On the Stability of Complex Ions in Ionic Liquid Ion Sources

by

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Abstract

Ionic liquids are molten salts at room temperature that consist of positive and negative ions. These liquids can be used in electrosprays to produce ion beams. Ionic liquid ion source (ILIS) beams typically consist of single ions and solvated ions. It has been observed that solvated ions are not always stable and can break up into lighter ions midflight. Past experiments show that the stability of solvated ions depends on the molecular composition of the ionic liquid. Based on these results, it has been hypothesized that the stability of solvated ions increases with increasing molecular complexity of the ions. The focus of this work is to test this hypothesis by characterizing ionic liquids of different molecular complexities under controlled conditions. A time of flight mass spectrometer and a retarding potential analyzer were developed specifically for this purpose. The ion beam composition and energy distribution were measured at various temperatures and source voltages for each ionic liquid. With some exceptions, the observed trend was in agreement with the results of past experiments and with the hypothesis. The exceptions to the expected trend may have resulted from the limitations of the detectors. The data from this work can be used to test the hypothesis with moderate confidence. Future study requires improvements to the detectors, namely the retarding potential analyzer, so that the hypothesis can be evaluated more conclusively.

Thesis Supervisor: Paulo C. Lozano
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Chapter 1

Introduction and Background

Ionic Liquid Ion Sources (ILIS) use ionic liquids to produce ion beams. Ionic liquids are molten salts at room temperature that consist of positive and negative ions. They are conductive and have nearly zero vapor pressure \(^{[1]}\), which makes them suitable for applications in vacuum. The most important property of these liquids is that ions can be evaporated from the liquid surface through the application of a strong electric field \(^{[1]}\). These ions can be electrostatically accelerated to high velocities, producing a few keV ion beam. ILIS beams can be used to produce thrust in ion electrospray thrusters and for etching and deposition in focused ion beam columns \(^{[2]}\). Figure 1-1 shows a diagram of a single emitter ILIS.

Figure 1-1: Diagram of an Ionic Liquid Ion Source \(^{[3]}\)
A single emitter ionic liquid ion source consists of a sharp tip, coated with ionic liquid, placed very close to a metal extraction plate with a hole in it. Approximately 1 kilovolt is applied between the tip and the extraction plate, denoted by the voltage $V_0$. The electric field at the tip stresses the surface of the liquid to a point where ions can be evaporated. The evaporated ions are accelerated through the hole, producing thrust. An array of sharp tips can be used as an ion electrospray thruster.

Electrospray thrusters have many advantages over plasma thrusters such as gridded ion thrusters or Hall effect thrusters. First, plasma thrusters require the production of a plasma from an inert gas. This requires energy and isn’t 100% efficient since some energy is spent exciting the atoms instead of ionizing them $^4$. In ILIS the ions come from the liquid, thus no energy is required for ionization. Second, a substantial fraction of the gas in plasma thrusters is never ionized and slowly leaks out the exit, reducing the specific impulse $^4$. In contrast, electrospray thrusters use nearly all of the propellant because they can produce beams of positive and negative ions by alternating the voltage polarity $^3$. Third, electrospray thrusters do not require the added complexity of a beam neutralizer because alternating the polarity creates a net neutral beam. The most significant advantage of electrospray thrusters over plasma devices is that they are very compact and can be used on small satellites. It is very difficult to scale down plasma thrusters for use on small spacecraft because the plasma density must be increased, which increases plasma collisions with the internal walls of the device and decreases the lifetime of the thruster $^5$. Because of this, electrospray propulsion has the potential to revolutionize the attitude and position control of small spacecraft.

Electrospray propulsive inefficiencies derive from non-uniform beam composition. ILIS beams consist of ions, solvated ions, and sometimes droplets $^6$. Solvated ions are ions attached to at least one neutral, which is a positive ion joined to a negative ion. Ions and solvated ions exit the thruster at different speeds due to their difference in masses, resulting in a reduced specific impulse $^6$. Solvated ions can break up in the acceleration region into a single ion and a neutral group. This process is called fragmentation, which further reduces the propulsive efficiency $^6$. The ratio of ions to
solvated ions and the stability of solvated species depends on the chemical composition of the ionic liquid [6]. The effect different liquids have on fragmentation is the focus of this work.

Ionic liquid ion sources have applications besides spacecraft propulsion that can drastically improve current technologies like ion beam deposition and ion beam etching. These applications require electrostatic focusing of the ion beam; the effectiveness of which depends on the energy distribution of the beam [7]. Fragmentation results in a non-uniform energy distribution [7]; therefore understanding fragmentation is very important for the use of ILIS in focused ion beam applications. Additionally having a complete understanding of the beam composition will allow for the prediction of the focusing performance and will aid in the selection of suitable ionic liquids. Current ion beam lithography technology uses liquid metal ion sources (LMIS) [2]. For LMIS, there are very limited options for the chemical composition of the beam [2]. With ILIS, there are hundreds of different ionic liquids available and many more that have not yet been synthesized [1]. This could have an enormous impact on industries that currently rely on LMIS and make technologies that require non-metal ion beams feasible.

1.1 ILIS Beam Composition and Fragmentation

Typically in ionic liquids, the cation is a heavy organic molecule and the anion is an inorganic molecule or single atom [6]. This work focuses on imidazolium-based ionic liquids like the 1-ethyl-3-methylimidazolium (EMI+) cation, shown in Figure 1-2.

![Molecular Structure of EMI+](image-url)

Figure 1-2: Molecular Structure of EMI+ [6]
The imidazolium-based ionic liquids tested in this work have a variety of different anions, which are shown in Figure 1-3.

Ion beams from ILIS can consist of several different types of ions. The simplest ion that can be evaporated from the liquid surface are single positive or negative ions, which are referred to as monomers. Solvated ions are typically present in the beam. A dimer is a monomer attached to a neutral, which is a cation-anion pair. The charge of a dimer is the same as that of a monomer, but dimers are considerably more massive. A positive monomer and dimer of EMI-BF$_4$ is shown in Figure 1-4.

Ions of higher degrees of solvation are also possible. For example, trimers are monomers attached to two neutrals. The production of solvated species has a very important effect on the propulsive efficiency of ionic liquid ion sources. Additionally solvated
ions are not necessarily stable and can fragment into lighter species. For example, a
dimer can break up into a monomer and a neutral. Fragmentation of solvated species
has an additional negative effect on the propulsive efficiency \[6\].

1.2 Polydispersive Efficiency

The polydispersive efficiency is a penalty for accelerating the beam constituents to
different velocities. This arises from the fact that an exhaust with particles travelling
at the same velocity is the most propulsively efficient \[6\]. Without fragmentation,
the beam is monoenergetic; however since monomers and solvated ions have different
masses, they have different velocities. Equation 1.1 shows the velocity of an electro-
statically accelerated ion that was not produced by a fragmentation event:

\[
v_i = \sqrt{\frac{2q_iV_0}{m_i}} \tag{1.1}
\]

where \(v_i\) is the velocity of the ion, \(q_i\) is the charge of the ion, \(V_0\) is the source voltage,
and \(m_i\) is the mass of the ion. From Equation 1.1, it is clear that the monomers have
a faster speed than the dimers. The expression for the polydispersive efficiency is
given by Equation 1.2 \[6\]:

\[
\eta_p = \frac{[1 + (\sqrt{\xi} - 1) f_0]^2}{1 + (\xi - 1) f_0} \tag{1.2}
\]

where \(\eta_p\) is the polydispersive efficiency, \(\xi\) is the charge to mass ratio of the dimer
divided by the charge to mass ratio of the monomer, and \(f_0\) is the monomer current
fraction \[6\]. Note that this is only valid for a beam of monomers and dimers; no other
solvated species are taken into account. The polydispersive efficiency is represented
graphically in Figure 1-5 for EMI-BF_4 in the positive and negative modes.
Figure 1-5: Polydispersive Efficiency for EMI-BF$_4$ without Fragmentation [3]

It is clear from Figure 1-5 that $\eta_p = 1$ when the beam consists entirely of either monomers or dimers. The efficiency reaches a minimum when there is a mix of the two species.

Fragmentation of dimers into monomers further reduces the polydispersive efficiency [6]. When a solvated ion breaks up into a lighter ion in the acceleration region, the lighter ion will be accelerated to a final kinetic energy less than the full accelerating potential. Since solvated ions can break up anywhere in the acceleration region, the broken ions are accelerated to a spread in kinetic energies and thus a spread in velocities. This is why fragmentation has a negative effect on the polydispersive efficiency. Equation 1.3 [6] shows the polydispersive efficiency for the case where dimers break up into monomers uniformly in the acceleration region. This means that there is no preferred potential for fragmentation to occur. It is not currently known what the break up distribution is, but past experiments support this notion [6].

$$\eta_p = \frac{[1 + (\sqrt{\xi} - 1)f_0 + \frac{1}{3}f_f(2\sqrt{\xi(1-\sqrt{\xi})} - 1)]^2}{1 + (\xi - 1)f_0}$$ (1.3)
where $f_f$ is the current fraction of dimers that fragment into monomers inside the acceleration region. The polydispersive efficiency is shown in Figure 1-6 for 0% and 100% fragmentation of dimers for EMI-BF$_4$ in the positive mode.

![Figure 1-6: Polydispersive Efficiency for EMI-BF$_4$ with Fragmentation](image)

It is clear that the production of solvated species and the fragmentation of solvated ions has a negative effect on the efficiency of ion electrospray thrusters. For a monomer fraction of zero, the efficiency is no longer 1 because of the fragmentation of dimers into monomers. Therefore it is important to study why different liquids fragment more than others and what processes lead to fragmentation.
1.3 Ionic Liquid Ion Source Theory

When conductive liquids are sufficiently electrically stressed, the liquid surface collapses into a Taylor cone \[^8\]. This phenomena is shown in Figure 1-7 for a capillary electrospray.

![Taylor Cone Diagram](image)

Figure 1-7: Capillary Electrospray with a Taylor Cone

The sharp geometry of a Taylor cone allows the electric field strength to reach values high enough to evaporate ions \[^11\]. Taylor cones form through the perfect balance of the surface tension pressure of the liquid and the electrostatic pressure of the applied field \[^11\]. This is shown in Equation 1.4:

\[
\frac{1}{2} \epsilon_0 E^2 = \frac{\gamma}{R_c}. \tag{1.4}
\]

where \( \epsilon_0 \) is the permittivity of free space, \( E \) is the electric field strength, \( \gamma \) is the surface tension of the liquid, and \( R_c \) is the radius of curvature of the liquid surface. Assuming a conical geometry of the liquid, the electric field can be expressed as the following:

\[
E = \sqrt{\frac{2\gamma \cot \theta_T}{\epsilon_0 r}} \tag{1.5}
\]
where \( r \) is the distance from the tip of the cone along the liquid surface and \( \theta_T \) is the half angle of the cone. Equation 1.5 shows that the electric field strength increases towards the tip of the cone. Near the tip, the field strength surpasses the threshold for ion emission and ions are evaporated from a localized region at the tip. This is depicted in Figure 1-8:

![Liquid Cone Evaporated Ions](image)

**Figure 1-8:** Pure Ion Emission from a Taylor Cone

By solving Laplace's equation using a conical geometry, the angle of the cone can be determined. The cone half angle, called the Taylor angle, is 49.3° for all applied voltages \(^{[1]}\). It is independent of the liquid properties and the geometry of the emitter.

In reality, the Taylor cone model breaks down very close to the tip since a singularity cannot exist. This occurs because ionic liquids have a finite conductivity, so it takes time for the charges to relax to the surface. At some distance \( r^* \) from the tip, the charges are no longer relaxed to the surface. In this case, assuming a spherical liquid surface, the pressure balance is given by Equation 1.6:

\[
\frac{1}{2} \varepsilon_0 E_*^2 - \frac{1}{2} \varepsilon_R \varepsilon_0 E_{in}^2 = \frac{2 \gamma}{r^*}
\]

(1.6)

where \( E_* \) is the critical electric field outside of the liquid, \( E_{in} \) is the electric field
inside of the liquid, \( \epsilon_R \) is the relative permittivity of the liquid, and \( r^* \) is the critical distance from the tip measured along the liquid surface. The quantity \( r^* \), shown in Equation 1.7, can be solved for by assuming that the charges are not relaxed. This means that \( E_{in} \) can be approximated as \( E_* / \epsilon_R \).

\[
r^* = \frac{4\gamma}{\epsilon_0 E_*^2} \left( \frac{\epsilon_R}{\epsilon_R - 1} \right)
\] (1.7)

The quantity \( r^* \) gives an estimate to the size of the emission region, which is typically tens of nanometers.

