The NH₃ monomer cross section had the greatest uncertainty which was 96.11 Å² ± 8.89 Å². This resulted in the collision probability of the monomer having a total uncertainty of 51.48 % ± 3.11 % (when the polarizability uncertainty is averaged). The uncertainty could be found in the literature and resulted in an uncertainty of 51.48 % ± 0.20 % collision probability due to the IE of the NH₃ monomer and 51.48 % ± 1.29 % collision probability due to the dipole [81,85]. Polarizability was the greatest contributor as it accounted for over half of the uncertainty in the NH₃ monomer calculations.

In the smallest clusters, polarizability produced a larger uncertainty than IE and dipole, mainly due to the distribution of values across the literature. In particular, the CRC handbook lists four different values for the polarizability of the NH₃ monomer [85]. While 2.2 Å³ was initially used for the NH₃ L cross section calculations, the values for polarizability ranged from 2.1 Å³ to 2.81 Å³. These minimum and maximum polarizability values would result in a minimum cross section of 94.5 Å² and a maximum of 103.2 Å². The corresponding collision probabilities at a Na-oven temperature of 498 K would be 50.9 % and 54.0 %, respectively, instead of 51.5 % (an average of ± 1.6 %). Most substances have more accurately known polarizabilities for small clusters (i.e. monomers), resulting in uncertainties less than 3%. These uncertainties were considered acceptable for the small clusters because they do not significantly change the result of the collision probability.

The polarizability of large clusters is generally not known and was estimated using Equation 3.11. This resulted in an increasing uncertainty as cluster size increased. The error due to this extrapolation was investigated by looking at H₂O, because its polarizability had been studied in the literature through theoretical calculations for larger clusters (i.e. n < 100) and showed a linear relationship [86]. In addition to this, experimental polarizabilities have also been reported in the literature for H₂O dimers and trimers [74]. The polarizability of larger H₂O clusters was estimated with less uncertainty. This difference in the way that the polarizability was estimated for larger clusters is shown in the error bars in Figure 3.6.
When the uncertainty of the L cross section was compared with the HS cross section in Figure 3.6, it was seen that there was no significant difference in which model describes each cluster size. The polarizability uncertainty became larger with increasing cluster size, however, the L cross section was not larger than the HS cross section for clusters with \( r > 0.5 \) nm. At the cluster sizes where the uncertainty became significant due to the large extrapolation of the polarizability, the HS cross section calculations more accurately described the clusters.

Figure 3.6 \( \text{NH}_3 \) cross section vs cluster size. Solid line is the cross section for the HS model and the dashed line is L model. Error bars are shown for the L cross section taking into account different values of \( \alpha \). The lower error bar is produced using \( \alpha = 2.1 \text{ Å}^3 \) and the higher error bar was produced using \( \alpha = 2.81 \text{ Å}^3 \).

For large clusters, the uncertainty in the HS model could have an effect upon the collision probability. The source of uncertainty for the HS cross sections was a result of the molecular density which was used to calculate the approximate number of molecules within the individual clusters (Figure 3.7). An estimate of this was found in the literature for CO\(_2\) [68], but it is generally not reported. The liquid densities of H\(_2\)O, NH\(_3\) and AA at their respective melting points were chosen and used with the radius of the clusters from the HS cross sections to calculate the number of molecules within the cluster. Because this may not be the state that the cluster was in, the uncertainty was calculated using the solid densities. It is not known whether
the clusters formed are liquid, solid, amorphous, or a combination thereof. The uncertainty calculated for 0.5 nm and 1.0 nm radii are shown in Figure 3.7.

![Figure 3.7 Collision cross section of H$_2$O. Solid line is HS cross section and dashed line is L cross section. Error bars shown for HS cross section are a result of different cluster densities.](image)

The uncertainties which were calculated for both the HS and the L model were not sufficient to significantly change the results of these calculations. These calculations show that the Na collisions with clusters larger than about 0.5 nm radius are dependent upon the geometric cross section, not on the properties of clusters. Lower clusters sizes, while they may be more dependent upon molecular properties, were calculated with < 5% uncertainty.

