DEVELOPMENT AND CHARACTERIZATION
OF A SINGLE PARTICLE MASS
SPECTROMETER WITH SOFT
PHOTOIONIZATION FOR ORGANIC AEROSOL
STUDIES

by

SARAH JANE HANNA

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Abstract

Aerosol particles, which are ubiquitous in the Earth’s atmosphere, can be 20-90% organic carbon by mass.1 These organic aerosols are thought to play an important role in climate, human health, and the chemistry of the atmosphere. Their composition, however, can be extremely complex, presenting a significant challenge to standard analytical techniques. Over the past several decades aerosol mass spectrometry has become an important tool for determining organic aerosol chemical composition.

This thesis describes the development and characterization of a new aerosol mass spectrometer designed for analysis of individual organic aerosol particles.

A unique vacuum UV source and custom monochromator, fully tunable from 7.4 to 10.2 eV (168 to 122 nm), was developed and characterized using gas phase analytes. The VUV source was coupled to a single particle mass spectrometer which uses a tunable CO$_2$ laser for particle vaporization and an ion trap for mass analysis.

Initial aerosol experiments were carried out using caffeine particles. The appearance energy of caffeine molecular ions from the vaporized particle was measured by scanning the VUV photon energy. The impact of increasing vaporization energy was also studied.

Following the caffeine experiments, a detailed study of oleic acid and 2,4-dihydroxybenzoic acid (DHB) aerosols was undertaken. The appearance energies of both the molecular and fragment ions were measured and the impact of ionization wavelength was determined. In addition, the results were compared to those from similar studies done with time-of-flight mass analyzers, allowing observation of the impact of long ion storage times on the mass spectra.

The final part of this thesis compares the IR laser vaporization of small, solid caffeine and DHB aerosols with larger, liquid oleic acid particles. The translational energy of the vaporized aerosol plume was followed by changing the delay between the vaporization and ionization events. The extent of fragmentation was monitored and was found to be dependent on both vaporization energy and ionization delay time. Both translational energy and the degree of fragmentation were seen to change with particle type, an effect which has important implications for pulsed laser desorption in aerosol mass spectrometry.
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<thead>
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<th>Description</th>
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<tbody>
<tr>
<td>a.u.</td>
<td>Arbitrary units</td>
</tr>
<tr>
<td>ADC</td>
<td>Analog to digital converter</td>
</tr>
<tr>
<td>AMS</td>
<td>Aerosol mass spectrometer (commercial instrument made by Aerodyne Research Inc.)</td>
</tr>
<tr>
<td>ATOFMS</td>
<td>Aerosol time of flight mass spectrometer (commercial instrument made by TSI Inc.)</td>
</tr>
<tr>
<td>CI</td>
<td>Chemical ionization</td>
</tr>
<tr>
<td>CPC</td>
<td>Condensation particle counter</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous wave</td>
</tr>
<tr>
<td>DHB</td>
<td>2,4-dihydroxybenzoic acid</td>
</tr>
<tr>
<td>DMA</td>
<td>Differential mobility analyzer</td>
</tr>
<tr>
<td>FPGA</td>
<td>Field programmable gate array</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared (spectrometer)</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>IE</td>
<td>Ionization energy</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>LDI</td>
<td>Laser desorption/ionization</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass to charge ratio</td>
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<tr>
<td>MALDI</td>
<td>Matrix-assisted laser desorption/ionization</td>
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<tr>
<td>Mb</td>
<td>Megabarn</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<td>--------------</td>
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<tr>
<td>MS</td>
<td>Mass spectrometry</td>
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<tr>
<td>MS/MS</td>
<td>Tandem mass spectrometry</td>
</tr>
<tr>
<td>OPO</td>
<td>Optical parametric oscillator</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbon</td>
</tr>
<tr>
<td>PAN</td>
<td>Peroxyacetyl nitrate</td>
</tr>
<tr>
<td>PERCI</td>
<td>Photoelectron resonance capture ionization</td>
</tr>
<tr>
<td>PIE</td>
<td>Photoionization efficiency</td>
</tr>
<tr>
<td>PILS</td>
<td>Particle-into-liquid sampler</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier tube</td>
</tr>
<tr>
<td>q_z</td>
<td>Mathieu equation parameter (used in determining the stability of an ion’s motion in the ion trap)</td>
</tr>
<tr>
<td>QMS</td>
<td>Quadrupole mass spectrometer</td>
</tr>
<tr>
<td>REMPI</td>
<td>Resonance enhanced multiphoton ionization</td>
</tr>
<tr>
<td>RF</td>
<td>Radiofrequency</td>
</tr>
<tr>
<td>SOA</td>
<td>Secondary organic aerosol</td>
</tr>
<tr>
<td>SPI</td>
<td>Single photon ionization</td>
</tr>
<tr>
<td>SWIFT</td>
<td>Stored waveform inverse Fourier transform</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>TEA-CO₂ laser</td>
<td>Transversely excited atmospheric CO₂ laser</td>
</tr>
<tr>
<td>TOF</td>
<td>Time of flight</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VOAG</td>
<td>Vibrating orifice aerosol generator</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic carbon</td>
</tr>
<tr>
<td>VUV</td>
<td>Vacuum ultraviolet</td>
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Chapter 1. Motivation for aerosol studies

1.1. Aerosol particles and their importance

An aerosol is defined as any particulate matter, solid or liquid, suspended in a gas phase medium. Individual aerosol particles can originate from a variety of sources and they can differ greatly in size, number concentration, and chemical composition. The exact physical properties of an aerosol particle are determined by the particle source and by any processing that the particle undergoes in the gas phase medium. Although aerosol particles are of interest in a wide range of human activities, for example as delivery agents for chemical or biological weapons, as contaminants in clean room activities, and as a workplace health hazard, they are of particular interest to the atmospheric science community.