The critical electric field to induce ion evaporation can be determined using the Schottky model for ion evaporation. Using the law of mass action, the current density for ion evaporation is given by Equation 1.8:

\[
 j = \frac{\sigma kT}{h} \exp \left( - \frac{1}{kT} \Delta G \right)
\] (1.8)

where \( j \) is the current density, \( \sigma \) is the surface charge density, \( k \) is Boltzmann’s constant, \( T \) is the temperature of the liquid, \( h \) is Planck’s constant, and \( \Delta G \) is the solvation energy of the ion in the liquid.

Equation 1.8 does not include the effect of an external electric field, which reduces the amount of work required to evaporate an ion. By minimizing the work done to remove an evaporated ion from the potential well, the exponential in Equation 1.8 can be modified to yield the expression in Equation 1.9:

\[
 j = \frac{\sigma kT}{h} \exp \left( - \frac{1}{kT} \left( \Delta G - \sqrt{\frac{e^3 E_*}{4\pi \epsilon_0}} \right) \right)
\] (1.9)

where \( e \) is the fundamental unit of charge. The critical field can be approximated by setting the term in the exponential of Equation 1.9 equal to zero. The critical field is given by Equation 1.10.

\[
 E_* = \frac{4\pi \epsilon_0}{e^3} \Delta G^2
\] (1.10)

Typically the solvation energy for ionic liquids is on the order of 1.5 eV \[^9\], so the
The required field strength is approximately 1.6 V/nm.

The emission current can also be estimated using the results of this model. By assuming a hemisphere of liquid at the tip, the current, \( I \), is given by Equation 1.11.

\[
I = 2\pi r_s^2 j
\]  

(1.11)

Assuming that the charges are not relaxed to the surface, the current density can be approximated as:

\[
j = K E_{in} = K \frac{E_s}{\epsilon_R}
\]  

(1.12)

Where \( K \) is the conductivity of the liquid. The current can then be expressed as:

\[
I = \frac{32\pi K \gamma^2}{\epsilon_0^2 E_s^3} \frac{\epsilon_R}{(\epsilon_R - 1)^2}
\]  

(1.13)

For EMI-BF₄, the surface tension is 0.052 N/m [1], the conductivity at 25°C is 1.3 Si/m [1], and the relative permittivity is about 10 [9]. This results in an emission current of about 146 nA. The conductivities of ionic liquids are varied, which results in a range of typical emission currents. Additionally, the conductivity changes with liquid temperature [1], which provides a way to control the current of the source without modifying the extraction potential.

The voltage required to create a Taylor cone can be determined by solving Laplace's equation for a given electrode geometry. Externally wetted tungsten needles can be modeled using prolate spheroidal coordinates. Once the expression for the electric field at the tip is determined, it can be used in Equation 1.6 to solve for the required voltage. The start-up voltage is given by the expression in Equation 1.14:

\[
V_{start} = \sqrt{\frac{\gamma R_c}{\epsilon_0 \ln \left( \frac{4d}{R_c} \right)}}
\]  

(1.14)

where \( V_{start} \) is the startup voltage of the ILIS, \( R_c \) is the radius of curvature of the emitter, and \( d \) is the distance between the tip of the emitter and the extractor plate. The only liquid property that affects the startup voltage is the surface tension; oth-
erwise the startup voltage is determined exclusively by the geometrical properties of the ion source. Typically the radius of curvature for the tip is on the order of 20 μm and the tip to extractor distance is about 500 μm. This results in a startup voltage of approximately 1250 V.
Chapter 2

Literature Review and Hypothesis

Fragmentation of solvated species in ILIS beams is not a well characterized process. It has been observed and measured in several different experiments; however it has not been thoroughly studied. The current fraction from fragmented species has been measured for a few different ionic liquids in ILIS. The observation from past work indicates that solvated species from different ionic liquids fragment in different amounts. This notion is also supported by molecular dynamics simulations of solvated ions. This section discusses past work in detail and presents the motivation for this work.

Fragmentation has been observed in both capillary and externally wetted ionic liquid ion sources. Capillary sources consist of a thin glass tube through which the flow of ionic liquid is controlled by an applied back pressure. A Taylor cone forms at the end of the capillary which can emit ions, droplets, or both depending on the operation regime. For high conductivity liquids, like ionic liquids, and for low flow rates, the pure ionic regime (PIR) is usually attained. Figure 2-1 shows the difference between capillary and externally wetted sources.
In 2005, the fragmentation of solvated ions from a sodium iodide formamide capillary source was observed \[^{11}\]. A quadrupole mass spectrometer was used to filter the ions by their mass and a retarding potential analyzer was used to measure the energy distribution for each ion species \[^{11}\]. It was found that the energy distributions for solvated ions with low degrees of solvation had low energy components \[^{11}\]. If there was no fragmentation, the beam would be monoenergetic with an energy corresponding to the extraction potential energy. When fragmentation occurs, the broken ions always have less energy than the extraction potential; thus the signature of fragmentation is low energy components in the ion beam.

Fragmentation of ionic liquid nanodoplets produced by a capillary electrospray has also been observed \[^{12}\]. The nanodrops were created by electrospraying droplets of ionic liquid diluted by a volatile solvent; the solvent evaporated while the positive and negative ions from the ionic liquid remained and formed a charged droplet \[^{12}\]. Some of the droplets were unstable and would break up, which was a nuisance because it was an unexpected effect that interfered with the measurements; the goal of the experiments was to determine the solvation energies for different ionic liquids \[^{12}\]. The charged nanodrops were sent through a differential mobility analyzer coupled with a mass spectrometer \[^{12}\]. The drops of a selected mobility made it into the detector where the mass spectrum of the drops was then determined; some drops fragmented inside the detector, which resulted in an erroneous mass spectrum for the selected mobility \[^{12}\]. This did not occur in all cases, but it did result in the loss of some useful
data [12].

Fragmentation has been studied using externally wetted emitters more thoroughly than with capillary sources. In 2006, the fragmentation of solvated ions from an externally wetted EMI-Im ionic liquid ion source was well characterized [7]. High resolution beam energy measurements were made using a retarding potential analyzer with a planar geometry [7]. Many low energy components were found in the ion beam, which were attributed to the fragmentation of dimers into monomers and trimers into dimers [7]. Low resolution retarding potential measurements were taken to estimate the total fragmentation current fraction, which was determined to be on the order of 20% [7]. Additionally, time of flight mass spectrometry measurements were used to detect fragmentation; unfortunately the combination of poor signal strength and low time resolution prevented any quantitative measurements from being made [7].

In 2009, the fragmentation of solvated ions from a BMI-I externally wetted ionic liquid ion source was observed [13]. Using a low resolution retarding potential analyzer with a planar geometry, the beam energy distribution was measured [13]. Signatures from the fragmentation of dimers into monomers and trimers into dimers in field-free space were found [13]. The vast majority of the fragmentation occurred inside of the acceleration region [13]. In this case the fragmentation fractions of the solvated ions was much higher than that of the EMI-Im ILIS discussed previously [13].

In 2012, the fragmentation of solvated ions from an EMI-BF$_4$ externally wetted ionic liquid ion source was studied [14]. A low resolution retarding potential analyzer with spherical geometry was used to measure the beam energy distribution for various liquid temperatures at a constant source voltage [14]. Low energy components of the beam were found, which corresponded to the fragmentation of dimers into monomers and trimers into dimers outside of the acceleration region [14]. The current fraction for fragmentation inside the acceleration region was less than that for fragmentation outside of the acceleration region [14]. This is likely due to the fact that the RPA collecting surface was placed far from the source [14], so the solvated ions had more time to break up in the field-free region. Interestingly, it was found that the current fraction for fragmentation inside of the acceleration region increased with increasing
temperature \textsuperscript{[14]}. The three experiments for externally wetted emitters show that different ionic liquids have different rates of fragmentation \textsuperscript{[6]}. EMI-Im solvated ions fragmented the least and BMI-I solvated ions fragmented the most. The results of the three experiments are summarized in Table 2.1.

Table 2.1: Summary of Experimental Results (Negative Mode) \textsuperscript{[3, 15]}

<table>
<thead>
<tr>
<th></th>
<th>EMI-Im</th>
<th>EMI-BF\textsubscript{4}</th>
<th>BMI-I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fragmentation Before Emission</td>
<td>3%</td>
<td>12%</td>
<td>50%</td>
</tr>
<tr>
<td>Total Fragmentation</td>
<td>11%</td>
<td>51%</td>
<td>65%</td>
</tr>
</tbody>
</table>

The cations for these liquids are nearly the same since EMI\textsuperscript{+} and BMI\textsuperscript{+} only differ by a few molecules. They both have an imidazolium ring, but BMI\textsuperscript{+} has a slightly longer carbon chain, a total of six extra atoms. Therefore the difference between the three liquids is mostly the anions. Figure 2-2 shows images of the three anions.

![Figure 2-2: Comparison of Anions used in Past Experiments \textsuperscript{[3, 6]}](image)

Im is a very complex molecule with many atoms and the EMI-Im solvated ions were shown to fragment the least. Iodine is a single atom, which has no complexity, and the BMI-I solvated ions fragmented the most. BF\textsubscript{4} is a molecule with mid-range complexity, consisting of five atoms, and the EMI-BF\textsubscript{4} solvated ion fragmentation
fraction was between that of EMI-Im and BMI-I. Therefore it appears that there may be a correlation between the complexity of the ion and the fragmentation rate. However these liquids were tested using different experimental setups under different conditions, so no concrete conclusions should be drawn from these results [6].

In addition to the experimental testing of ionic liquids, molecular dynamics simulations have been used to study the stability of solvated ions. A wide range of EMI+ based ionic liquids were compared by testing the stability of a negative dimer of that liquid. The atoms of the dimer were given a random distribution of velocities; the total energy imparted to the dimer was similar across all tests [6]. A dimer of each liquid was simulated 10,000 times to see if it would break up [6]. The results of the molecular dynamics simulations support the past experimental observations in that more complex molecules fragment less frequently [6]. The results are summarized in Table 2.2.

Table 2.2: Results of Molecular Dynamics Simulations [6]

<table>
<thead>
<tr>
<th>Anion</th>
<th>Number of Negative Dimer Atoms</th>
<th>Fragmentation Fraction within 200 ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br</td>
<td>21</td>
<td>94.6%</td>
</tr>
<tr>
<td>Cl</td>
<td>21</td>
<td>98.6%</td>
</tr>
<tr>
<td>BF₄</td>
<td>29</td>
<td>86.3%</td>
</tr>
<tr>
<td>FSI</td>
<td>37</td>
<td>72.7%</td>
</tr>
<tr>
<td>Im</td>
<td>49</td>
<td>26.7%</td>
</tr>
<tr>
<td>MPI</td>
<td>69</td>
<td>3.5%</td>
</tr>
</tbody>
</table>

Through experimental testing of ionic liquids in ionic liquid ion sources and molecular dynamics simulations, it has been shown that the fraction of fragmentation decreases with increasing ion complexity [6]. It is hypothesized that excess energy is imparted to the solvated species as they are extracted from the surface of the liquid [6]. This excess energy can go into stretching the individual ions apart and can
possibly lead to fragmentation \cite{6}. Complex molecules have many atoms, so the excess energy can be redistributed throughout the many bonds between atoms \cite{6}. This leaves less energy to stretch the individual ions in a solvated ion apart and potentially reduces the probability of fragmentation \cite{6}.