### 3.2 Lifetime of Na-Cluster Complexes and Fragmentation

After a collision between a cluster and a Na atom occurs it travels to the ionization region. During this time, energy from the collision is redistributed and fragmentation of the cluster can occur. Calculations were done in our group to predict the average lifetimes of the small Na-acetic acid (AA) collision complexes using the SACM (statistical adiabatic channel model). The results are shown in Table 3.3 and published in reference [1] where further explanation of the theory...
and results may be found. It was found that rearrangement of the cluster after a Na atom was picked up released enough energy to evaporate a couple molecules from the cluster. The weakly bound molecules had similar binding energy to that which was released from the molecular rearrangement. Similarly, when rearrangement occurs once the cluster is ionized and enough excess energy is present to evaporate a few more molecules. This was seen to happen in acetic acid, which had a total of two acetic acid molecules evaporate from the trimers and tetramers before they hit the detector (see Section 4.1.1). Corresponding calculations for large clusters cannot be performed, but a similar degree of fragmentation is expected, i.e. a few molecules per particle.

<table>
<thead>
<tr>
<th>Collision Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-AA</td>
</tr>
<tr>
<td>Na-(AA)₂</td>
</tr>
<tr>
<td>Na-(AA)₃</td>
</tr>
<tr>
<td>Na-(AA)₄</td>
</tr>
<tr>
<td>( \tau_1 ) †</td>
</tr>
<tr>
<td>2 ps</td>
</tr>
<tr>
<td>( \infty )</td>
</tr>
<tr>
<td>140 ns</td>
</tr>
<tr>
<td>50 ps</td>
</tr>
<tr>
<td>( \tau_2 ) †</td>
</tr>
<tr>
<td>100 ps</td>
</tr>
<tr>
<td>7.5 µs</td>
</tr>
<tr>
<td>500 ns</td>
</tr>
<tr>
<td>( \tau_3 ) †</td>
</tr>
<tr>
<td>70 µs</td>
</tr>
<tr>
<td>( \infty )</td>
</tr>
<tr>
<td>( \tau_4 ) †</td>
</tr>
<tr>
<td>( 10 ) s</td>
</tr>
</tbody>
</table>

Table 3.3 Decay times, \( \tau \), for different Na acetic acid collision complexes. † The decay time for decay channel Na-(AA)ₙ → Na(AA)ₙ₋₁ + (AA) is \( \tau = \frac{1}{k\langle E \rangle \langle \ell_{\text{max}} \rangle} \), where the decay rate, \( k \), is a function of the average collision energy, \( \langle E \rangle \), and the angular momentum quantum number, \( \langle \ell_{\text{max}} \rangle = j \). Further details can be found in reference [1].

### 3.3 Ionization Efficiency

The probability of ionization of the doped clusters, \( p_{\text{ion}} \), is calculated using Equation 3.12. The initial number of photons, \( N_o \), was calculated using equation 3.13. The number of photons which are not absorbed by a cluster, \( N \), is calculated using Equation 3.14, where \( \frac{I}{I_o} \) is the intensity ration found using the Beer-Lambert law (Equation 3.15). The concentration of AA used was \( 10^{19} \) clusters/m³, and the volume was \( \pi r^2 \ell \). The path length, \( \ell \), is the overlap of the laser beam with the molecular beam, and was estimated to be 1.0 mm. The radius of the molecular beam, \( r \), was estimated to be 1.0 mm.
\[ p_{\text{ion}} = \frac{N_o - N}{[AA] \times \text{volume}} \times 100 \]  
\[ N_o = \frac{\lambda E}{hc} \]  
\[ N = N_o \frac{I}{I_o} \]  
\[ \frac{I}{I_o} = e^{-\sigma_{Na}[AA]} \]

\[ \lambda = 266\text{nm}, \] the wavelength of the laser light and \( E = 7.0mJ \) which is the energy of the laser, \( h \) is Plank’s constant and \( c \) is the speed of light. The photoionization cross section of Na, \( \sigma_{Na} \), in Equation 3.15 was \( 10^{-22} \text{m}^2 \) [87–89]. It was assumed that each interaction between a photon and a cluster resulted in an ionized cluster, thus the total number of ionized clusters is \( N_o - N \). The Beer-Lambert law provided a rough estimate of the number of ions that will be formed from the doped clusters. The number of clusters which are ionized is estimated on the order of 30%.

The collision cross section calculations, the life-time of the cluster complexes and the ionization cross section calculations provide a clear picture of the processes involved in this method. The results of the calculations presented here show that collision complexes will form and will be ionized, if they remain intact. Therefore, it is the life-time of the collision complexes which has the greatest uncertainty and is currently being investigated further in our research group.
Chapter 4 Experimental Cluster / Aerosol Mass Spectra

Ionizing clusters with laser radiation near the ionization energy (IE) of molecules which make up the cluster can cause several problems. First, fragmentation of the cluster is a common side effect of excess energy. How dramatic this effect is depends upon what forces hold the cluster together and the energies used to ionize. A cluster held together by Van der Waals forces will be easier to fragment than a cluster formed with hydrogen-bonding. Clusters can be prevented from significant fragmentation by ionizing near the IE of the cluster. This should reduce the amount of excess energy available to fragment large clusters [18,31]. The second problem is chemistry within the cluster. Once a molecule is ionized it can undergo chemical changes and structural rearrangements before reaching the detector. This can produce further fragmentation of the cluster as more excess energy may be released. Another problem is that the original chemical information is lost when bonds are broken and molecular fragments are created.