Aerosol particles are ubiquitous in the atmosphere, with number concentrations ranging from approximately $10^2$ to $10^5$ cm$^{-3}$ in the lower atmosphere (troposphere). In remote areas over the ocean number concentrations are on the order of $10^2$ cm$^{-3}$, while in remote continental areas this rises to approximately $10^4$ cm$^{-3}$. In polluted urban environments the number concentrations can be greater than $10^5$ cm$^{-3}$.

Atmospheric aerosol particles come from a wide range of sources and have a considerable impact on climate, visibility, and human health. Aerosol particles affect climate both directly and indirectly. The direct aerosol effect involves the absorption and scattering of radiation by the particles themselves. The indirect effect refers to the absorption and scattering of light from clouds which have formed due to the presence of aerosol particles acting as cloud condensation nuclei. Because of these two effects, an increase in the atmospheric particle load can cause a reduction in the amount of solar radiation reaching the earth’s surface, an effect known as global dimming. Data proving the long term occurrence of global dimming is scarce, but satellite data collected between 1981 and the present seem to suggest a correlation between the aerosol load of the atmosphere and the amount of solar radiation reaching the surface. The impact that
aerosols have on the extinction of incoming solar radiation can be more readily observed following volcanic eruptions, such as the 1991 eruption of Mt Pinatubo.\textsuperscript{10,11}

On a local scale the scattering and absorption of light by aerosol particles can limit visibility. In an aerosol free environment the human visual range would be around 300 km. However, in polluted regions aerosols typically reduce the range of visibility by an order of magnitude.\textsuperscript{12} Smog formation in heavily polluted urban areas has been known to reduce visibility to only a few meters.\textsuperscript{9}

Particulate matter is also known to have a significant impact on human health. In health matters particles under 2.5 $\mu$m in diameter are considered most important because it is these particles that can penetrate deep into the respiratory system when inhaled.\textsuperscript{9,13} Airborne particulate matter can impact respiratory, cardiovascular, infectious, and allergic diseases.\textsuperscript{8}

1.2. Sources, sizes, and composition of atmospheric particles

1.2.1. Particle sources

Atmospheric particles can be liquids or solids and can originate from a wide range of sources, both natural and anthropogenic. Natural sources include wind driven suspension of soil, ocean spray, volcanoes, biomass burning (forest fires), and biogenic emissions (i.e. leaf abrasion, pollen, spores, microorganisms, and condensation of oxidized gaseous precursors emitted from plants and phytoplankton).\textsuperscript{2,8,14} Anthropogenic sources include biomass burning, incomplete fossil fuel combustion in vehicles and home heating, wood-burning stoves, dust particles produced by vehicle or farming activities, and particles produced by industrial processes.\textsuperscript{2,15-17} Small scale sources of anthropogenic aerosols include cigarette smoking and meat cooking operations.\textsuperscript{18,19}

Aerosol particles can be emitted directly into the atmosphere or they can form by nucleation and condensation of gas phase precursors.\textsuperscript{8,9} In addition, molecules in the gas phase can undergo reactions which lower their vapor pressure and cause them to
condense on existing particle surfaces. Once formed, aerosol particles can undergo various physical and chemical transformations (known as particle aging) which can alter their size and chemical composition.

1.2.2. Particle sizes

Aerosol particles range in diameter from approximately 0.002 to 100 µm. The lower limit of this range is only approximate since the size where a cluster of molecules becomes a particle is not well defined. The upper limit is set as the size where the particles are so large that they quickly precipitate out of the gas phase medium. In the atmosphere particles less than 10 µm in diameter are the most significant.

The size of atmospheric particles is closely tied to their source. In general aerosol particles greater than 2.5 µm in diameter are called coarse mode particles, while those less than 2.5 µm in diameter are called fine mode particles.

Coarse mode particles are typically produced by mechanical means. This includes particles produced from ocean spray which is caused by wind and wave action, and mineral dust particles generated by wind or by driving and farming activities. Other sources of coarse mode aerosols include industrial processes which produce large particles such as fly ash and some biological sources which produce materials such as spores and pollen. These large particles tend to be removed from the atmosphere rather quickly via gravitational settling, although there are some circumstances, such as convective episodes, where they can be transported over very long distances.

Fine mode particles have longer atmospheric lifetimes and can be further broken down into two additional size ranges. The transient, or Aitken, nuclei mode consists of particles from 0.01 to 0.08 µm (10 to 80 nm) in diameter, while the accumulation mode consists of particles from 0.08 µm to ~1-2 µm in diameter.