The hypothesis for this work is that complex ions fragment at slower rates. To test this hypothesis, measurements of the fragmentation fractions for several different ionic liquids must be made under very controlled conditions. Beam energy measurements are critical for the detection of fragmentation in both the acceleration region and in field-free space. Additionally the beam composition should be measured to support the beam energy measurements. Therefore, a retarding potential analyzer is used to measure the beam energy distribution and a time of flight mass spectrometer is used to determine the beam composition. These two measurements will need to be made under the same conditions, which means that the vacuum chamber should not be vented between experiments. This makes the design of the detectors challenging, which is the subject of Chapter 3.
Chapter 3

Experimental Methods

The experimental goal for this work is to measure the beam composition and fragmentation fractions under different conditions. The parameters for the experiments are listed in Table 3.1.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>BMI-I, EMI-BF₄, EMI-Im, EMI-MPI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source Voltage</td>
<td>± 1050V-1950V</td>
</tr>
<tr>
<td>Temperature</td>
<td>30°C, 50°C, 70°C, 90°C</td>
</tr>
<tr>
<td>Extractor Hole Size</td>
<td>~1.6 mm</td>
</tr>
<tr>
<td>Needle Radius of Curvature</td>
<td>~20 microns</td>
</tr>
<tr>
<td>Extraction Distance</td>
<td>~200 microns</td>
</tr>
</tbody>
</table>

Four different imidazole-based ionic liquids are tested. Three are EMI⁺ based and one is BMI⁺ (1-butly-3-methylimidazolium) based. The anions for these liquids span a wide spectrum of complexity. Figure 1-3 shows diagrams of the different anions.

In order to compare these liquids on equal grounds, the emitter geometry is fixed. The same externally wetted tungsten needle is used for all experiments. Additionally the extractor hole size and the distance between the tip of the needle and the extractor are kept as constant as possible across all experiments. This ensures that
the potential distribution in the acceleration region, which is hypothesized to affect the fragmentation [6], is kept consistent for all experiments. The variables include the source voltage and the liquid temperature. The source voltage is varied across a range where the emission current is stable. Data is acquired at the same set of voltages for all experiments so that a fair comparison can be made. Temperature control is used so that all experiments can be taken at the same temperature. Note that some low conductivity liquids, namely BMI-I [13], need to be heated to a minimum temperature before consistent ion emission can be achieved.

Two experimental techniques are used to determine the beam composition and fragmentation fraction. First is the retarding potential analyzer (RPA), which is used to probe the energy of the beam. It yields the fragmentation fractions for break up in the acceleration region and in field-free space. The second is time of flight mass spectrometry (TOF), which yields the beam composition. With a high enough time resolution, the fragmentation in the acceleration region can be characterized for each solvated species using TOF. These methods are detailed in section 3.3 and 3.4.

3.1 Vacuum System

All experiments are carried out in the same vacuum chamber. The chamber has two 140 l/s turbo molecular pumps. Typical operation pressures range from $10^{-7}$ Torr to $10^{-5}$ Torr. The main chamber is approximately 0.5 m long and has a small extension for the time of flight detector. In order to do both RPA and TOF experiments under the same conditions, some of the experimental apparatus is mounted on a linear stage. The stage is moved up and down to change experiments without having to vent the chamber. Figure 3-1 shows a diagram of the chamber with the ion source and detectors installed.
3.2 Ion Source

The ion source consists of an externally wetted tungsten needle. Figure 3-2 shows a scanning electron microscope image of the tungsten needle wetted with ionic liquid.

Figure 3-2: Image of the Externally Wetted Tungsten Needle
A distal contact electrode is used as a reservoir for the ionic liquid while providing electrical contact between the stainless steel and the tungsten needle. Figure 3-3 shows a photo of the ion source without the extractor plate on the left and with the extractor plate on the right. Note that a flashlight was used to illuminate the ionic liquid to improve the contrast in the photos.

![Figure 3-3: Ionic Liquid Ion Source Setup](image)

A distal contact is used so that the high voltage is applied to the stainless steel cylinder rather than to the needle directly. This helps prevent electrochemical reactions from degrading the tip \(^\text{[16]}\). The stainless steel cylinder is fitted into a copper block where the high voltage is applied to the copper block through a wire secured to the block by a screw. The copper block and needle are mounted to a boron nitride holder. A ceramic heater is installed in the boron nitride, which is used to heat the ionic liquid. A K-type thermocouple is held in place by the same PEEK bracket that is used to secure the shaft of the needle. The boron nitride holder is mounted to a compact, manual 3-axis stage that is used to precisely position the tip of the needle with respect to the extractor hole. A view of the setup mounted on the vacuum chamber flange without the extractor plate is shown in Figure 3-4. Note that the
aforementioned PEEK bracket was originally made of boron nitride, as shown in the photo; the boron nitride bracket was very fragile and broke, so a PEEK replacement was made and used for all experiments in this work.

Figure 3-4: Ion Source Mounted on Vacuum Chamber Flange

The temperature control was achieved by using a proportional integral control algorithm. An Arduino UNO was used to open and close the heater circuit while measuring the temperature from the thermocouple. Figure 3-5 shows a schematic of the heater circuit. The Arduino monitors the temperature using a MAX31855 thermocouple breakout board (purchased from Adafruit.com) and a K-type thermocouple. A PI control algorithm was used to control the heater circuit to maintain a certain temperature. The output of the Arduino was a pulse-width modulation (PWM) signal, which was used to control a TIP41C transistor as shown in Figure 3-5. The ceramic resistive heater is operated using a DC power supply. To control how long the voltage is applied to the heater, the heater circuit is connected across the transistor. When the PWM signal tells the transistor to allow current to flow,
the DC voltage is applied to the heater. When the PWM signal tells the transistor to break the circuit, no current can flow and no voltage is applied to the heater.

The voltage of the source was controlled using a high voltage power supply with the capability to measure the emitted current as well as the current intercepted on the extractor. Note that the source voltages referred to in the text are actually the control signal input to the high voltage amplifier since it is easier to refer to round numbers. The actual voltage applied to the needle was typically about 10V-20V higher than the control signal due to some overshoot. However the measured source voltage was used in all plots like RPA curves and current-voltage curves. The applied voltage, emitted current, and intercepted current were measured using a data acquisition system. Table 3.2 summarizes the instruments, equipment, and materials used for the source.
Table 3.2: Materials and Equipment Used for Ion Source

<table>
<thead>
<tr>
<th>Material/Instrument</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newport Stages (M-MT-XYZ)</td>
<td>Position control of needle relative to the extractor</td>
</tr>
<tr>
<td>Saint-Gobain Boron Nitride (Combat AX05)</td>
<td>Heat transfer and electrical isolation between heater and high voltage needle</td>
</tr>
<tr>
<td>Goodfellow Tungsten Straight Wire (W 005350/19)</td>
<td>Needle</td>
</tr>
<tr>
<td>Watlow Ceramic Resistive Heater (WS-CER-1-01-00335)</td>
<td>Heat ionic liquid</td>
</tr>
<tr>
<td>Omega K-Type Thermocouple (5TC-TT-K-30-36)</td>
<td>Temperature measurement</td>
</tr>
<tr>
<td>RSR DC Power Supply (HY3005F-3)</td>
<td>Heater voltage</td>
</tr>
<tr>
<td>Arduino UNO</td>
<td>Heater circuit control</td>
</tr>
<tr>
<td>Matsusada High Voltage Amplifier (AP-3B1-L2)</td>
<td>High voltage supply for needle</td>
</tr>
<tr>
<td>National Instruments DAQ (NI-USB-6119)</td>
<td>Data acquisition system</td>
</tr>
</tbody>
</table>

3.3 Retarding Potential Analysis

The energy distribution of the ion beam provides the fragmentation fraction of solvated ions. The fragmentation that occurs inside of the acceleration region can be distinguished from that in field-free space. A retarding potential analyzer is used to probe the energy of the beam through the use of semi-transparent grids biased to high voltage.

An RPA typically consists of several grids placed in front of a current collecting
plate. The front grid is grounded to ensure that the potential is zero in the region between the source and the detector. The middle set of grids are the retarding grids. The voltage on the retarding grids is varied continuously from zero to approximately 1.5 times the source voltage. When the retarding grids reach a voltage that corresponds to the kinetic energy of an ion, that ion is stopped and is not collected by the detector. Finally there is a third grid placed right before the collector plate, which is used to repel secondary electrons that are created when ions impact the metal surface of the collector. In the case of these experiments, the collector plate is a Faraday cup current collector.

### 3.3.1 Theory

The kinetic energy of ions that are not produced by fragmentation events should be nearly equal to that of the source voltage. There are voltage losses incurred during the extraction process, but they are very small (< 5%) [7,17]. In the case where there is no fragmentation, the beam should be monoenergetic. However fragmentation does occur, and the broken ions that are produced have kinetic energies less than the source voltage.

The kinetic energy of a broken ion produced from a fragmentation event occurring in field-free space is very simple to determine. When the solvated ion is in field-free space, it is no longer being accelerated and thus has a constant velocity. When the solvated ion breaks up, the broken ion will have that same velocity; however the kinetic energy is less because the mass of the broken ion is less than that of the solvated ion. The kinetic energy of a broken ion is given by Equation 3.1 [7]:

\[
K_{bi} = \frac{m_i}{m_{pi}} q_i V_0
\]

where \(K_{bi}\) is the kinetic energy of the broken ion, \(m_i\) is the mass of the broken ion, \(m_{pi}\) is the mass of the parent ion, \(q_i\) is the charge of the broken ion, and \(V_0\) is the accelerating potential. This is actually the minimum kinetic energy that a broken ion can have.
The ratio of the kinetic energy of a broken ion to the acceleration potential is simply just the ratio of the mass of the broken ion to that of the parent ion. This means that monomers resulting from the fragmentation of dimers in field-free space will have a different kinetic energy from dimers resulting from the fragmentation of trimers in field-free space. This fact makes it very simple to distinguish the difference between the fragmentation fraction of dimers versus the fragmentation fraction of trimers in field-free space. Figure 3-6 shows an ideal RPA scan for an ILIS beam with no fragmentation. The collected current normalized by the maximum collected current is plotted as a function of the retarding potential normalized by the accelerating potential. The beam is clearly monoenergetic, with an energy of $V_0$ in eV’s.

![Figure 3-6: RPA for Monoenergetic Beam](image)

Figure 3-7 shows an ideal RPA scan for fragmentation of dimers into monomers occurring only in field-free space. Again the collected current normalized by the maximum collected current is plotted as a function of the retarding potential normalized by the accelerating potential.
The percentage of the total current that corresponds to fragmentation of dimers into monomers in field-free space is the height of the step at $V/V_0 = m_i/m_{di}$.

Fragmentation in the acceleration region is somewhat more difficult because the solvated ion is still being accelerated when it breaks up. Then the lighter ion is further accelerated until it is emitted at some velocity. The kinetic energy of a broken ion that results from the fragmentation of a solvated ion in the acceleration region is given by Equation 3.2 [7]:

$$K_{bi} = q_i \left( \frac{m_i}{m_{pi}} - 1 \right) V_B + V_0$$  \hspace{1cm} (3.2)

where $K_{bi}$ is the kinetic energy of the broken ion, $q_i$ is the charge of the ion, $m_i$ is the mass of the broken ion, $m_{pi}$ is the mass of the parent ion, $V_B$ is the local value of the potential where the parent ion broke up, and $V_0$ is the accelerating potential. This expression was determined using the conservation of energy. The kinetic energy from Equation 3.2 normalized by the source potential energy is given by Equation 3.3.

$$\frac{K_{bi}}{q_i V_0} = 1 - \left( 1 - \frac{m_i}{m_{pi}} \right) \frac{V_B}{V_0}$$  \hspace{1cm} (3.3)

It is clear that this quantity is always less than one. It also depends on the local
value of the potential in the acceleration region where the solvated ion broke up. Since solvated ions can break up anywhere in the acceleration region, this means that the broken ions will be accelerated to a spread in final kinetic energies. This range of energies will always be greater than that given by Equation 3.1 and will always be less than the full accelerating potential.

Determining the fraction of fragmentation that occurs inside the acceleration region is not difficult. However, determining which species of solvated ions that broke up in the acceleration region is not possible using RPA. Note that it is possible using time of flight mass spectrometry; see Section 3.4 for more information about time of flight measurements. Figure 3-8 shows an ideal RPA scan for fragmentation that occurs both in the acceleration region and in field-free space.