The present work suggests the use of the Na-doping method to solve these problems. Doping the clusters decreased the IE of the clusters to \( \leq 241 \text{ nm} \) (\( \leq 5.14 \text{ eV} \)). This allows one to use a UV photon for ionization. It is expected that the clusters / particles still lose a few molecules as some excess energy is still be present, but much less compared to XUV ionization. Because the Na atom is ionized and not the molecules that make up the cluster, chemical changes should be prevented. Section 4.1 addresses the fragmentation that occurs in the doped clusters and compares the cluster size distributions taken with XUV and UV ionization.

The laser energy used to ionize the doped clusters should not need to be as high as the IE of Na, 5.14 eV (241 nm) for ionization to occur. For example, the IEs for Na(NH$_3$)$_n$ have been studied and it was found that for $n = 1$, the IE = 4.27 eV which corresponds to a $\lambda = 290.4 \text{ nm}$ [43]. As $n$ increases the energy required to ionize the cluster decreases. A (NH$_3$) cluster with a radius of 0.5 nm requires less than 2.5 eV (496 nm) to ionize it. Not all clusters will have as dramatic a decrease in IE as ammonia. Na doped methanol clusters, for example, have an IE of 3.19 eV (389 nm) for $n = 6 – 40$ [49].
While there will be sufficient energy to ionize doped clusters regardless of whether the wavelength is slightly above or below 241 nm, it is not known if there will be any benefit to using less energetic photons. It is known that the electron removes most of the excess energy from small clusters when they are ionized directly [20]; however, it is not clear whether or not this is true for larger clusters. For this reason, the spectra resulting from different UV wavelengths used for photoionization are compared in Section 4.2.

It was found in Section 3.1.3 that the oven temperature could significantly affect the collision rate of the clusters with Na due to the vapor pressure of Na. Experiments were done and are presented in Section 4.3 comparing the spectra of small doped ammonia clusters at oven temperatures ranging from 448 K to 548 K.

4.1 Comparison of XUV and UV Mass Spectra

Several experiments were done in order to characterize the Na-doping method. First, small acetic acid (AA) clusters were studied. These were clusters with less than 10 AA molecules, generally focusing on monomers to tetramers. This was done in order to characterize the fragmentation process after the Na collision and ionization. Clusters of this size were studied because they could be isolated in the molecular beam from larger clusters. Secondly, the distributions of larger clusters (n > 10) were studied. This was done to demonstrate that this method is applicable to larger clusters and ultrafine aerosols. Through the comparison of the spectra of the doped clusters, ionized with UV light, with the spectra of the undoped clusters, ionized with XUV light, it is demonstrated that the Na-doping technique allows for a softer ionization than other available techniques.

4.1.1 Small Acetic Acid Clusters

Small acetic acid clusters have been studied in the literature and are known to fragment in a particular pattern upon ionization by XUV laser light [1,90,91]. The expected fragments of AA clusters are shown in Table 4.1, and this was used to characterize the AA spectra taken using XUV.
Masses of fragments after XUV ionization

\[(AA)_n^+ + h\nu_{XUV} \rightarrow (AA)_n^+ \rightarrow F_i^+ + \sum F_j\]

<table>
<thead>
<tr>
<th>Original ion</th>
<th>Fragment ions</th>
<th>Mass of (F_i^+) / amu</th>
</tr>
</thead>
<tbody>
<tr>
<td>(AA)_n^+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AA^+</td>
<td>(CH_3CO^+)</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>(COOH^+)</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>AA^+</td>
<td>60</td>
</tr>
<tr>
<td>(AA)_2^+</td>
<td>((AA)H^+)</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>((AA)COOH^+)</td>
<td>105</td>
</tr>
<tr>
<td>(AA)_3^+</td>
<td>((AA)H^+)</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>((AA)CH_3CO^+)</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>((AA)_2H^+)</td>
<td>121</td>
</tr>
<tr>
<td>(AA)_4^+</td>
<td>((AA)_3H^+)</td>
<td>181</td>
</tr>
<tr>
<td>(AA)_n^+</td>
<td>((AA)_{n-1}H^+)</td>
<td>(1 + 60(n-1))</td>
</tr>
</tbody>
</table>

Table 4.1 Characteristic fragments and masses of acetic acid and its clusters after XUV ionization \([90,91]\).