Particles in the nuclei mode originate from gas-to-particle conversion processes, often during combustion where hot, supersaturated vapors are formed and subsequently condense to form particles. Particles can also be generated by other nucleation processes such as binary nucleation, involving water and sulfuric acid, or tertiary nucleation involving water, ammonia, and sulfuric acid. Particles in the nuclei mode tend to
coagulate or act as nuclei for further condensation and therefore grow in size towards the accumulation mode range.²

Accumulation mode particles have much weaker sinks than particles in either the coarse or nuclei modes and therefore they persist for longer in the atmosphere. Whereas the other two modes have atmospheric lifetimes on the order of a day, accumulation mode particles can persist for days to weeks.⁹ These particles can be generated directly during combustion processes, or can be formed by coagulation of smaller particles.² ⁹

1.2.3. Atmospheric particle composition

As illustrated in the previous section, the source of atmospheric particles has a large impact on their size. In a similar manner, the aerosol source, along with any aging processes that occur in the atmosphere, also has a significant impact on particle composition. Dust and ocean spray-derived particles often contain large quantities of inorganic species such as mineral compounds and sea salt.² Other major inorganic components of atmospheric particles include \( \text{SO}_4^{2-} \), \( \text{NO}_3^- \), and \( \text{NH}_4^+ \).⁹ Organic carbon also makes up a significant fraction of many aerosol particles. Depending on location, organic carbon species can comprise anywhere from 20 to 90% of the submicron aerosol composition.¹ This is illustrated in Figure 1.1 which is adapted from a study by Hueglin et al. In this study the chemical composition of particles at urban and rural sites was measured and a significant fraction of organic matter was observed.²³ However, when looking at studies such as this, it is important to remember that particle sources and aging processes can vary extensively from location to location and season to season, and that an individual study is not representative of all possible scenarios. In addition most studies have been conducted in northern hemisphere locations and very little information about the southern hemisphere is included in most pictures of global aerosol composition.
Despite their abundance the exact chemical composition of organic aerosols is not well understood,\textsuperscript{20, 24} nor are the exact mechanisms and products resulting from organic aerosol aging in the atmosphere.

In comparison with the inorganic fraction, which generally consists of only a few major species, the organic fraction of the aerosol composition can contain hundreds of different compounds.\textsuperscript{25, 26} Even if classes of compound rather than individual species are considered, there can still be a wide variation in chemical and physical properties.

Classes of compounds present in atmospheric particles include dicarboxylic acids, keto acids, polyols, n-alkanes, n-alkanoic acids, and polycyclic aromatic hydrocarbons.
(PAHs). Some species are more robust under analysis and others are extremely labile. All of these considerations have made characterization of the organic fraction of atmospheric aerosols a considerable analytical challenge.

This thesis describes the development and characterization of a new aerosol mass spectrometer designed for laboratory studies of organic particles. Potential laboratory investigations include studies of heterogeneous reactions (reactions between gas phase oxidants and aerosol particles) to better understand organic aging in the atmosphere and studies of organic aerosol formation from gas phase reactions (secondary organic aerosol or SOA formation). Although this instrument was not designed specifically for field measurements, information gained from its use could potentially be used when designing the next generation of aerosol field instruments.

1.3. **Traditional particle analysis techniques**

Traditional aerosol analysis techniques typically consist of off-line measurements where particles are gathered by filter collection, inertial impaction, or gravitational sedimentation. A wide variety of methods are then employed for analysis of both individual particles and the bulk sample, including, but not limited to, atomic absorption spectroscopy, ion chromatography, scanning electron microscopy, transmission electron microscopy, and laser microprobe mass spectrometry. These traditional methods have many strengths, including the ability to directly visualize particles through various microscopy techniques and robust collection methods that can be used in almost any environment. However, for all types of off-line analysis long collection and storage times can lead to artifacts from evaporation of particle components and/or condensation of gas phase species onto the particles or collection substrate. In addition, off-line analysis is necessarily slow since samples must be collected and sometimes transported prior to analysis.

For organic aerosol species in particular, off line analysis methods present some challenges. For organic aerosols, filter collection followed by gas chromatography coupled to a mass spectrometer (GCMS) has been by far the most commonly used
Although it has been successful in showing that organic aerosols are composed of many different compounds, there are serious drawbacks to the technique when attempting to determine the precise chemical composition of atmospheric particles. In the initial stages of the analysis, the collected particles must be extracted from filters or impactor plates. If the sample is to be introduced to a GC column, polar solvents cannot be used which limits the amount and type of material that can be analyzed. In addition, the extraction process itself may induce changes in the compounds observed. Ultrasonic extraction is a commonly used technique, but the high pressures and temperatures that occur in cavitating air bubbles may cause alterations of some compounds. Once the extraction is complete, and the extract is injected onto the GC column, there can be additional problems. Somewhat polar compounds or high molecular weight species which have been successfully extracted can bind very strongly to the column and fail to elute. In addition, of the compounds that do elute, only a fraction may be separated enough to identify individual species. The result of these issues is that only about 10-15% of the organic mass from an ambient aerosol sample can be resolved into individual compounds.

In an effort to mitigate some of the issues inherent in off-line analysis, a number of different on-line, and in some cases real-time, techniques have been developed for both organic and inorganic particle analysis. In these methods, particles are either accumulated for a short time (seconds to minutes) and then analyzed (on-line) or analyzed immediately upon sampling, with no collection stage involved (real-time). Some examples of these techniques are the particle-into-liquid sampler (PILS) coupled to an ion chromatograph which is used for inorganic aerosol characterization and the various aerosol mass spectrometers which are discussed in more detail below. These techniques have the benefit of providing high temporal resolution and allowing minimal time for chemical modification.
Chapter 2. Aerosol mass spectrometry

2.1. Introduction to aerosol mass spectrometry

Over the past three and a half decades, aerosol mass spectrometry has been developed as a means of conducting on-line chemical analysis of both inorganic and organic aerosol particles. For the complex organic fraction in particular, aerosol mass spectrometry provides an appealing option to traditional techniques. Aerosol mass spectrometers sample particles from a region of atmospheric pressure (either ambient air or samples in a laboratory environment) and analyze them in a matter of seconds. Some instruments collect particles for a short time prior to analysis and others operate in real-time, analyzing particles immediately after sampling. Aerosol mass spectrometers avoid the complications associated with collection and storage, and allow analysis of the entire particle composition without difficulties from compounds that cannot be extracted from a filter or eluted from a GC column. In addition, most instruments also gather size information about the particles, allowing relationships between particle size and composition to be determined.