![Figure 3-8: RPA for Fragmentation Everywhere](image)

The fragmentation that occurs in field-free space is distinguished by the sharp vertical step features as discussed previously. Fragmentation in the acceleration region looks like a sloped line because the broken ions are accelerated to a spread in final kinetic energies, not just a singular value. The fragmentation in the acceleration region may not necessarily appear as a straight slope, which corresponds to uniform break up in the acceleration region. In the cases where break up occurs preferentially near the emission region or perhaps closer to the extractor, the measured signal will not be a straight line.
3.3.2 Experimental Apparatus

The sample RPA signals shown in Figures 3-6 – 3-8 are idealized. There are several non-ideal effects that can occur when making RPA measurements. The first is that the retarding grids may not produce a completely uniform region of a given potential. If the grid is fairly coarse, the value of the potential between the wires that make up the grid will be less than that close to the wires. When the potential is less than expected in some regions, the ions that should have been stopped by the applied potential can still make it to the detector. This is called sagging, which causes some spreading in the RPA features and shifts the RPA curve to higher potentials [2]. This effect is remedied by using finer grids at the expense of the signal strength; the signal is decreased because more signal is blocked by the lower transparency grids.

Another major effect occurs because the grids typically have planar geometry and the beam expands spherically outward. This results in the spreading of the RPA features [2]. On-axis ions have their kinetic energy completely in the axial direction, which requires the application of the full accelerating potential to the retarding grids to stop them from getting to the detector. Ions that are not on-axis will have a fraction of their kinetic energy directed perpendicular to the axial direction. The grids only need to stop the ions from moving in the axial direction to keep them from getting to the detector. Therefore, since off-axis ions have less than the full accelerating potential energy in the axial direction, a potential less than the source potential can stop the ions. This means that ions with the same kinetic energy will be stopped at slightly different potentials and thus results in the spreading out of the steps in the RPA curves. Figure 3-9 shows an ideal RPA curve for a monoenergetic beam with beam spreading.
Spreading is more difficult to counteract than sagging. One way to remove the effects of spreading is to collimate the beam with an electrostatic lens. However, this method is not suitable for studying the fragmentation properties of ILIS beams because the high voltage used to focus the beam could induce fragmentation and modify the energy distribution. Another way to counteract spreading is to make an RPA detector that has spherical geometry. Making spherical grids is very challenging so this method was not employed. Instead, an aperture was placed in front of the planar grids so that a small solid angle of the beam is sampled. Equation 3.4 shows how much spreading can occur for a given beam spread angle:

$$\frac{V_{\text{min}}}{V_0} = \cos^2 \theta_B$$

(3.4)

where $\theta_B$ is the half angle spread of the beam and $V_{\text{min}}$ is the minimum voltage for which spreading can occur. The minimum voltage for which spreading can occur for a 20° half angle beam is 0.88$V_0$. For a 3/16" aperture placed 1 cm from the source, the minimum voltage increases to 0.95$V_0$. Using an aperture reduces the effect of spreading enough so that the major RPA features can be identified.

Figure 3-10 shows a diagram of the RPA setup.
The grounded grid and the electron repelling grid are both coarse since the flatness of the potential for these grids is not as critical as that for the retarding grids. There are four retarding grids made from stainless steel plates, each with a large aperture, with parallel tungsten wires spot welded across the aperture \( [7] \). The grids are placed such that the direction of the tungsten wires of one grid are oriented at a right angle to those of the grid next to it. Figure 3-11 shows photos of the RPA used in this work.

![RPA Detector Diagram](image)

Figure 3-10: RPA Detector Diagram \([3]\)

**3.3.3 Data Acquisition**

The current collected by the Faraday cup was amplified using a current amplifier. The output of the current amplifier was measured and recorded with an oscilloscope. A signal generator was used to control the waveform of the high voltage power supply.
to create a high voltage triangular wave for the retarding grids. The oscilloscope was triggered to the triangular wave so that the current signal could be averaged a few times before the data was recorded. Table 3.3 shows the apparatus required for the RPA experiments.

Table 3.3: Instruments Used for RPA Measurements

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matsusada (AMS-5B6)</td>
<td>High voltage for RPA retarding grids</td>
</tr>
<tr>
<td>Agilent Signal Generator (33220A)</td>
<td>Control signal for Matsusada to scan retarding grids</td>
</tr>
<tr>
<td>Keithley Current Amplifier (428-PROG)</td>
<td>Amplify current collected from the Faraday cup</td>
</tr>
<tr>
<td>Agilent Oscilloscope (Infinium 54835A)</td>
<td>Measure and record RPA and retarding voltage signals</td>
</tr>
<tr>
<td>DC Power Supply (RSR HY3005F-3)</td>
<td>Voltage for secondary electron repelling grid</td>
</tr>
</tbody>
</table>

3.4 Time of Flight Mass Spectrometry

Time of flight mass spectrometry provides the composition of the ion beam. Additionally it can yield the fraction of current from each species that fragments in the acceleration region. The ions in ILIS beams have the same kinetic energy, except for those produced from fragmentation events. The beam consists of monomers and solvated ions, which have dramatically different masses and thus exit the acceleration region at different velocities. Since various ion species have different velocities, they can be distinguished by their flight times along some distance. Therefore the ion beam composition can be deduced by measuring the current collected by a detector, placed far from the source, as a function of time.
Fragmentation of solvated ions in the acceleration region complicates the time of flight signal. When a solvated ion breaks up in the acceleration region, the broken ion will be accelerated to a slower final velocity than if it had been produced at the tip of the needle. Since solvated ions can break up anywhere in the acceleration region, the broken ions will be accelerated to a spread in final velocities. This means that the fragmented ions of a given species will have a spread in flight times rather than a single, distinct flight time. Despite this, the current fraction from fragmented ions is easily measured from the time of flight signal. Additionally the distribution of fragmentation inside the acceleration region with respect to the potential can be determined.

### 3.4.1 Theory

The velocity of an ion electrostatically accelerated through a given potential is given by Equation 1.1. The flight time to travel through some distance $d$ is given by Equation 3.5.

$$t = d \sqrt{\frac{m_i}{2q_i V_0}}. \quad (3.5)$$

When a solvated ion breaks up, the broken ion is accelerated to a different velocity than that given by Equation 1.1. By the conservation of energy, the velocity of the broken ion, $v_{bi}$, is:

$$v_{bi} = \sqrt{\frac{2q_i V_0}{m_i} \left(1 - \frac{V_B}{V_0} \left(1 - \frac{m_i}{m_{pi}}\right)\right)} \quad (3.6)$$

The flight time of the broken ion is given by Equation 3.7.

$$t_{bi} = \frac{d}{\sqrt{\frac{2q_i V_0}{m_i} \left(1 - \frac{V_B}{V_0} \left(1 - \frac{m_i}{m_{pi}}\right)\right)}} \quad (3.7)$$

For example, when a dimer breaks up into a monomer somewhere in the acceleration region, that monomer will be accelerated to a final velocity slower than monomers
that are emitted from the tip directly. If the dimer breaks up close to the emission region, the final velocity of the broken monomer will be close to the monomer velocity. If the dimer breaks up towards the end of the acceleration region, the final velocity of the broken monomer will be close to that of the dimers.

The beam composition can be determined by measuring the current collected by a detector as a function of time. Based on Equation 1.1, it is clear that the monomers are the first ions to arrive at the detector because they are the fastest. Then, assuming that there is no fragmentation, the dimers arrive at a later time because their velocity is slower. An ideal time of flight measurement for a monoenergetic beam is shown in Figure 3-12. Note that this data is synthetic and is not from a real measurement.

![Ideal Time of Flight Measurement of a Monoenergetic Beam](image)

Figure 3-12: Ideal Time of Flight Measurement of a Monoenergetic Beam

This synthetic time of flight curve corresponds to EMI-BF$_4$ in the positive mode with an applied voltage of 1500 V and a flight distance of 0.8 m. The beam consists of only monomers and dimers; there are no fragmented species. The beam composition can be determined by the current fractions indicated in Figure 3-12, in this case the beam consists of 50% monomers and 50% dimers.

The effect of fragmentation is shown in Figure 3-13, where 50% of the dimers fragment in the acceleration region.
The signature from the fragmentation of dimers into monomers is distinct. In this case, the fragmentation of dimers into monomers occurs uniformly in the acceleration region. This means that there is no preferred potential for fragmentation to occur. This assumption is not necessarily correct, although it has been supported in the literature [6].

With a fast time of flight detector, the distribution of break up with respect to the potential in the acceleration region can be determined. The derivative of the time of flight signal with respect to time yields the distribution of current for each species of ion. Therefore the derivative of the fragmentation current signal is the distribution of fragmentation in the acceleration region.

3.4.2 Experimental Apparatus

A time of flight mass spectrometer typically consists of a gate, used to interrupt the ion beam, and a detector, used to measure the current. A diagram of a time of flight setup is shown in Figure 3-14.
When the beam is interrupted, no current is measured at the detector. When the gate is reopened, the current measured at the detector is the time of flight signal. The beam is periodically interrupted, such that the time of flight signal can be averaged over many cycles. The challenges of making time of flight measurements arise from low signal strength at the detector and slow electronic response time. To increase the flight times and reduce the requirements on the measurement electronics, the flight distance can be increased; however this reduces the magnitude of the current collected at the detector.

One way to have both a long flight distance and good signal strength is to use a large metal collector plate. The current collected is measured by an electrometer with a fast response time. The major issue with this method comes from the fact that ILIS beams expand spherically outward. Typically the spread in the beam is approximately a 20° half angle. The ions travelling axially arrive at the detector sooner than those that travel off-axis; the off-axis flight distance is longer which makes the flight time longer. This means that ions of a single species will have a spread in flight times. Depending on the goal of the time of flight measurements, this may not be an issue; however for measuring the fragmentation signal, this is not an acceptable design.

To avoid spreading in the time of flight signal due to the spread of the beam, a smaller detector area should be used. The current density arriving at the detector can be very low, depending on the flight distance. This requires the use of an amplifier to increase the signal strength before the measurement is recorded with an oscilloscope.
High gain, high bandwidth amplifiers exist, but they may not be able to provide the required gain with a fast enough response time. In the case where only tens of picoamps are collected by the metal plate, a fast electrometer or a basic non-inverting amplifier with gain is not sufficient.

An electrostatic lens can be used to focus the full current of the beam onto the small metal plate. This greatly reduces the gain requirement on the measurement electronics and removes the spread in the beam. Unfortunately electrostatic lenses involve applying high voltage to the ion beam, which could induce fragmentation inside the lens \[ T \]. Another issue is that electrostatic lenses focus the beam based on the energy of the ions \[ T \]. Ions from fragmentation events have lower energies than those of unfragmented species. Therefore if the lens is tuned to focus the unfragmented species, the lower energy components of the beam will be defocused and will not be measured at the detector. Thus to study the fragmentation properties of different ionic liquids, an electrostatic lens should not be used. This places challenging requirements on the detector and electronics.

Instead of using a metal plate for a detector, an electron multiplier with a small entrance aperture can be used. Electron multipliers have very high gains, so even if the current reaching the detector is very low, the output current of the electron multiplier can still be high enough to measure. There are several types of electron multipliers including Channeltron electron multipliers (CEM) and micro-channel plates (MCP). The detector selected for these experiments is a Channeltron electron multiplier. The output signal from the CEM is only a few microamps of current, so a fast non-inverting amplifier with gain is used to amplify the signal before measuring with an oscilloscope.

**Gate**

Several types of gates are used for electrospray time of flight experiments: stopping, deflector, and interleaved comb. A stopping gate consists of a fine grid that is biased to a high enough potential to completely stop the ion beam from travelling through the gate. This imposes constraints on the allowed potentials used to operate the
source. A deflection gate uses deflector plates biased to high voltage to turn the ion beam away from the detector. An interleaved comb gate is basically several very thin deflector gates placed next to each other, which allows for effective interruption of a spread out beam.

The deflector gate has a very simple design and does not impose strong constraints on the operating voltage of the source, which is why this type of gate was selected. A diagram of a deflector gate is shown in Figure 3-15.