The protonation of the AA clusters can be seen in Figure 4.1, which shows the TOF spectra of AA resulting from ionization with 74.2 nm XUV. This was published in [1]. The characteristic protonated AA peaks are present. The AA dimer is the predominant form of AA in the vapor phase due to strong H-bonds. It can be seen as a protonated monomer 61 m/z in Figure 4.1 a-d as well as the AA and carboxylic acid peak at 105 m/z. The timing of the molecular beam relative to the laser could be changed in order to probe different parts of the molecular beam (for more details refer to Section 2.1). When this was done to include trimer in addition to the monomer and dimer, several peaks appeared in the spectra. In Figure 4.1 b, the trimer can be seen at 121 m/z (dimer plus proton) as well at 103 m/z as indicated in Table 4.1. The presence of the tetramer in Figure 4.1 c was noted as the appearance of a peak at 181 m/z (trimer plus proton). The Figure 4.1 d shows that clusters up to \(n = 8\) were made as peaks increased in steps of 60 m/z.
Figure 4.1 XUV-TOF spectra recorded under different conditions: Molecular beam contains a: monomer AA and dimer (AA)$_2$; b: monomer AA, dimer (AA)$_2$, and trimer (AA)$_3$ (amount of tetramer is very small); c: monomer AA, dimer (AA)$_2$, trimer (AA)$_3$, and tetramer (AA)$_4$; d: large clusters. The species are identified by their characteristic fragments given in Table 4.1.

The UV spectra recorded under the same molecular beam conditions as the XUV spectra are shown in Figure 4.2. The clusters were doped with Na then ionized with UV laser radiation at 240 nm.
Figure 4.2 TOF spectra of Na-doped acetic acid clusters recorded under different molecular beam conditions as specified in Figure 4.1: a: same conditions as in Figure 4.1 a (up to the trimer); b: same conditions as in Figure 4.1 b (up to the tetramer); c: same conditions as in Figure 4.1 c (including large clusters). The masses of the various Na-doped acetic acid clusters are given in Table 4.1.

To understand the UV spectra of doped AA clusters, Table 4.1 lists the peaks which were found upon UV ionization. In general, it was expected that there would be peaks at 60 m/z increments starting at 83 m/z.

<table>
<thead>
<tr>
<th>Masses of Na doped clusters expected after UV ionization</th>
<th>Ion</th>
<th>Mass of ion / amu</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Na(AA)_n^+$</td>
<td>$Na(AA)$</td>
<td>83</td>
</tr>
<tr>
<td>$Na(AA)_2^+$</td>
<td>$Na(AA)$$_2$</td>
<td>143</td>
</tr>
<tr>
<td>$Na(AA)_3^+$</td>
<td>$Na(AA)$$_3$</td>
<td>203</td>
</tr>
<tr>
<td>$Na(AA)_4^+$</td>
<td>$Na(AA)$$_4$</td>
<td>263</td>
</tr>
</tbody>
</table>
Table 4.2 Expected ions of Na doped acetic acid and its clusters after UV ionization.

The conditions depicted in the XUV spectrum in Figure 4.1 a were optimized for monomer and dimer signal, with no trimer or larger clusters. The corresponding UV spectrum in Figure 4.2 a showed no peaks. Thus it can be stated that when the conditions in Figure 4.1 b were optimized to have the maximum trimer signal while minimizing tetramer signal, the signal seen in Figure 4.2 b was a result of the trimer (and possibly a small amount of tetramer). A peak at 83 m/z and a very small peak at 143 m/z were observed. When the tetramer signal was maximized while keeping all larger peaks minimized (Figure 4.1 c and Figure 4.2 c), the peak at 143 m/z increased relative to the peak at 83 m/z indicating that the two peaks are the result of two different clusters in the molecular beam, namely the tetramer and trimer, respectively.

The peak at 83 m/z and 143 m/z, doped monomer and dimer ions, originated from trimers and tetramers clusters in the molecular beam. Two AA molecules evaporated between the time that the cluster picked up a Na atom and when the ion reached the detector. Calculations (see Section 3.2) were done to help understand how the two molecules were lost [1]. The loss can be from excess energy from collision with the Na atom or after Na was ionized. A few molecules may be lost at each step. This was a significant loss for small acetic acid clusters, and does not necessarily make this method more advantageous than others for the very smallest of clusters. However, this amount of fragmentation is insignificant for larger clusters. The sodium doping technique would be very advantageous in measuring size distributions much closer to those of the original distribution within the molecular beam than other techniques.