2.2. General characteristics of aerosol mass spectrometers

The general function of an aerosol mass spectrometer is to draw particles from a region of atmospheric pressure into a vacuum chamber where they can be vaporized, ionized, and the components analyzed with a mass spectrometer. In general aerosol mass spectrometers can be divided into two categories; those which perform single particle analysis and those which average data from an ensemble of aerosols. Both types of instrument must have an inlet system to transfer particles from regions of atmospheric pressure into the vacuum of the mass analyzer. Often this is followed by a sizing region. The final stage is vaporization, ionization, and mass analysis. It is in this final stage that most of the differences between existing instruments occur. A generic aerosol mass
The purpose of the aerosol inlet is to transfer particles into the vacuum region of the instrument with high efficiency and minimal changes in chemical composition.\textsuperscript{32,36} Although orifices and capillaries were generally used in early instruments,\textsuperscript{30} the most commonly used inlet in current instruments is the aerodynamic lens. An aerodynamic lens consists of a series of apertures of decreasing diameter that successively focus a range of particle sizes onto the centerline of the inlet. The pressure in the lens is generally on the order of 1-5 Torr, and at the exit of the lens the particle beam is delivered through an accelerating nozzle into the high vacuum of the analysis region.\textsuperscript{37} The aerodynamic lens provides superior focusing of the particles and produces a well collimated beam which can give efficient particle transmission to analysis regions tens of centimeters downstream from the lens outlet. Chemical composition changes in the inlet are typically minor because of the relatively short residence time of particles in the lens.
2.2.2. Particle sizing

Particle sizing can be achieved either by light scattering from a single laser\textsuperscript{38-40} or by velocity measurements.\textsuperscript{41-45} Light scattering from a single laser can be used to detect a particle in the analysis region but the sizing information obtained is subject to some artifacts. In addition to being a function of particle diameter, the scattering depends on particle shape and refractive index\textsuperscript{46} and can thus vary from aerosol to aerosol.

Two options are currently employed for measuring particle velocities in aerosol mass spectrometry. In the commercially available Aerosol Mass Spectrometer (Aerodyne) a chopper wheel is used. In this system the time between the opening of chopper wheel and the detection of ion signal is used as a measure of particle velocity.\textsuperscript{41} In other instruments velocity is often determined by the particle’s transit time between two light scattering points. In this arrangement two CW (continuous wave) lasers are typically used and the particle velocity is calculated based on the known distance between the two scattering events.\textsuperscript{42-45}

2.2.3. Vaporization

A variety of different vaporization schemes have been implemented in aerosol mass spectrometers. In many instruments vaporization and ionization are combined in a single step. Early aerosol mass spectrometers used impaction on a heated rhenium or tungsten filament for combined vaporization and ionization.\textsuperscript{30} This was followed by single laser desorption/ionization (LDI) with either excimer lasers,\textsuperscript{39, 40} Nd:Yag lasers,\textsuperscript{47} or a CO\textsubscript{2} laser.\textsuperscript{47} Single laser desorption/ionization is still widely used and is employed in one of the two commercially available instruments (TSI Aerosol Time of Flight Mass Spectrometer (ATOFMS)). Single laser LDI is especially well suited for analysis of particles containing salts or mineral dust which can be difficult to vaporize and ionize with softer methods.\textsuperscript{29, 48} For organic molecules the laser intensity necessary to perform both desorption and ionization in a single step results in extensive fragmentation. In an effort to avoid this problem some researchers have separated the desorption and ionization into two independent steps which can be individually optimized.\textsuperscript{45, 49} This also
has the added benefit of reducing the number of ion-molecule reactions that occur in the dense cloud of vaporized molecules and ions immediately following the vaporization/ionization laser pulse. In a two-stage instrument, vaporization is commonly achieved with either a heated surface which vaporizes particles upon impact, or a pulsed laser. Although a heater has been used for single particle analysis it is most commonly employed for vaporization of particle ensembles. For single particle analysis pulsed IR lasers are most commonly used.

2.2.4. Ionization

In instruments with separate vaporization and ionization stages, a wide variety of ionization methods are available. For ensembles of particles where a defined vaporization time does not exist, continuous ionization sources are often used. Some of the ionization methods that have been employed include electron impact, chemical ionization (CI), metal attachment, and continuous vacuum UV photoionization. Many other aerosol mass spectrometers employ pulsed ionization sources. For single particle analysis in particular these are often used. Pulsed ionization sources in use include resonance enhanced multiphoton ionization (REMPI), pulsed VUV photoionization, and photoelectron resonance capture ionization (PERCI).

2.2.5. Mass analysis

The three main methods of mass analysis employed in aerosol instruments are time-of-flight (TOF), quadrupole, and ion trap mass analyzers. The commercially available Aerodyne Aerosol Mass Spectrometer (AMS) uses either a quadrupole or TOF analyzer while the TSI Aerosol Time of Flight Aerosol Mass Spectrometer (ATOFMS) uses a dual TOF to look at both positive and negative ions. Ion traps are less widely used, but a number have been employed.