![Diagram of a deflector gate](image)

Figure 3-15: Side View of Deflector Gate

The angle through which the beam is deflected is given by Equation 3.8:

$$\theta_d = \arctan \left( \frac{L \cdot V_G}{4d \cdot V_0} \right)$$  \hspace{1cm} (3.8)

where $L$ is the thickness of the deflector plates, $d$ is the diameter of the aperture, $V_G$ is the potential between the plates, and $V_0$ is the voltage applied to the source. The deflection angle is $7.2^\circ$ for a plate thickness of 0.1", an aperture of 0.25", a gate voltage of 1900 V, and a source voltage of 1500 V. The required deflection angle is given by Equation 3.9, which depends on the aperture size of the detector and the flight distance:

$$\theta_{\text{required}} = \arctan \left( \frac{d}{2L} \right)$$  \hspace{1cm} (3.9)

where $d$ is the diameter of the detector entrance and $L$ is the flight length. The required deflection angle for a detector aperture of 0.25" and a flight length of 0.8 m
is approximately 0.23°. Therefore the gate design presented above is sufficient for use with the detector. Figure 3-16 shows photos of the deflector gate used in this work.

![Deflector Gate](image)

**Figure 3-16: Deflector Gate**

After performing several time of flight experiments, it was found that the needle did not consistently fire axially. Instead, sometimes the ion beam was off-axis which resulted in less signal, or none at all, measured at the time of flight detector. This occurred because the angular current distribution of the ion beam is not uniform. The angular current distribution approximately follows a parabolic shape with the maximum current at the center of the beam \(^1,1^7\). When the center of the beam reaches the detector, the measured signal is strong. If the beam is off-center, the tails of the ion beam reach the detector, resulting in a low signal. The angular species distribution of an ILIS beam has not been studied. If it is not uniform, off-axis measurements will be different from on-axis measurements. This could make interpreting the results from different experiments difficult. A set of deflector plates was installed in front of the time of flight gate to ensure that the center of the beam is sampled by the detector.

Figure 3-17 shows a diagram of the deflector plates. Two sets of plates are used to steer the beam in the two directions perpendicular to the axial direction. The magnitude of the voltage applied to opposite plates is the same, but one plate is biased positive and the other negative to ensure that the potential in the middle of the plates is zero.
The angle through which the plates can deflect the beam is given by Equation 3.8. The required voltage on each plate to turn the beam 10° is about 130 V for a plate length of 1", a plate separation of 0.25", and a source voltage of 1500 V.

By adjusting the voltages applied to the deflector plates, the signal at the detector can be maximized. This is assumed to occur when the center of the beam is reaching the detector. Figure 3-18 shows photos of the final time of flight gate with deflector plates installed.
Detector

The time of flight detector is an electron multiplier. Electron multipliers use tubes coated with silicon oxide, a material that produces electrons when a particle collides with the surface $^{18}$. When an ion enters the detector, it impacts the interior surface of the tube and several electrons are produced. A strong electric field is used to accelerate these electrons down the tube, where they collide with the walls and produce even more electrons. The electron cascade dramatically increases the current and allows for the detection of low ion currents. A diagram of an electron cascade is shown for a single channel CEM in Figure 3-19.

![Diagram of an Electron Multiplier](image)

There are two types of electron multipliers: Channeltron electron multipliers and microchannel plates. CEM’s typically consist of a single tube and have small entrance apertures of about 0.25''-0.5'' in diameter $^{18}$. Microchannel plates (MCP’s) are planar detectors that have many tiny electron multiplier tubes in an array across the surface. MCP’s have much larger collection areas than CEM’s, usually 1-2'' in diameter $^{19}$. Electron multipliers have very high gains, but they have a maximum output current
where the detector saturates. Table 3.4 shows typical gains and maximum output currents for a few types of electron multipliers.

Table 3.4: Typical Characteristics of Electron Multipliers

<table>
<thead>
<tr>
<th>Electron Multiplier</th>
<th>Gain</th>
<th>Maximum Output Current (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM 4700 Series [18]</td>
<td>$10^2 - 10^6$</td>
<td>5-10</td>
</tr>
<tr>
<td>CEM 5900 Magnum [20]</td>
<td>$10^5 - 10^8$</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>MCP (single) [19]</td>
<td>$1.5 \times 10^3 - 4 \times 10^4$</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The choice of detector requires that the input current from the source and the gain and saturation current of the detector are compatible. The approximate flight distance for the chamber used in these experiments is 0.8 m. The typical size of the entrance aperture for a CEM is about 0.25" in diameter. This means that the current reaching the detector is approximately 7000 times less than the current of the source. Equation 3.10 was used for this calculation:

$$I_{detector} = \frac{D^2}{8L^2(1 - \cos \theta_B)} I_{source} \quad (3.10)$$

where $I_{detector}$ is the current reaching the detector, $I_{source}$ is the current of the source, $D$ is the diameter of the detector aperture, $L$ is the distance between the source and the detector, and $\theta_B$ is the beam spread angle. This estimation was made by assuming that the beam expands spherically outward and that the current density is uniform across the 20° half angle spread. In reality, the current is not uniformly distributed across the beam [1], but this was ignored for the sake of a simple estimation. For a source current of 200 nA, the current reaching the detector will be about 30 pA. For a saturation current of 1 μA, the maximum gain allowable is about $3.5 \times 10^4$. A small microchannel plate has approximately 16 times the collection area, which means that the maximum allowable gain is $2.2 \times 10^3$. This is below the typical gain for MCP’s, so an MCP should not be used.

The Channeltron 5900 Magnum was selected for use in these experiments. The
5900 is a special type of CEM that has six tubes instead of one; note that the 5900 looks different from the CEM depicted in Figure 3-19. Multiple tubes allow for a much higher gain and saturation current. The characteristics for the CEM used in these experiments are shown in Table 3.5.

Table 3.5: Characteristics of the Channeltron 5900 Magnum.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Output Current</td>
<td>13 μA</td>
</tr>
<tr>
<td>Gain[20]</td>
<td>10⁵ – 10⁸</td>
</tr>
<tr>
<td>Operating Voltage[20]</td>
<td>1500V - 3000V</td>
</tr>
</tbody>
</table>

The minimum gain is 10⁵ [20], and the saturation current is approximately 13 μA, which is known because the CEM was tested by the manufacturer. With a source to detector distance of 0.85 m, the maximum allowable source current is approximately 1 μA. The minimum source current that can saturate the detector is approximately 1 nA. The 5900 can be used with a large range of source currents that cover the spectrum of possible ILIS beam currents, which is why it was selected.

Figure 3-20 shows a photo of the CEM installed in a custom-made housing. The housing is made of teflon since some of the external surfaces of the Channeltron are either at high voltage or carry current.
Amplifier

The positive mode is the simplest configuration for operating the Channeltron. A schematic of the CEM connections for the positive mode is shown in Figure 3-21.

For positive ion detection the front of the Channeltron is biased to high negative voltage and the back is grounded \[18\]. Therefore the collector plate can safely be connected to ground through a termination resistor. In the case of negative ion detection, the collector plate must be biased to high voltage which requires an isolation capacitor between the collector plate and the amplifier \[18\]. The schematic for this
configuration is shown in Figure 3-22.

![Channeltron Electron Multiplier Diagram]

Figure 3-22: Negative Mode Channeltron Circuit

The current output from the Channeltron is approximately 10 μA. This signal needs to be amplified to a level that an oscilloscope can measure and the amplifier must have a high enough bandwidth so that the resolution of the time of flight signal is sufficient. The required resolution is given by Equation 3.11 [7]:

\[
\frac{\Delta t}{t} = \frac{1}{2} \frac{V_0 - V_B}{V_0}
\]  

(3.11)

where \( \Delta t \) is the required time resolution, \( t \) is the average flight time, \( V_0 \) is the source voltage, and \( V_B \) is the potential where a solvated ion broke up in the acceleration region. For example, to be able to detect the difference between monomers with 100% of the applied potential energy and broken monomers with only 95% of the applied potential energy, the required resolution is 2.5%. The estimated flight times are on the order of tens of microseconds so this corresponds to a response time of a few hundred nanoseconds.

Ideally the signal should be about 1 V in amplitude, but 100 mV is also reasonable. Therefore the required gain of the amplifier should be around \( 10^5 \). The simplest way to convert a 10 μA current to a 1 V signal is to terminate the current to ground through a 100 kΩ resistor. However, the response time for this situation is limited by the RC charging time. The coaxial feedthroughs and cables used have an inherent capacitance, approximately 50 pF. The response time for an RC circuit is given by
Equation 3.12 \cite{21}:

\[ t_R = 2.2RC \]  \hspace{1cm} (3.12)

where \( t_R \) is the 10\% to 90\% rise time, \( R \) is the resistance, and \( C \) is the capacitance. Therefore with a capacitance of 50 pF and a resistance of 100 k\( \Omega \), the response time is 11 \( \mu s \), which is much too slow for the required time of flight measurements. Using Equation 3.12, the maximum resistance that can be used for a response time of around 100 ns is about 1 k\( \Omega \). This results in a gain of 1000, which leaves a required gain of about 100 remaining.

The solution is to use a non-inverting amplifier with gain to accomplish the remaining required amplification. Suitable high gain, high bandwidth amplifiers can be somewhat challenging to find. The one selected for these experiments is the Analog Devices AD8067. Some of the characteristics are shown in Table 3.6.

Table 3.6: Analog Devices AD8067 Characteristics \cite{22}

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gain Bandwidth Product</td>
<td>300 MHz</td>
</tr>
<tr>
<td>Settling Time to 0.1%</td>
<td>27 ns</td>
</tr>
<tr>
<td>Input Impedance</td>
<td>( 1000 \ G\Omega \ \parallel \ 1.5pF )</td>
</tr>
<tr>
<td>Output Impedance ((G = 10, 10MHz))</td>
<td>( \sim 3\Omega )</td>
</tr>
<tr>
<td>Bandwidth ((G = 50))</td>
<td>6 MHz</td>
</tr>
</tbody>
</table>

A gain of 50 was used, which should allow for a bandwidth of 6 MHz \cite{22}; this corresponds to a response time of 58 ns. The circuit schematic is shown in Figure 3-23. Note that the capacitors used to stabilize the voltage terminals are not shown. Each power supply pin was connected to a 0.1 \( \mu F \) capacitor and a 10 \( \mu F \) capacitor placed in parallel, terminated to ground. Note that the input capacitance of the amplifier is approximately 50 pF due to the capacitance of the coaxial cables used.
For the negative mode, an isolation capacitor is needed to protect the non-inverting amplifier from the DC high voltage. Using recommendations from Schwartz et al., the capacitance selected is 2.5 nF [23]. The resistor used to connect the high voltage for the Channeltron to the collector plate is 10 MΩ. The amplifier was made using a Texas Instruments evaluation board (p/n 551012875-001/NOPB). Surface mount components were soldered to the evaluation board to create a non-inverting amplifier with gain; note that the isolation capacitor was not a surface mount component. The power for the amplifier was supplied by two 9 V batteries. L7805 and L7905 voltage regulators were used to apply ±5V to the amplifier power terminals. Note that two separate amplifiers were built: one for the positive mode and one for the negative mode. The amplifiers are identical except that the positive mode amplifier does not have the 2.5 pF isolation capacitor.

3.4.3 Data Acquisition

Table 3.7 shows the instruments required for time of flight measurements. The pulse generator for the gate is supplied power by an Acopian power supply. The control signal for the pulse generator is supplied by the Agilent signal generator. The voltage for each deflector plate is provided by several different high voltage power supplies.
The high voltage for the Channeltron was supplied by a Bertran high voltage power supply. The output of the Channeltron was inputted to the custom-made fast amplifier, and the output of the amplifier was sent to the oscilloscope (50 Ω input). The gate signal from the Agilent signal generator was also measured and recorded by the oscilloscope. The oscilloscope measurements were triggered on the gate signal so that the time of flight signal from the Channeltron could be averaged many times.