4.1.2 Larger Clusters

Spectra were taken using both XUV to ionize large undoped clusters and UV to ionize large doped clusters, to compare the two methods. The XUV ionization induces a significant amount of fragmentation of clusters and molecules. The UV light was a softer ionization method because there was not enough excess energy to fragment individual molecules. Dimethyl ether (DME), water, AA, mixed DME and water and ammonia were investigated ionized using both ionization methods.
Neat DME clusters were doped with Na and ionized with 266 nm UV light, as well as being directly ionized by XUV light at 17 eV. It can be seen in Figure 4.3 a that there is a significant amount of molecular fragmentation of DME as a result of ionizing with XUV light. The spectrum is dominated by the peaks from the fragmentation of DME molecules at 15, 28 and 44 m/z. There are also smaller peaks from the ionized DME clusters; however they can only be seen to about 1500 m/z. These peaks in the XUV spectrum were also protonated, which is consistent with the literature [92]. UV light, on the other hand, causes no molecular fragmentation in the doped DME clusters. This can be seen in Figure 4.3 b as there are no significant peaks below 69 m/z. Na-doping technique produced clusters which were not protonated and the cluster distribution extends out to about 3000 m/z.

Figure 4.3 TOF spectra of dimethyl ether. a: XUV spectrum of DME. Peaks resulting from the fragmentation of DME molecules are the most intense peaks and have m/z < 43. b: Spectrum of doped DME clusters using UV ionization with 266 nm laser radiation.

The differences between Figure 4.3 a and b show that the UV ionization of Na-doped clusters is a much softer ionization method than direct ionization with XUV. More accurate cluster
distributions can be observed, and the spectra are easier to assign because the peaks present are only cluster ions, and do not contain molecular fragments or protonated clusters.

The UV spectrum reveals a cluster distribution closer to the original distribution within the molecular beam than the XUV because it is a softer ionization technique. This has been seen in both DME and water clusters, but it is large acetic acid clusters which have the most dramatic difference between the XUV and UV spectra (Figure 4.4). The XUV spectrum, Figure 4.4 (a), shows clusters were present with up to about 27 AA molecules; however, it can be seen in Figure 4.4(b) that the Na-doping technique reveals that the molecular beam originally contained clusters with up to about 75 molecules. In addition to this a distribution with the maximum signal at about 39 molecules can be seen in the when ionizing with UV (266 nm). The UV spectrum contains very few clusters below n = 23, whereas in the XUV spectrum this is where almost all of the clusters are seen.

Figure 4.4 Large acetic acid clusters a: undoped clusters ionized with XUV light b: Na-doped clusters ionized with UV light (the increase in signal of alternating peaks may be a result of the abundance of dimer in the gas phase when the clusters were formed).
Water clusters were made by seeding with He at 3.5 bar and differences in the spectra could again be seen between the XUV and UV spectra. The spectra are shown in Figure 4.5. When XUV ionization was used, the water clusters can be observed up to \( n \approx 12 \) (217 m/z). Like DME and AA, these peaks are protonated water clusters. UV ionization of doped water clusters, Figure 4.5 b, had clusters up to \( n \approx 20 \) (about 383 m/z). The largest clusters seen in the XUV spectrum are about 166 m/z lower than the largest clusters seen in the UV spectrum. In addition to this, the most intense peaks shifted from the monomer to the trimer. This is not as significant an increase in the distribution as was seen by DME. This may be because XUV is still fairly soft as there are fewer reaction channels available in water than DME and AA. However, the differences between the spectra show that for water, the Na-doping method is still a softer ionization than XUV ionization.

\[
\begin{array}{c}
\text{Signal / mV} \\
\hline
0 & -0.5 \\
-0.1 & -0.4 \\
0 & -0.3 \\
0 & -0.2 \\
0 & -0.1 \\
0 & 0 \\
0 & 0.1 \\
0 & 0.2 \\
0 & 0.3 \\
0 & 0.4 \\
0 & 0.5 \\
\end{array}
\]

\[
\begin{array}{c}
\text{m / z} \\
0 & 0 \\
200 & -1 \\
400 & -2 \\
600 & -3 \\
800 & -4 \\
\end{array}
\]

Figure 4.5 TOF-MS spectra of water clusters seeded in 3.5 bar He. a: Water clusters ionized using XUV. b: Doped water clusters ionized using UV
One of the advantages in using the molecular beam machine TOF-MS with Na oven is its ability to detect and distinguish between a variety of different cluster types. The lack of fragmentation allows the peak masses to be more easily used to identify their constituent species. Spectra of neat clusters have been shown; including AA (Figure 4.2), DME (Figure 4.3), and H$_2$O (Figure 4.5). Mixed clusters have also been detected. Figure 4.6 shows mixed DME and H$_2$O clusters. The inset of Figure 4.6 shows the Na(DME)$_n$ for n = 11 - 20. Peaks corresponding to Na(DME)$_n$H$_2$O for the same n values can also be seen.