Each of the three mass analyzers has some advantages and disadvantages. For continuous measurements quadrupoles offer the advantage of being able to constantly monitor a particular mass to charge ratio, an advantage in situations were there is a single
compound of interest. A disadvantage of quadrupoles is that they are unable to obtain a full mass spectrum from a single aerosol particle. TOF and ion trap mass analyzers do have the ability to obtain a mass spectrum from an individual aerosol particle and both are well matched to single particle instruments with pulsed vaporization and ionization sources. TOF systems have the advantage of a fairly high duty cycle when compared with ion traps and a simpler electronic configuration. In contrast ion traps require less physical space, an advantage in field instruments, and have the capability to perform tandem MS. In tandem MS ions of a single mass to charge ratio can be trapped, collisionally dissociated, and the fragments mass analyzed to provide additional chemical information.

2.3. Commercially available instruments

As mentioned above, two aerosol mass spectrometers are commercially available. These are the Aerodyne Aerosol Mass Spectrometer (AMS) and the TSI Aerosol Time of Flight Aerosol Mass Spectrometer (ATOFMS). The Aerodyne instrument analyzes aerosol composition using a heater for thermal vaporization and electron impact for ionization. The original version uses a quadrupole mass analyzer, but newer versions are available with TOF analyzers. Unlike the quadrupole, the TOF has the advantage of collecting a complete mass spectrum every time the extraction voltage is pulsed although each mass spectrum does not necessarily come from a single aerosol particle. Electron impact ionization also has several advantages. It is a universally applicable ionization technique with few chemical biases, but it can cause extensive fragmentation of organic ions. Currently several new soft ionization methods are under development for the AMS, including a VUV lamp for photoionization, Li\(^+\) ion attachment, and dissociative electron attachment.

In the TSI instrument particle detection and sizing are accomplished by velocity measurements using two CW 532 nm Nd:YAG lasers. Vaporization and ionization are combined in a single step using a 266 nm pulsed Nd:YAG laser and mass analysis is done with a dual-TOF setup that collects both positive and negative ion information for
individual aerosol particles. The dual-TOF setup maximizes the amount of information that is collected for each particle, but single laser desorption/ionization causes most organics to fragment indiscriminately.49, 77

2.4. Challenges specific to organic aerosol analysis and instruments that incorporate soft ionization sources

Instruments that use a single laser for desorption and ionization have been very successful at characterizing the inorganic fraction of atmospheric particles, and they give some indication of the amount and type of organic carbon present.40 However, the high laser intensities needed to vaporize and ionize particles in a single step cause extensive fragmentation and matrix effects.29, 40, 49, 77 Separation of vaporization and ionization eliminates some of these issues, but high energy ionization techniques such as 70 eV electron impact still cause extensive fragmentation of many organics.49

In the past decade considerable effort has been made to develop soft ionization sources for aerosol mass spectrometry. In these methods the ions are generated with a minimum of excess energy in an attempt to reduce the extent of fragmentation. The ultimate goal is to obtain mass spectra with only molecular ion peaks, reducing the complexity of the spectra and making molecular identification much more straightforward. This is particularly important for particles of mixed composition.

To date, several research groups have coupled aerosol mass spectrometers with soft ionization sources, some examples of which include photoelectron resonance capture ionization (PERCI),78 chemical ionization (CI),5, 56 metal attachment,55 resonance enhanced multiphoton ionization (REMPI),44, 45, 49, 50, 53 and single photon ionization.51, 52, 58-60, 63, 65-67, 79
2.5. Applications of aerosol mass spectrometry

For atmospheric studies of organic particles, aerosol mass spectrometers have been employed extensively in both the field and the laboratory. In field work aerosol mass spectrometers have been used to study ambient conditions and to collect information on sources, transport, and aging of aerosol particles. In the laboratory detailed studies can be conducted into specific particles types or mechanisms of particle aging.

Perhaps the main use of field instruments to date has been characterization of the spatial and temporal variation in ambient particle composition. Field studies have been conducted around the world and have deepened our understanding of the regional variability of aerosol types. In addition, the high temporal resolution possible with on-line analysis has helped us better understand short term variations in particle concentration and composition. In most field studies meteorological information is collected alongside aerosol measurements and can be used to determine the trajectories taken by air masses and assign sources to particle emissions. This information can help us better understand the aging of aerosol particles in the atmosphere.

Field and laboratory studies complement one another in expanding our knowledge of atmospheric processes. Often the focus of lab studies is influenced by findings in the field, and the more detailed knowledge of processes investigated in a controlled environment can enhance our understanding of the complex chemistry occurring in the atmosphere.

Laboratory studies can examine particle composition and aging in considerable detail, looking at particular particles or processes in isolation, something which is often not possible in a complex real-world environment. One focus of laboratory based aerosol studies has been the determination of products and mechanisms for reactions of aerosols with gas phase species, known as heterogeneous chemistry. Heterogeneous reactions between aerosols and atmospheric oxidants are an important process in atmospheric particle aging and a number of different research groups have used aerosol mass spectrometers to study these systems in a laboratory setting.
Another interesting avenue for laboratory based aerosol studies has been the use of smog chambers. Chambers such as the one in the Laboratory of Atmospheric Chemistry at the Paul Scherrer Institute are used to study reactions of particles in a simulated atmospheric environment. In one study this smog chamber was used to identify polymers formed during photooxidation of aromatic compounds, a previously unobserved process and one that could drastically change the chemistry of particles in the atmosphere.\textsuperscript{85} The well controlled conditions of a smog chamber and the wide array of instrumentation that can be brought to bear in them make these types of laboratory experiments particularly useful for investigating reactions under realistic atmospheric conditions.