Table 3.7: Instruments Required for TOF Measurements

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agilent Signal Generator (33220A)</td>
<td>Gate control signal (TTL)</td>
</tr>
<tr>
<td>DEI Pulse Generator (PVM-4210)</td>
<td>Pulse generator for gate plates</td>
</tr>
<tr>
<td>Acopian DC Power Supply (BG25G30)</td>
<td>Supplies voltage for pulse generator</td>
</tr>
<tr>
<td>Matsusada (AMS-5B6)</td>
<td>Two Matsudas provide high voltage for a set of deflector plates</td>
</tr>
<tr>
<td>Acopian Negative High Voltage Power Supply (NO3.5HP17)</td>
<td>Provides voltage for a single deflector plate</td>
</tr>
<tr>
<td>Acopian Positive High Voltage Power Supply (PO3.5HP17)</td>
<td>Provides voltage for a single deflector plate</td>
</tr>
<tr>
<td>Bertran High Voltage Power Supply (230-05R)</td>
<td>Provides high voltage for operating the Channeltron</td>
</tr>
<tr>
<td>Custom-Made Amplifier</td>
<td>Amplifies the output signal from Channeltron</td>
</tr>
<tr>
<td>Agilent Oscilloscope (Infinium 54835A)</td>
<td>Measures and records gate control and Channeltron output signals</td>
</tr>
</tbody>
</table>
Chapter 4

Results and Discussion

Four imidazolium-based ionic liquids were tested using the RPA and TOF apparatuses in order to evaluate the stability of their solvated species. This was done under controlled conditions so the liquids could be compared on an equal basis. RPA and TOF scans were taken at the same set of temperatures across a range of voltages, in 50 V increments, for which the source produced stable emission.

4.1 Source Stability

Current-voltage curves were taken to determine the stable ranges of operation of different ionic liquids. Figure 4-1 shows the current voltage curve for EMI-BF₄ in the positive mode for various liquid temperatures. In this case, a single Taylor cone exists stably for a fairly wide range of voltages, generally between 1400V-1700V. The current increases with increasing temperature because the electrical conductivity of the liquid increases with temperature \(^1\). The source voltage range of stable emission was not as large for all liquids. For example, EMI-Im formed several Taylor cones as the voltage was increased. Figure 4-2 shows the current-voltage curve for EMI-Im in the positive mode at various temperatures. See Appendix A for IV curves for all liquids and for both source voltage polarities.

For the purposes of this work, only the TOF and RPA curves for the single Taylor cone mode were used. The effects of operating in multi-cone mode may be an area of
Figure 4-1: EMI-BF$_4$ IV Curve, Positive Mode

Figure 4-2: EMI-Im IV Curve, Positive Mode
future study. Multi-cone emission is particularly troublesome for RPA measurements because the ions from each cone enter the detector at different angles. This results in a beam spreading effect that can blur the steps from fragmentation in field-free space or create anomalous features. Additionally, there is no guarantee that each cone operates in the same regime. As for time of flight mass spectrometry, operating in multi-cone mode would result in the detector sampling a different solid angle of the ion beam than for the single-cone mode. It is also possible that a mix of species from both cones could reach the detector. The angular distribution of the beam composition is not well characterized. An experiment using the deflector plates was conducted to see how the monoenergetic population varies across the spread of the beam. While no definite conclusions about the distribution can be made at this time, it was clear from the experiment that the composition does vary to some degree. Comparing the results from multi-cone emission to single-cone emission may not be straightforward, thus single-cone emission is the focus of this work.

4.2 Time of Flight Mass Spectrometry

The time of flight detector was operated in nearly the same way across all experiments. The gate was pulsed to $\pm 950$ V at a frequency of 500 Hz. The channeltron voltage was set somewhere between -1800 V and -1900 V depending on the strength of the signal at the detector. The same non-inverting amplifier was used for all experiments. The oscilloscope acquired 8192 points across the set time range and averaged the scans 4096 times. Two time ranges were used, each of which corresponded to a different acquisition rate: 25 MSa/s for the shortest time range and 10 MSa/s for the longer time range. The shorter time range, approximately 300 $\mu$s in width, was used to get a high resolution scan of the ion population and the longer time range, approximately 500 $\mu$s in width, was used to capture the droplet tail if present.

The deflector plates were kept grounded since the beam was on-axis for the most part. Electrostatic deflection plates deflect the ions to some angle based on the energy of the ion. Since the fragmented species have lower energies than the monoenergetic
population, they will be deflected to a different angle. This modifies the relative fractions of the beam constituents as measured by the time of flight detector. Using the deflector plates is good to determine the angular distribution of the composition of the monoenergetic population, but their use is not ideal for studying the fragmented population. This is a topic that requires careful study and is discussed as an area of future work in Chapter 5.

Time of flight spectra were taken for the positive mode only due to difficulties with the negative mode amplifier. The negative mode amplifier detailed in Chapter 3 was successfully built and tested. The positive mode spectra measured by the negative mode amplifier was in sufficient agreement with that measured by the positive mode amplifier. Negative mode time of flight spectra were taken for some of the ionic liquids tested for this thesis; however the amplifier failed before all liquids were tested. Although the exact failure mechanism is not well understood at this time, it likely has to do with the lack of proper isolation from the high voltage applied to the Channeltron. Improvements will be made in the future so that the negative mode can also be studied.

4.2.1 Source Stability Range

Using the measured source voltage and current for each TOF spectra for a given liquid, an IV curve can be reconstructed to see how the source was behaving. Figure 4-3 shows the reconstructed IV curve for the EMI-BF$_4$ time of flight data. For completeness the reconstructed IV curve for the EMI-Im time of flight data is shown in Figure 4-4. The sudden rise in current associated with the onset of multi-cone mode is apparent for EMI-Im. The data points for single-cone mode were the only ones used in the subsequent analysis. The reconstructed IV curves from the TOF data for all liquids is shown in Appendix A.
Figure 4-3: EMI-BF$_4$ TOF IV Curve

Figure 4-4: EMI-Im TOF IV Curve
4.2.2 Data Processing

The raw time of flight curve was calibrated using a time of flight scan in which the source was turned off. The non-inverting amplifier has an inherent voltage offset which is easily removed by subtracting the calibration curve. The pulse generator causes a distinct, repeatable ringing signature within the first few microseconds of the TOF scan, which is also reduced by subtracting the calibration. This does not have a significant impact on the TOF curve because the ions do not arrive until after about 10 μs. A final calibration is to subtract 90 ns from the flight times to account for the approximate delay of the pulse generator. Once the curve has been calibrated, it is normalized so that the current fractions can easily be read from the curve. The zero current point is determined by averaging the signal between 0 μs and 10 μs, which is subtracted from the TOF signal. The maximum current occurs at the longest flight times, so the TOF signal from the last 10 μs is averaged to estimate the maximum signal value. The TOF curve is then divided by this averaged maximum value to normalize the curve.

A normalized TOF curve for BMI-I at 90°C and 1500 V is shown in Figure 4-5. The arrival times of the monomers and dimers are labeled. No droplets are present, so the source is said to be operating in the Pure Ionic Regime (PIR) [10]. The slope between the arrival of the monomers and the arrival of the dimers is not due to slow electronic response time. The response time of the amplification system is on the order of a few hundred nanoseconds, so this slope is actually due to the dimers that fragment in the acceleration region. A closer view of the ionic TOF curve is shown in Figure 4-6. The fragmented dimers and fragmented trimers are labeled. The shape of the fragmentation TOF signal indicates whether or not the break up of solvated ions occurs uniformly with respect to the accelerating potential. The break up of dimers into monomers does not quite look like the expected shape for uniform break up as shown in 3-13. Further study is required to determine the distribution of break up using higher resolution, better quality TOF curves.
Figure 4-5: BMI-I TOF Curve (90°C, 1500 V)

Figure 4-6: BMI-I TOF Curve, Zoom (90°C, 1500 V)
By carefully measuring the heights of the steps of the TOF curves, the current fractions of the different species can be determined. The following quantities were measured: monomer current fraction, fragmented dimer current fraction, dimer current fraction, fragmented trimer current fraction, and trimer current fraction. This process became complicated when the mixed ion-droplet regime was observed, namely for EMI-Im and EMI-MPI at higher temperatures. See Appendix B for a sampling of TOF curves of the different liquids. A cutoff time was defined to differentiate between the ion population and the droplet population. The pentamer flight time was used as this cutoff, since the production of highly solvated ions is very small compared to that of monomers and dimers. The value of the normalized TOF signal at this cutoff was used to determine the current fractions relative to the current fraction of ions. This removes the effect of the droplet current fraction on the current fractions of the different ion species so that these quantities for different liquids can be compared in a more useful manner.

Once the relative current fractions of the ionic species were determined for each TOF curve, they were averaged across a narrow voltage band for a given temperature and liquid. The voltage band corresponds to voltages for which stable emission was observed for all liquids at all temperatures, which was approximately between 1400V-1500V. This was done so that the quantities for each liquid could be easily compared at a given temperature. Each liquid is assigned a complexity factor, which is simply the number of atoms in an anion. This is an over-simplified way of determining the complexity, but for the purposes of this work it is sufficient. The relevant quantities, like the dimer fragmentation percentage, can be plotted as a function of this complexity factor at a given temperature. This is the focus of the next sections.

4.2.3 Ion Population Fractions

A few common trends across the different ionic liquids were observed regarding the relative fractions of different ion populations. See Appendix B for supplementary plots that are described in this section. For all ionic liquids, the monomer current fraction of ions tends to decrease with increasing temperature. The total dimer cur-
rent fraction of ions, which includes the fragmented dimers, tends to stay nearly constant or increase slightly with increasing temperature. The trimer current fraction of ions, which includes the fragmented trimers, tends to increase slightly with increasing temperature. The monomer to total dimer ratio tends to decrease with increasing temperature. The current fraction of ions from fragmented species, which includes fragmented dimers, fragmented trimers, as well as heavy fragments that have flight times between the trimer time and the pentamer time, tends to increase with increasing temperature. The effect of temperature on the dimer fragmentation percentage is less clear. Most liquids show a decrease with increasing temperature, but the dimer fragmentation percentage for EMI-BF$_4$ remains constant across 30°C - 70°C and then increases at 90°C.

It is important to note that the dependence on temperature is not isolated from the dependence on emitted current. Increased temperature can dramatically increase the current at constant voltage, which means that these quantities vary with both temperature and current. It is not clear which has the stronger effect, although an argument can be made for the current being the more important factor since it varies over a much larger range than the liquid temperature. Future work should be conducted to isolate the effects of temperature and current on the ion beam composition and fragmentation characteristics.

BMI-I has the highest monomer current fraction of ions across all temperatures except for 30°C because it does not fire consistently at lower temperatures. EMI-Im has the lowest monomer current fraction of ions across all temperatures. EMI-BF$_4$ and EMI-MPI show an intermediate amount of monomers. EMI-Im has the largest total dimer current fraction of ions across all temperatures. The dimer fractions for other liquids are similar across all temperatures, although BMI-I and EMI-MPI tend to have the lowest. EMI-Im also has the highest ion current fraction of trimers, which includes fragmented trimers, across all temperatures. BMI-I and EMI-BF$_4$ tend to have the least trimers. EMI-Im has the lowest monomer to total dimer ratio while BMI-I has the highest. EMI-Im has the highest total fragmentation current fraction of ions across all temperatures, although at higher temperatures all liquids have similar...
total fragmentation fractions.

4.2.4 Analysis of Solvated Ion Stability

The stability of positive dimers can be estimated by the percentage of dimers that undergo fragmentation in the acceleration region. The current fraction of fragmented dimers is not sufficient to determine the stability because this quantity depends on the total current fraction of dimers emitted from the tip. The total current fraction of dimers emitted from the tip is the sum of the current fraction of dimers that fragment in the acceleration region and the current fraction of dimers that survive the acceleration region. Therefore the figure of merit for estimating the stability of dimers is the current fraction of fragmented dimers divided by the current fraction of all dimers. The dimer fragmentation percentage is shown as a function of ionic liquid complexity at 70°C in Figure 4-7. The voltage band at 30°C and 50°C is 1400V-1500V and at 70°C and 90°C is 1400V-1450V. Note that the error bars are the standard deviation of the points averaged in the voltage band. See Appendix B for data at other temperatures.
Figure 4-7: Dimer Fragmentation Percentage for All Liquids at 70°C [3]

It is clear from Figure 4-7 that BMI-I has the largest dimer fragmentation percentage in the acceleration region out of all of the ionic liquids tested. EMI-BF₄ shows a lower dimer fragmentation percentage than BMI-I and a higher dimer fragmentation percentage than EMI-Im. This is in agreement with the past observations discussed in Chapter 2. Based on the hypothesis, one would expect EMI-MPI to show the lowest dimer fragmentation percentage; however this is not what is observed. Instead EMI-MPI shows a dimer fragmentation percentage somewhat larger than EMI-BF₄. This trend is also observed at other temperatures.