![Graph showing Na-doped clusters of DME and DME-water clusters.](image)

**Figure 4.6** Na doped clusters of DME and DME-water clusters. Insert: shows the area highlighted by the box and corresponds to m/z 500 – 1000, showing the mixed DME – water clusters as smaller peaks beside the large DME clusters.

The Na-doping technique has allowed the detection of a variety of molecules and differentiation between the types of molecules. This has great potential for studying aerosols for several reasons. First, it gives a reliable size distribution of neutral clusters. Secondly, these clusters which have been used to show that the method works with both volatile (DME) and semi-volatile (H$_2$O and AA). In addition to this, mixed clusters have been detected ((DME)$_n$H$_2$O). This shows
that the Na-doping technique has promise to help determine the composition of gases and aerosols from small clusters to ultrafine aerosols. In the future, it may be useful in the analysis of more complicated systems.

The photoion spectrometer with Na oven was made to be able to detect cluster sizes consisting of only a few molecules up to clusters with a 10 nm radius. In order to show that this size range has been realized in the detection of volatile clusters, large ammonia clusters were made. The size distribution of clusters was varied by changing the backing pressure of the gases. Higher backing pressures enabled larger clusters to form because more molecules were available to cluster. Temperature of the nozzle was also changed as it increased the saturation of the gas.

Ammonia clusters were doped with Na then ionized with 266 nm laser light with backing pressures ranging from 1 to 8 bar abs. The temperature of the nozzle was also changed from room temperature down to -2 °C. This resulted in the clusters increasing their mean radius from 0.8 nm to 6 nm. This corresponds to Na(NH₃)ₙ where n ≈ 45 to n ≈ 15,000, respectively. The resultant spectra, shown in Figure 4.8, indicate that the molecular beam machine was able to produce and detect clusters as desired. It can be seen in Figure 4.7 d that clusters 10 nm in diameter and larger were present in the molecular beam.
The collision probability calculations between the clusters and Na predicted that all large clusters would pick up Na (see Section 3.1.3). It is not known how accurate these calculations are in regards to the actual number of clusters which pick up a Na atom; however, these preliminary results indicate that this method is in principle, reliable. Ammonia clusters have been detected throughout the size range that was intended for this experimental setup.

4.2 Comparison of Tunable UV and Fixed Wavelength 266 nm UV

UV light is sufficient to ionize Na doped clusters and provides a more accurate size distribution than other soft ionization techniques. Preliminary studies into which UV wavelength is the best choice and how dependent this is on the cluster type were done. While Na doped clusters do not
have the broad range of IE that the undoped clusters do, they still are not equal \([43,49,51,58]\). If all of the clusters are to be ionized with a single wavelength, a balance between ionizing the clusters and keeping a minimum excess energy must be maintained. Two different lasers were used, the tunable Sirah laser and the fixed wavelength Quantel laser. The Sirah laser is a dye laser pumped by the 2\(^{\text{nd}}\) harmonic of a Nd:YAG laser. It is frequency doubled using a BBO crystal. The Quantel laser is a fixed wavelength laser, producing 266 nm laser radiation \((4^{\text{th}}\) harmonic of Nd:YAG, 1064 nm). This laser was chosen because it is hoped that one day this instrument will be scaled down into a field instrument. The Quantel laser is robust and portable thus will be able to be used for this purpose. In order to compare the Sirah laser to the Quantel laser as ionization sources, several types of clusters were investigated.

Na doped water clusters seeded in 3.5 bar He were investigated by ionizing with UV laser radiation from both the Sirah and Quantel lasers. The resultant spectra are shown in Figure 4.8. The Sirah laser was tuned to produce 245 nm laser radiation. The Sirah laser produces laser beam with a lower power \((\sim 1 \text{ mJ})\) than the Quantel laser \((\sim 7 \text{ mJ})\). The signal from the Sirah laser was scaled so that a direct comparison could be made. The spectrum scales linearly with laser power. It could be seen that the spectra both return to baseline at about 1200 m/z. The spectra also have very similar distributions. The main exception to this was the peak at 46 m/z which was Na\(_2\). This was not present in B because the laser wavelength was below its IE. The similarity between the Sirah and Quantel spectra shows two things. The first is that the IE are all high enough for ionization to occur. The second is that the shorter wavelength is not causing noticeable evaporation of the molecules.
Figure 4.8 UV TOF spectra of water seeded with 3.5 bar He. a: Doped water clusters ionized with 245 nm UV light from the Sirah laser. b: Doped water clustered ionized with UV from the Quantel laser.