2.6. Motivation for this work

The work described in this thesis was motivated by the ongoing need to develop new instrumentation for organic aerosol analysis. Here the development and characterization of a novel single particle aerosol mass spectrometer which combines a tunable single photon ionization source with an ion trap for mass analysis is described.

As discussed earlier, single photon ionization is a soft technique which deposits a minimum of excess energy in the ionized molecule. Tunable single photon ionization provides the added benefit of allowing the photon energy to be set very close to the ionization threshold of the molecule of interest giving the gentlest possible ionization. A tunable source also has the advantage of being able to function as an "ionization chromatograph" and separate compounds by their ionization energy. Tunable single photon ionization has been used for organic aerosol analysis in the past, but never for a single particle system and never coupled with an ion trap mass spectrometer.

In this instrument an ion trap mass analyzer has been employed to give the option of tandem mass spectrometry. Since organic aerosol composition can be very complex, this additional tool for determining chemical structure and the presence of particular functional groups could be very useful in unraveling which compounds are present in a particle. In addition, soft ionization sources which aim to minimize fragmentation sacrifice a considerable amount of chemical information when spectra with only
molecular ion peaks are generated. By using an ion trap this information can be regained via tandem MS.
Chapter 3. Thesis overview

This thesis describes the development and characterization of a novel single particle aerosol mass spectrometer designed for laboratory studies of organic particles. Although a wide variety of instrumentation exists for aerosol particle analysis, there are still many challenges in the field which necessitate further innovation.

In Chapter 4 an overview of the instrument is given. In this section the particle inlet, the sizing region, and the ion trap mass spectrometer are described in some detail. The vaporization and ionization stages are briefly discussed, but as these are covered in more depth in the remainder of the thesis, the description of them in Chapter 4 is brief.

In Chapter 5 a detailed description of the tunable VUV source and custom-built VUV monochromator is given. A full characterization of the source was carried out using gas-phase species and its first application to aerosol mass spectrometry was undertaken using caffeine particles. Mass spectra were collected for particles down to 300 nm in diameter and the tunability of the source was used to measure the appearance energy of caffeine from particles.

In Chapter 6 a comprehensive study of two different organic aerosols is described. Liquid particles of oleic acid, a long chain fatty acid and a component of meat cooking aerosols, were studied alongside solid particles of 2,4-dihydroxybenzoic acid. Mass spectra were collected as a function of both vaporization energy and ionization wavelength and the impact of both on the degree of fragmentation was examined. The results from this study are compared with those from similar experiments undertaken with time-of-flight (TOF) mass analyzers and the differences are explored in some detail. This comparison sheds some light on the fragmentation process and may prove helpful for others considering the development of an aerosol mass spectrometer.

One area of considerable importance in single particle mass spectrometry is the desorption stage, where pulsed IR lasers are often used to vaporize the aerosol particles. The dynamics of pulsed laser desorption are not very well understood and a number of experimental studies and molecular dynamics simulations have been undertaken to investigate the process. In Chapter 7 the vaporization of three different organic
aerosols, one liquid (oleic acid) and two solids (2,4-dihydroxybenzoic acid and caffeine) is examined in some detail. The total ion signal is measured as a function of the IR laser energy and the expansion of the vaporized plume is followed by scanning the delay between the IR and VUV pulses. Changes in the degree of fragmentation are observed as a function of both the IR pulse energy and the delay between the two laser events. Although many questions remain with regard to the laser vaporization process, this work provides some insight into the impact that changes in particle type have on the vaporization process.

The final chapter in this thesis gives a summary of the work done and explores some potential areas of future research.
Chapter 4. Instrument description

The single particle aerosol mass spectrometer described in this thesis has many of the components outlined in section 2.2. This includes an aerodynamic lens which serves as an inlet and provides particle focusing, aerosol velocity and size measurement, separate vaporization and ionization stages, and mass analysis. A schematic of the instrument is shown in Figure 4.1. In this chapter a brief description of the various components is given. The vaporization and ionization stages will be discussed in more detail in subsequent chapters.

Figure 4.1 Schematic of the single particle aerosol mass spectrometer
4.1. Particle inlet and sizing

In this instrument particles are drawn from a region of atmospheric pressure through a 100 µm critical orifice. This is followed by a 25 cm equilibration region which allows the flow to relax from turbulent to laminar. After the equilibration region, the particles enter an aerodynamic lens which focuses a range of particle sizes with a Stokes number around 1 along the centerline of the instrument. The aerodynamic lens used in this instrument operates at a pressure of 1.6 Torr and consists of a series of five apertures followed by a nozzle outlet. As the carrier gas stream contracts to pass through each aperture, particles are moved towards the centerline of the lens. Because of their inertia, the particles do not exactly follow the carrier gas stream as it expands after each aperture and they become concentrated on the centerline of the instrument. Optimal focusing of different particle sizes is achieved by different aperture widths, so a series of different diameter apertures is able to focus a range of particle sizes. This system uses the original set of aperture sizes described by Liu et al. which has been shown to achieve good focusing of particles in the 0.1 to 1 µm range. This size range is in the accumulation mode (0.08 µm to ~1-2 µm in diameter, described in section 1.2.2) and is of particular interest for atmospheric studies given the long lifetime and potential negative health impact of these particles.