One of the major limitations of the TOF detector is the fact that it only samples a very small solid angle of the beam. The TOF curves do not measure the full-beam population of ions and instead only provide the populations for a tiny section of the beam. It has yet to be determined how well the small solid angle represents the full beam. Past experiments indicate that the relative ion populations vary angularly across the beam. This means that if the beam is not perfectly on-axis with the TOF...
detector, the ion populations measured may not be the same as that for the high current density center of the beam. While deflector plates can be used to ensure that the center of the beam is pointed onto the TOF detector, they disturb the relative populations of ions with different energies. So for this work, the deflector plates were not used other than to check how well the beam was centered on the detector. For the most part, having the deflector plates grounded maximized the current measured at the TOF detector. However it is possible that in some cases the beam was off-axis and the TOF detector was sampling the fringes of the ion beam.

In the case of EMI-MPI, perhaps the beam was slightly off-axis and the TOF detector sampled the edges of the beam where fragmented species could be more abundant. This would result in a higher than expected percentage of fragmented dimers relative to measurements made by sampling the center of the beam. Unfortunately it is challenging to get ILIS beams that are on-axis. While using the same emitter across all experiments improves the probability that the same portion of the beam is sampled, it does not guarantee it. The needle is removed from the setup every time a new liquid is used, which means that the needle was in slightly different positions for each experiment. Therefore, the data presented in this work is not sufficient to determine the validity of the hypothesis due to these limitations. Further experiments are required to evaluate the validity of the hypothesis which are the subject of Chapter 5. Retarding potential analysis can provide more insight by supplementing the TOF data, which is the subject of the next section.

### 4.3 Retarding Potential Analysis

The retarding potential analyzer was operated in the same way for all experiments. The retarding grid voltage was varied using a triangular wave with a 5 s period, the amplitude of which varied slightly depending on the operating voltages of the source. The electron repelling grid was set to approximately -10 V in all cases. The current amplifier was set with a gain of either $10^7$ or $10^8$ depending on how much signal was measured by the Faraday cup. The oscilloscope was set to sample at 1 kSa/s and 6000
points across all experiments. Each scan on the oscilloscope includes two RPA scans: one where the retarding grid voltage is rising and another where the retarding grid voltage is falling. When the source was sufficiently stable, averaging could be done using the oscilloscope. The number of averages ranges from 5 to 20 depending on how well-behaved the source was. If the source was not well-behaved, meaning that the emission would shut off briefly during the timescale of the RPA scan, single scans where the source was stable were saved and later averaged together using MATLAB code. These averaged RPA scans were later calibrated and used to determine the stability of dimers of both polarities.

4.3.1 Source Stability Range

In the same fashion as the time of flight analysis, reconstructed IV curves were made for the RPA results. Figure 4-8 shows the reconstructed IV curve for the EMI-BF$_4$ positive mode RPA data. The IV curve is very smooth with no discontinuities, which indicates that the source was operating in single-cone mode. This is the desired mode of operation for retarding potential analysis. The reconstructed IV curves from the RPA data for all liquids are shown in Appendix C.
4.3.2 Data Processing

There are several steps required to calibrate the RPA curves and smooth them so that they can be used to determine the dimer fragmentation fraction. The time varying high voltage on the retarding grids induces a capacitive current in the measured signal. This is easily removed by taking an RPA scan for when the source is off. The capacitive current for the rising retarding potential and for the falling retarding potential were estimated by taking the average current of the calibration curve in the appropriate time range. These quantities were simply subtracted from the appropriate RPA signals. The measured retarding grid voltage had a small amount of inherent noise, so a line was fitted to the measured voltage to smooth it out. Finally each calibrated RPA curve was averaged into 5 V bins to smooth out the curve. Figure 4-9 shows an RPA scan for BMI-I at 90°C and 1750V.

Figure 4-8: EMI-BF₄ Positive RPA IV Curve
Unfortunately the RPA data was far from ideal, and the only useful quantity that can be gleaned from the data is the dimer fragmentation fraction in field-free space. One major problem was the lack of perfect alignment between the RPA entrance aperture and the extractor hole. Due to some design issues, the RPA and extractor were misaligned by a few millimeters. The misalignment is on the order of the RPA aperture size, which means that the full center of the beam probably was not captured by the detector. The aperture did not help with the beam spreading as much as hoped, which means that the current distribution of ions with slightly less energy than the source potential could not be studied. The aperture ended up hurting the quality of the results because of the lower signal measured by the Faraday cup. Also there were anomalous features, like rises and dips in the collected current that were present for intermediate retarding voltages. This may be the result of some sort of electrostatic focusing and defocusing effect from the high voltage retarding grids. The slopes from fragmentation in the acceleration region were superimposed on these anomalous features, making it impossible to distinguish them. The only feature that remained
intact was the step associated with the fragmentation of dimers into monomers in field-free space. Figure 4-10 shows the step height marked by red horizontal lines. The black vertical line shows the normalized voltage corresponding to the energy of dimers that fragment into monomers in field-free space.

![Figure 4-10: BMI-I Positive RPA Curve with Marked Step (90°C, 1750 V)](image)

The step height for the fragmentation of dimers into monomers in field-free space was measured for each RPA curve. This was difficult to determine in some cases because of beam spreading. The spreading out of the step makes it challenging to determine exactly where the step begins and ends. This provides further motivation to construct an improved RPA detector. In most cases, the RPA current did not go to zero at voltages past the source voltage. The base current at these high voltages was determined so that it could be used to calculate the total collected beam current. In almost all cases, the collected current continued to increase past the dimer to monomer step with decreasing retarding grid voltage. This is not a true feature of the ionic energy distribution and it has been seen in past experiments[^14]. Because of
this, the peak current of the RPA curve was not used to determine the total collected beam current and instead the top of the dimer to monomer step was used as the maximum collected beam current. Thus the total collected beam current is the top of the dimer to monomer step minus the base current found at high voltages. The current fraction of fragmented dimers in field-free space can then be determined by dividing the step height by the calculated maximum collected beam current.

Through the analysis of the RPA curves, it was determined that the EMI-BF₄ dataset was anomalous. EMI-BF₄ is a very well tested ionic liquid [1, 10, 14], so the general characteristics of EMI-BF₄ RPA curves are known. The RPA curves from this work show a significant low energy population and a severely depleted monoenergetic population, which is highly unusual. Additionally, the step for the fragmentation of dimers into monomers in field-free space is unusually large. This could be the result of the misalignment of the RPA detector aperture and the source extractor hole. If the beam fired off-axis in an unfavorable direction relative to the misalignment, perhaps only the fringes of the ion beam entered the RPA. As discussed in the previous section, the fringes of the beam may have a higher fragmented population than the center of the beam, which could explain the high abundance of low energy ions. Fortunately some older EMI-BF₄ data that was taken using the same needle, temperatures, voltages, and detectors was available for analysis. The reason that this older data was not included in the original dataset was because the TOF data was low quality and was not sufficient for the required analysis detailed in the previous section. This is why EMI-BF₄ was tested again to obtain better quality TOF data and RPA data under the exact same conditions. The older EMI-BF₄ dataset was processed using the same method described in this section and is included in subsequent analysis. Note that the RPA curves for this older dataset were taken with an 8 s retarding grid period rather than a 5 s period.

4.3.3 Analysis of Solvated Ion Stability

It was found that the current fraction from the fragmentation of dimers into monomers in field-free space did not vary strongly with the source voltage. Therefore this quan-
tity was averaged across all voltages for each liquid at each temperature. Figure 4-11 shows the current fraction of fragmented positive dimers in field-free space as a function of the ionic liquid complexity factor at 70°C. The older dataset of EMI-BF$_4$ is labeled by the date it was taken: 4/10.

Figure 4-11: Positive Dimer Fragmentation Fraction at 70°C (Field-Free Space) [3]

Figure 4-12 shows the current fraction of fragmented negative dimers in field-free space as a function of the ionic liquid complexity factor at 70°C. See Appendix C for plots at other temperatures.
The first observation from Figures 4-11 and 4-12 is that EMI-Im and EMI-MPI show the lowest current fraction of fragmented dimers in field-free space. The original EMI-BF$_4$ data shows a very large dimer fragmentation current fraction, which did not come as a surprise since the RPA curves were highly unusual. The older dataset for EMI-BF$_4$ taken on 4/10 shows a lower fragmentation fraction than the anomalous dataset, which makes sense because the RPA curves from the older dataset looked like what was expected for EMI-BF$_4$. Finally BMI-I shows a moderate fragmentation current fraction, which is actually less than that for both EMI-BF$_4$ datasets. Note that the same trends were observed at other temperatures.

It is critical to stress that the current fraction from fragmented dimers in field-free space is not a good way to evaluate the stability of dimers because this quantity is dependent on the current fraction of dimers that survive the acceleration region. The current fraction of dimers that survive the acceleration region is likely not the same for all liquids. Figure 4-13 shows the ion current fraction of positive dimers that...
survive the acceleration region as a function of the ionic liquid complexity factor at 70°C.

![Graph showing current fraction of dimers that survive the acceleration region as a function of the number of atoms (anion).]

Figure 4-13: Current Fraction of Dimers that Survive Acceleration Region (70°C)

It is apparent from 4-13 that different liquids have different current fractions of dimers that survive the acceleration region. Most importantly, it can be seen that EMI-BF$_4$ has a higher current fraction of surviving dimers than BMI-I. This may offset the higher current fraction of fragmented dimers in field-free space for EMI-BF$_4$ as shown in Figures 4-11 and 4-12.

The current fraction of dimers that survive the acceleration region is also the current fraction of dimers that can break up in field-free space. Therefore to test the stability of dimers in field-free space, the current fraction of fragmented dimers in field-free space should be divided by the current fraction of dimers that survive the acceleration region. Unfortunately the time of flight data is only available for the positive mode, so only the positive RPA data can be corrected to evaluate the stability of dimers in field-free space. As mentioned in the previous section, high quality TOF
data is not available for the older EMI-BF4 dataset. It is not unreasonable to use the TOF data from the more recent EMI-BF4 dataset because the experiments were taken under nearly the same conditions. The anomalous RPA data was likely caused by the misalignment of the RPA detector, which would not affect the TOF measurements. Thus the newer TOF data was used with the older RPA data in order to get an estimate of the fragmentation percentage of dimers in field-free space for EMI-BF4. Figure 4-14 shows the fraction of dimers that survived the acceleration region that break up in field-free space as a function of the ionic liquid complexity factor at 70°C. See Appendix C for the results at other temperatures.

Figure 4-14: Positive Dimer Fragmentation Percentage in Field-Free Space (70°C) [3]

Figure 4-14 shows that BMI-I has the highest fragmentation percentage, disregarding the anomalous EMI-BF4 data. The older EMI-BF4 dataset has a lower fragmentation percentage than BMI-I. EMI-Im and EMI-MPI show the least fragmentation percentages. It appears that EMI-Im may show a slightly higher fragmentation
percentage than EMI-MPI. Note that the same trends are observed at different temperatures. The corrected data supports the past observations and the hypothesis that more complex ionic liquids fragment less. However this result cannot be used to conclusively validate the hypothesis due to the instrumental limitations and the mixing of datasets. The RPA detector does not collect the full current of the beam, so like the TOF detector, it is vulnerable to the non-uniform angular beam composition. For the hypothesis to be tested with high confidence, full-beam RPA data is required, which is discussed further in Chapter 5.
Chapter 5

Conclusions and Future Work

Ionic liquid ion sources produce beams with diverse ion populations. Single ions, or monomers, and singly solvated ions, or dimers, are the most abundant ions in ILIS beams. Highly solvated species such as trimers and tetramers are less common. Solvated species are metastable and can fragment into lighter ions and charge neutral clusters of ions. Past experimental work has shown that the amount of fragmentation depends on the ionic liquid\textsuperscript{[6]}. It has been hypothesized that molecularly complex ionic liquids will fragment less than molecularly simple ionic liquids\textsuperscript{[6]}. The goal of this work was to investigate the validity of this hypothesis by testing several different ionic liquids under controlled conditions. Time of flight mass spectrometry was used to determine the beam composition and to detect fragmentation in the acceleration region. Retarding potential analysis was used to measure the beam energy distribution and to study the fragmentation in field-free space.