Spectra of doped DME clusters, shown in Figure 4.9, were taken by ionizing with 2 different wavelengths on the Sirah laser as well as 266 nm from the Quantel laser. The Sirah was tuned to just above and just below the IE of a lone Na atom (241 nm). As the laser power was different between each wavelength and between lasers, the signals were scaled linearly for comparison. It can be seen in Figure 4.9a that there is a peak at 23 m/z as a result of lone Na atoms being ionized. This peak, which is highlighted in a does not appear in b or c, because both are below the IE of Na. Na₂ is highlighted in Figure 4.9b and appears in a but not in c. Only the peaks resulting from Na (23 m/z) or Na₂ (46 m/z) change between the spectra. Clusters of DME have the same maximum cluster size and similar distributions. This shows that the excess energy from 241 nm laser radiation is no more destructive to the clusters than the 244 or 266 nm. The 266 nm laser radiation has also ionized all of the DME clusters which were ionized by 241 nm.
The Quantel laser, while limited to a specific wavelength, was sufficient to ionize the Na doped clusters. It did not produce spectra which were significantly different from the Sirah laser at the IE of Na. These preliminary results show that the Quantel laser can be used for reliable ionization.

### 4.3 Dependence of Na Capture on the Temperature of the Na Oven

In Section 3.1.3, it was predicted that the temperature of the Na oven would have a large effect upon the rate of collisions between clusters and Na atoms due to the change in the vapor pressure of Na. This was tested in an experiment done soon after the installation of the Na oven into the experimental setup. Spectra of doped ammonia clusters were taken by increasing the Na oven in increments of 25 K from 448 K to 548 K.
The results of the experiment roughly corroborate what was predicted by the calculations in Chapter 3. A significant increase in signal of the ammonia peaks can be seen in Figure 4.10 between the 448 K (a), 273 K (b) and 498 K (c) oven settings. The dimer signal was \( \sim 7.5 \text{ mV} \) in Figure 4.10 a which increases to about \( \sim 22 \text{ mV} \) in Figure 4.10 b. Increasing the temperature a further 25 °C, Figure 4.10 c, quadrupled the signal to \( \sim 86 \text{ mV} \). Figure 3.4 shows the predicted collision probabilities for the same Na oven temperatures. The calculations predicted that there would be about 5 %, 16 % and 45 % probability of picking up Na, respectively. The signal produced from the 498 K oven is strong enough to see large clusters. However, when the oven is set to 473 K, the signal has decreased, but remains strong enough to detect large clusters. Turning the oven down to 448 K decreased the signal enough that it becomes difficult to distinguish larger clusters from the baseline. Clusters with lower concentrations may be missed when the oven is set to 448 K but should be seen at both 473 K and 498 K.
The strength of the signal was due to the increase in the Na vapor pressure. Because more Na was available for collisions, more collisions were able to occur. While a stronger signal is good, the Na oven has been seen to produce a beam of Na which causes contamination in the vacuum system and damages the detector over time. The experiments were performed with the Na oven set between 473 K and 498 K. In order to balance protecting the MCPs with a good signal, the Na oven would ideally be used at lower temperatures (473 K).

In Figure 4.11, the Na oven was increased from 498 K (a) to 523 K (b) and 548 K (c) to see if there was a significant advantage in the increasing signal at these temperatures to warrant the risk to the MCP. It was found, however, that as the Na oven temperature rose, the increased availability of the Na atoms caused not an increase in signal, but an increase in the number of Na atoms picked up by the clusters. Double doping (2 Na atoms added to the cluster), and triple doping (3 Na atoms added to the cluster), both occurred at 548 K. The effect that the excess doping had upon the ammonia spectra can be seen in Figure 4.11, as the spectra became increasingly cluttered with additional peaks. While the double doped peaks can be seen at 523 K (b), it is at 548 K (c) that the doping significantly decreases the signal of the singly doped peaks.
Figure 4.11 Na doping of ammonia clusters using high temperatures for the Na oven a: 498 K (same as Figure 4.10 c) b: 523 K and c: 548 K