After exiting the aerodynamic lens the particles pass through a 5 mm skimmer and enter the sizing region. At the exit of the lens the pressure is approximately 1.4 x 10^{-2} Torr, but after the skimmer this drops to approximately 7 x 10^{-5} Torr.

Particle velocities are measured by detecting scattered light as the aerosols pass through two 532 nm CW laser beams located 6 cm apart in the sizing region (Figure 4.1). Since the particles are accelerated to a size-dependent terminal velocity at the exit of the aerodynamic lens, the measured particle speeds can be used to determine aerodynamic diameter. Polystyrene latex nanosphere standards (Duke Scientific Corp) with diameters ranging from 200 to 800 nm were used to calibrate the particle sizing system.

Two different scattering laser arrangements were tested during the development of the instrument. In the first setup the output of a single laser (100 mW 532 nm CW DPSS Nd:YAG laser; Crystalaser Ltd.) was divided by a 50/50 beamsplitter. The two beams
were independently focused to give ~80 µm laser spots at the points where they intersected the aerosol stream. A small focus size means a high photon flux and increased scattering intensity for particles that pass through the laser spot. However, the small focus proved to be problematic when the aerosol size was changed. Because the aerodynamic lens is in a horizontal orientation, gravitational settling of larger particles meant that the focus positions had to be adjusted as the particle size was altered. In the second arrangement two independent lasers were used (single mode 100 mW 532 nm CW Nd:YAG; Spectra-Physics Excelsior). The outputs from both lasers were focused to a spot size of ~280 µm. The higher intensity and larger spot size of the two-laser arrangement meant that particles down to 300 nm in diameter could be detected without the necessity of adjusting the beam position when the particle size was changed.

In the sizing region the scattered light from the particles is collected by two custom elliptical mirrors (Optiform Ltd) and focused onto a pair of miniature photomultiplier tubes (PMT 9001 V; Electron Tubes Ltd). The scattering lasers and elliptical mirrors are oriented at opposing 45° angles to minimize false triggers. A field programmable gate array (FPGA) (PCI-7831R; National Instruments) is used to record the particle velocities, generate triggers for firing the desorption and ionization lasers, and control the clock for the MS acquisition software. This real-time software control allows particle size information to be collected and retrieved from memory at a later time. This can be done independently from the actual laser triggering, allowing the size distributions of sampled as well as analyzed aerosols to be collected.

The detection efficiency for particles of different diameters in the sizing region was assessed by comparing the number of particles which passed through both scattering points with the number of particles detected by a condensation particle counter (CPC; TSI W3782) running in parallel to the aerosol mass spectrometer. The results from this measurement are shown in Figure 4.2 for both the one and two laser setups (reproduced from Simpson et al.97). For the one-laser setup slight adjustments in the height of the scattering lasers were made.
Figure 4.2 Particle detection efficiencies for polystyrene latex nanospheres as a function of geometric particle diameter.

The particle detection efficiency is very good for particles with diameters of 400 nm or greater. This compares well with other single particle systems. Zelenyuk and Imre reported detection efficiencies of roughly 90% at 400 nm with decreasing efficiency at larger and smaller sizes,\textsuperscript{44} Su et al. reported sizing efficiencies of close to 50% for 300 nm particles,\textsuperscript{46} and Harris et al. reported 95% efficiency at 548 and 740 nm.\textsuperscript{98}

The detection limit for the current aerosol sizing setup is ~225 nm.\textsuperscript{97} In work with similar instruments Su et al. reported detection of particles down to 95 nm in diameter\textsuperscript{46} and Zelenyuk et al. reported detection of particles down to 98 nm in diameter.\textsuperscript{44} However, in the current configuration of this instrument a large amount of light is scattered off of the input windows. Since the scattering response is background rather than signal limited a lower detection limit can very likely be achieved with increased
suppression of scattered light. One means to achieve this is the introduction of a baffle system similar to the one described by Zelenyuk and Imre\textsuperscript{44} or the one described by Pruett and Zare.\textsuperscript{99}

4.2. Vaporization and ionization

After exiting the sizing region, particles enter the ion trap through a 2 mm hole in the ring electrode (Figure 4.1). The instrument control software provides a trigger to fire the desorption laser when a particle reaches the center of the ion trap. After a variable delay, the VUV laser is fired and a mass spectrum is acquired.

For particle vaporization a pulsed TEA-CO\textsubscript{2} laser (MTL-3G Edinburgh Instruments Ltd) is used. This laser has a single mode output which allows for a uniform, Gaussian laser spot in the ion trap. A ZnSe lens is used to focus the laser pulse to a spot size of approximately 0.9 mm (FWHM). The CO\textsubscript{2} laser is also tunable across 60 rotational lines between 9.2 μm (1087 cm\textsuperscript{-1}) and 10.8 μm (926 cm\textsuperscript{-1}), allowing a wavelength to be chosen where the material of interest has a suitable absorption cross-section. The energy output of the laser varies from wavelength to wavelength and has a maximum value of approximately 50 mJ/pulse (~5 × 10\textsuperscript{7} W/cm\textsuperscript{2}). The temporal profile of the laser pulse consists of a sharp 140 ns spike containing approximately 50% of the total energy followed by a broad tail ~1 μs long.

Soft, single photon ionization of the vaporized aerosol components is achieved using a pulse of vacuum UV light generated by a custom-built VUV source which is described in detail in Chapter 5.