Time of flight mass spectrometry was used to determine the fraction of positive dimers that undergo fragmentation in the acceleration region. It was found that BMI-I has the highest percentage of fragmented dimers in this region. EMI-BF\textsubscript{4} has a lower percentage, and EMI-Im has the lowest percentage. The results for these three liquids are in agreement with the observations of past experiments. The observed trend agrees with the hypothesis that complex ions fragment less. However EMI-MPI was an outlier and showed a higher percentage of fragmented dimers than EMI-BF\textsubscript{4}. One of the major limitations of the time of flight detector is that it samples
a small solid angle of the beam. It is very likely that the beam composition is not angularly uniform, so if the beam is slightly off-axis, the measured relative abundances of different species will be different from that in the center of the beam. It is possible that the beam was off-axis for the EMI-MPI TOF measurements, which could result in a higher than expected population of fragmented species. The fact that the TOF detector does not measure the composition of the full beam means that the results cannot be used to evaluate the hypothesis with high confidence. Further work is required to determine the angular beam composition and the effect it could have on these results.

Retarding potential analysis was used to determine the fraction of dimers that fragment in field-free space. The current fraction of dimers that fragment into monomers in field-free space was measured from the RPA curves. This quantity is not sufficient to compare the fragmentation properties of different liquids because it depends on the current fraction of dimers that survive the acceleration region. Using the TOF data, it was found that different liquids have different current fractions of dimers that survive the acceleration region. For the positive mode only, the current fraction of dimers that fragment in field free space was normalized by the current fraction of dimers that survive the acceleration region. This quantity is sufficient for comparing between the different liquids and indicates which liquids have the most stable solvated species.

It was found that BMI-I has the highest percentage of dimers that fragment in field-free space and both EMI-Im and EMI-MPI have the lowest percentages. The results for EMI-BF₄ are less reliable because the RPA dataset was highly unusual in that low energy ions dominated the energy distribution. EMI-BF₄ is a very well characterized ionic liquid [1, 10, 14], so it was clear that the anomalous results were in fact anomalous. A different, more reliable EMI-BF₄ dataset was included in the analysis, with some caveats as detailed in Chapter 4. It was shown that EMI-BF₄ has a dimer fragmentation percentage in field-free space lower than BMI-I and higher than EMI-Im and EMI-MPI. Therefore the RPA analysis supports the hypothesis and is in agreement with past observations. However since the RPA detector did not measure
the full beam current, these results cannot be used to validate the hypothesis.

The results of both the TOF and RPA measurements tend to support the hypothesis, with some caveats. Unfortunately these results cannot be used to validate the hypothesis due to the limitations of both detectors. Instead future work is required to obtain unambiguous data. An RPA detector that measures the full beam current would ensure that the data would be unaffected by the angular dependence of the beam composition. The RPA detector used in this work is small and was placed close to the source. To help distinguish the field-free space fragmentation features from noise or other anomalous features, the RPA should be placed farther away. This means that the detector will need to be much larger in order to collect the full beam. To reduce the effects of beam spreading, the geometry of the RPA should be spherical. This will allow the steps from field-free space fragmentation to be more well-defined. Additionally a spherical RPA would make it possible to study the ions that have slightly less energy than the full accelerating potential. Using a more stable source will also help with improving the quality of the RPA curves.

A full-beam time of flight detector would be ideal, but it probably is not practical for studying the fragmented ion population. Capturing the full beam would require electrostatic focusing, which could potentially induce more fragmentation than expected. The focal distance depends on the ion energy, which makes focusing a non-monoenergetic beam challenging. It is not clear that using an electrostatic lens would help improve the reliability of the TOF results. The angular distribution of the beam composition should be studied in order to determine how much it could affect the results of the dimer stability analysis. This can be accomplished by using a set of deflector plates. It is possible that the TOF detector could continue to be used as is if the effects of an off-axis beam could be well characterized.

While it may not be possible to have a full-beam TOF detector that can be used to study fragmented ions, it is possible to test how well the TOF data represents the characteristics of the full beam. The TOF spectra can be converted into an energy distribution, since the flight times give the ion energy. Note that in doing this the mass of the fragmented species must be assumed; for example, one would have to
assume that any ion arriving between the monomer time and the dimer time has
the mass of a monomer because it most likely orginated from a dimer to monomer
fragmentation event. The TOF energy distribution can be compared to the energy
distribution measured using a full-beam RPA. If the distributions are in agreement,
then it can be said that the small solid angle of the beam that the TOF detector
samples is representative of the whole beam. This would allow the TOF data to be
used to test the hypothesis with higher confidence. To do this, high quality TOF and
RPA data is required. The quality of the data presented in this work can probably
be improved with more averaging and by using a very stable source.

Once the RPA and TOF detectors have been sufficiently improved, a large set
of ionic liquids should be tested. The complexity factor used in this work is over-
simplified. The fragmentation characterisitcs of different ionic liquids probabably de-
pend on more than just the number of atoms in the ions. Through testing a large
set of liquids, perhaps the effect of the molecular structure and bonding could be
determined. The effects of macroscopic liquid properties such as the conductivity,
viscosity, and surface tension could also be investigated. Additionally it is important
to determine the effect of the operating conditions, namely the source voltage and
emitted current, on the beam composition and fragmentation fractions. Ideally, the
results of thoroughly testing a large sample could be used to predict the performance
of untested ionic liquids. If the performance of ionic liquids is predictable, then the
synthesis of new liquids could be driven by the demands of relevant applications. The
development of ion electrospray propulsion technologies and ILIS focused ion beam
applications would undoubtedly benefit from this high level of characterization of
ionic liquids.
Appendix A

Current-Voltage Curves

This appendix contains the IV curves for all ionic liquids at different temperatures and source voltage polarities. Additionally the reconstructed IV curves for the RPA and TOF data are included for all liquids. IV curves begin on the next page.
Figure A-1: Positive Mode IV Curve for EMI-BF$_4$

Figure A-2: Negative Mode IV Curve for EMI-BF$_4$
Figure A-3: Positive Mode IV Curve for EMI-Im

Figure A-4: Negative Mode IV Curve for EMI-Im
Figure A-5: Positive Mode IV Curve for EMI-MPI

Figure A-6: Negative Mode IV Curve for EMI-MPI
Figure A-7: Positive Mode IV Curve for BMI-I

Figure A-8: Negative Mode IV Curve for BMI-I
Figure A-9: Positive Mode IV Curve for EMI-BF$_4$ TOF Data

Figure A-10: Positive Mode IV Curve for EMI-Im TOF Data
Figure A-11: Positive Mode IV Curve for EMI-MPI TOF Data

Figure A-12: Positive Mode IV Curve for BMI-I TOF Data
Figure A-13: Positive Mode IV Curve for EMI-BF$_4$ RPA Data

Figure A-14: Negative Mode IV Curve for EMI-BF$_4$ RPA Data
Figure A-15: Positive Mode IV Curve for EMI-Im RPA Data

Figure A-16: Negative Mode IV Curve for EMI-Im RPA Data
Figure A-17: Positive Mode IV Curve for EMI-MPI RPA Data

Figure A-18: Negative Mode IV Curve for EMI-MPI RPA Data
Figure A-19: Positive Mode IV Curve for BMI-I RPA Data

Figure A-20: Negative Mode IV Curve for BMI-I RPA Data
Appendix B

Supplementary Time of Flight Mass Spectrometry Data

This appendix contains supplementary TOF data.

Figure B-1: EMI-BF$_4$ TOF Curves at 30°C
Figure B-2: EMI-BF$_4$ TOF Curves at 50°C

Figure B-3: EMI-BF$_4$ TOF Curves at 70°C
Figure B-4: EMI-BF$_4$ TOF Curves at 90°C

Figure B-5: EMI-Im TOF Curves at 30°C
Figure B-6: EMI-Im TOF Curves at 50°C

Figure B-7: EMI-Im TOF Curves at 70°C
Figure B-8: EMI-Im TOF Curves at 90°C

Figure B-9: EMI-MPI TOF Curves at 30°C
Figure B-10: EMI-MPI TOF Curves at 50°C

Figure B-11: EMI-MPI TOF Curves at 70°C
Figure B-12: EMI-MPI TOF Curves at 90°C

Figure B-13: BMI-I TOF Curves at 50°C
Figure B-14: BMI-I TOF Curves at 70°C

Figure B-15: BMI-I TOF Curves at 90°C
Figure B-16: Monomer Current Fraction of Ions at 30°C

Figure B-17: Monomer Current Fraction of Ions at 50°C
Figure B-18: Monomer Current Fraction of Ions at 70°C

Figure B-19: Monomer Current Fraction of Ions at 90°C
Figure B-20: Dimer Current Fraction of Ions at 30°C

Figure B-21: Dimer Current Fraction of Ions at 50°C
Figure B-22: Dimer Current Fraction of Ions at 70°C

Figure B-23: Dimer Current Fraction of Ions at 90°C
Figure B-24: Trimer Current Fraction of Ions at 30°C

Figure B-25: Trimer Current Fraction of Ions at 50°C
Figure B-26: Trimer Current Fraction of Ions at 70°C

Figure B-27: Trimer Current Fraction of Ions at 90°C
Figure B-28: Monomer to Dimer Ratio (Includes Fragments) at 30°C

Figure B-29: Monomer to Dimer Ratio (Includes Fragments) at 50°C
Figure B-30: Monomer to Dimer Ratio (Includes Fragments) at 70°C

Figure B-31: Monomer to Dimer Ratio (Includes Fragments) at 90°C
Figure B-32: Dimer Fragmentation Percentage at 30°C

Figure B-33: Dimer Fragmentation Percentage at 50°C
Figure B-34: Dimer Fragmentation Percentage at 70°C [3]

Figure B-35: Dimer Fragmentation Percentage at 90°C
Figure B-36: Total Fragmentation Percentage of Ions at 30°C

Figure B-37: Total Fragmentation Percentage of Ions at 50°C
Figure B-38: Total Fragmentation Percentage of Ions at 70°C

Figure B-39: Total Fragmentation Percentage of Ions at 90°C
Figure B-40: Survived Dimer Fraction of Ions at 30°C

Figure B-41: Survived Dimer Fraction of Ions at 50°C
Figure B-42: Survived Dimer Fraction of Ions at 70°C

Figure B-43: Survived Dimer Fraction of Ions at 90°C
Appendix C

Supplementary Retarding Potential Analysis Data

This appendix contains supplementary RPA data. A sampling of RPA curves begins on the next page. The supplementary plots of the fragmentation fractions and percentages at different temperatures are provided after the RPA curves.
Figure C-1: EMI-BF₄ Positive RPA \((V_0 = 1400V)\)

Figure C-2: EMI-BF₄ Negative RPA \((V_0 = -1400V)\)
Figure C-3: EMI-BF$_4$ (4/10) Positive RPA ($V_0 = 1400$V)

Figure C-4: EMI-BF$_4$ (4/10) Negative RPA ($V_0 = -1400$V)
Figure C-5: EMI-Im Positive RPA ($V_0 = 1400V$)

Figure C-6: EMI-Im Negative RPA ($V_0 = -1400V$)
Figure C-7: EMI-MPI Positive RPA ($V_0 = 1400V$)

Figure C-8: EMI-MPI Negative RPA ($V_0 = -1400V$)
Figure C-9: BMI-I Positive RPA ($V_0 = 1750V$)

Figure C-10: BMI-I Negative RPA ($V_0 = -1750V$)
Figure C-11: Positive Dimer Fragmentation Current Fraction at 30°C

Figure C-12: Positive Dimer Fragmentation Current Fraction at 50°C
Figure C-13: Positive Dimer Fragmentation Current Fraction at 70°C [3]

Figure C-14: Positive Dimer Fragmentation Current Fraction at 90°C
Figure C-15: Negative Dimer Fragmentation Current Fraction at 30°C

Figure C-16: Negative Dimer Fragmentation Current Fraction at 50°C
Figure C-17: Negative Dimer Fragmentation Current Fraction at 70°C [3]

Figure C-18: Negative Dimer Fragmentation Current Fraction at 90°C
Figure C-19: Positive Dimer Fragmentation Percentage at 30°C

Figure C-20: Positive Dimer Fragmentation Percentage at 50°C
Figure C-21: Positive Dimer Fragmentation Percentage at 70°C [3]

Figure C-22: Positive Dimer Fragmentation Percentage at 90°C
Bibliography