There was a 20 mV increase in signal between Figure 4.11 a and Figure 4.11 b. However, it was not as dramatic an increase as was seen between Figure 4.10 b and Figure 4.10 c. The beam created by the Na vapor emerging from the Na oven is likely to be more detrimental at this temperature than increase in signal could justify. More importantly, the double doping was strong enough to cause ambiguity in the spectrum.
Chapter 5 Conclusion and Outlook

This thesis has investigated a number of key points in the application of the technique of sodium doping followed by UV photoionization to the sizing of clusters and ultrafine aerosol particles (r ≤ 10 nm). First, it was demonstrated that the probability of collisions between Na atoms and clusters / aerosol particles within the Na oven employed in the Na-doping technique is sufficient to dope them. It was shown in which temperature range the Na-oven must be operated at for the Na capture probability to be sufficiently high. Secondly it was demonstrated that more accurate (i.e. less fragmented) size distributions were obtained with the Na-doping technique than could be from other ionization techniques. In addition the present work shows that accurate chemical information about the clusters could be obtained as their mass to charge ratios were not affected by molecular fragmentation. Furthermore, it was shown through experiments that this technique can be used to detect clusters with different chemical properties.

Two models were used to calculate the cross sections for the collisions of the clusters / aerosol particles with Na atoms: the Langevin model and the hard sphere model. Both models predict Na capture probabilities on the same order of magnitude. For small clusters, the Langevin cross section is larger than the hard sphere cross section because the capture is dominated by intermolecular interactions. For clusters radii > 0.5 nm, the capture is dominated by the geometric size.

Calculations have shown that when the Na oven is at a temperature between 200 °C and 225 °C, about half of the small clusters capture a Na atom. At these temperatures, capture probabilities of larger clusters lie at 100 %. Lower temperatures will cause the collision probability of the small clusters to drop to < 10%. This was also confirmed by experiments because the ion signal decreased as the temperature of the Na oven was lowered. Experiments also showed that at T ≥ 250 °C, undesirable double doping and even triple doping occurs. The combination of these calculations and experiment reveal that for the most efficient single doping of the clusters, the oven should be in the temperature range of 200 to 225 °C.
A comparison with “soft” XUV ionization showed that sodium doping followed by UV photoionization is a softer ionization technique which allows even volatile or semi-volatile clusters to be detected with only a minimal amount of evaporation. The size distributions obtained using the sodium doping technique, were different (larger) from those obtained using XUV photoionization. While the UV spectra show complete size distributions, the XUV size distributions are the result of extensive fragmentation. Additionally, the UV mass spectra do not indicate any chemical changes. The XUV mass spectra, by contrast, clearly show fragmented cluster masses. XUV ionization is generally considered a soft technique, for example, compared to electron ionization. However, it was shown to be much harsher than doping with Na and subsequent ionization with UV laser radiation.

Preliminary studies have shown that the sodium doping technique is applicable to a wide range of substances. These include an acid (CH$_3$COOH), a base (NH$_3$), water and an ether. Mixed clusters of these substances with water have also been detected. The ability to distinguish between neat and mixed clusters, while maintaining an accurate size distribution has been realized.

In the context of cluster / aerosol particle sizing, the Na-doping technique is shown to be applicable to species ranging from small clusters to aerosol particles with diameters of many nanometers. While much progress has been made, there are still several major points in need of further work. Systematic studies will be needed to characterize the system for a broad variety of atmospherically relevant species. Additional substances could include thiols, amines, hydrocarbons and fluorinated hydrocarbons. Systematic studies can be done on all of these substances and include both neat clusters and a variety of mixtures of known concentrations. These can all be generated \textit{in situ} in the molecular beam machine for characterization purposes, and different size distributions can be obtained by varying the expansion temperature and pressure.

Additional theoretical work will be needed to explain observations. It has been shown in this work that sufficient collisions occur to allow Na doping; however, some Na-cluster complexes are more prone to lose the Na atom before reaching the detector than others. Carbon dioxide
clusters, for example, have not yet been successfully observed using the current system. In order to obtain a greater understanding of the effects of energy redistribution following a collision with a Na atom, calculations for the average Na-cluster complex lifetime of large systems would be beneficial. Additionally, more quantitative estimates of the ionization cross section would also be helpful.

The scope of the Na-doping technique has been extended to larger clusters for the application of sizing ultrafine atmospheric aerosol particles. This has been done through both calculations and experimental work, and it has been shown that this technique is very promising for the construction of a generic particle sizer for volatile and semi-volatile aerosol particles down to the sub-nanometer range.
Bibliography


[38] TSI Incorporated, Model 3022A Condensation Particle Counter, I (TSI Incorporated, St Paul, MN, 2002).