The pump laser for VUV generation is a pulsed Nd:YAG which presents some unique challenges for the instrument control software. The arrival of an aerosol in the ion trap is a random, unpredictable event, however, Nd:YAG lasers are susceptible to fluctuations in power stability and beam quality if the firing rate of the laser is not kept constant. In addition, the laser flashlamps must be triggered ~150 μs prior to the Q-switch opening to emit a laser pulse, so the arrival of a particle must be predicted at least 150 μs prior to its entering the ion trap. In the past these kinds of laser triggering issues have been
addressed using custom hardware solutions. In this system the real-time control software keeps track of the timing of the laser shots and maintains the average firing rate of the Nd:YAG laser at 10 Hz. If no particles are detected by the sizing system, the laser simply fires at a constant frequency. If a particle is detected, the software determines when the last laser shot was fired and, if possible, shifts the triggering for the ionization pulse by up to 60 ms to coincide with the particle’s arrival in the ion trap. When compared to the constant frequency mode, this irregular triggering shows no decline in the power stability or beam quality of the laser.

4.3. Mass analysis

After the vaporized particle constituents have been ionized a mass spectrum can obtained. In this system a 3D quadrupole ion trap is used (Figure 4.1). The ion trap electrodes were built in house and mounted in a custom vacuum manifold which allows access through the center of the ring electrode and along two diagonal paths between the ring and endcap electrodes (Figure 4.1).

Ions generated by the VUV pulse are trapped by the application of a 967 kHz radiofrequency (RF) potential on the ring electrode (generated by a customized Extrel QMS power supply; Mod 011-10). Although the ion trap chamber is operated at approximately 10⁻⁶ Torr, a pressure of ~1 mTorr of helium gas is maintained in the center of the ion trap. Collisions with the helium background gas lower the translational energy of the ions and confine them to trajectories near the center of the ion trap. This has the effect of substantially increasing the resolution of mass spectrum. The ions are cooled in this manner for 1 - 10 ms and then ejected. In this system the ion trap is operated in mass selective instability mode, where the amplitude of the RF voltage is linearly ramped to eject ions of increasing mass to charge ratio at qₑ=0.908 and generate a mass spectrum. The ejected ions exit the trap through small holes in the endcap electrodes and are detected by an electron multiplier (ETP AF 138). The resulting ion signal is amplified by a shaping amplifier (Keithley 427) and then recorded by a 16 bit ADC Card (PCI-6030E, National Instruments). This ADC card is also used to generate the RF
amplitude ramp. Mass calibration of the ion trap is done using 70 eV electron impact ionization of small amounts of perfluorotributylamine.

Because the ionization laser is fired at a continuous (average) 10 Hz frequency, there can be interference from the buildup of background ions in the trap between particle events. To avoid this, the trapping voltage is briefly dropped to zero after every mass scan and after every non-aerosol laser shot. In this manner each mass spectrum is recorded from a “clean” ion trap.

The mass range for this instrument in the mass selective instability mode is 10-340 Da. Supplemental waveforms can be applied to the endcap electrodes to extend the mass range via resonant ejection (masses of up to ~2000 Da can be accessed in this mode) or to isolate and dissociate ions for tandem MS. Resonant ejection was not used in this work, but tandem MS experiments were carried out. In these experiments the ions are trapped and cooled as they would be in the mass selective ejection mode, however, instead of ramping the RF voltage, a particular ion of interest is isolated by applying one or two notched broadband SWIFT (stored waveform inverse Fourier transform) waveforms sequentially to the endcap electrodes. After isolation, the selected ions are collisionally dissociated and the fragments mass analyzed. The collisional dissociation is accomplished by resonantly exciting the ions so that their trajectories carry them away from the center of the trap towards areas of higher potential. The higher potential increases the kinetic energy of the ions and subsequent collisions with helium gas lead to dissociation. The resulting fragments can then be analyzed in the usual manner (mass selective instability mode) and can offer additional clues as to the structure of a particular ion.
Chapter 5. Development of a new broadly tunable (7.4 to 10.2 eV) laser based VUV light source and its first application to aerosol mass spectrometry

5.1. Introduction

Single photon ionization (SPI) using vacuum ultraviolet (VUV) light is a very effective soft ionization method for analytical mass spectrometry. It has been used in measurements as diverse as diagnostics of automobile exhaust, analysis of amino acids, and monitoring of waste incineration flue gas. Unlike multiphoton ionization, no intermediate molecular resonances are required, making SPI a universal ionization technique. As long as the photon energy is higher than the ionization energy of the molecule of interest, ionization will occur.

Many SPI sources operate at a fixed photon energy, but tunable sources have several advantages. They allow the photon energy to be set very close to the ionization threshold minimizing fragmentation. In addition, a tunable source makes it possible to differentiate mixtures by the appearance energies of the components. A tunable source also makes it possible to measure ionization energies (IEs). Having both the IE and the SPI mass spectrum of the molecule is a powerful combination for product identification in analytical applications.

Pulsed lasers are an excellent source of VUV light. Unlike synchrotrons, they are laboratory based instruments, and although considerably more complex than discharge lamps, they can produce high intensity pulses of coherent radiation. The coherent light from a laser source has several advantages. It is highly collimated and can be steered over considerable distances by conventional optics. In addition the bandwidth can be very narrow, the spectral purity can be high, and the polarization can be easily controlled. There is also no higher order VUV radiation which can be an issue with synchrotron undulator sources. Pulsed lasers sources are also well suited for measuring discreet events, such as in pump-probe experiments or single particle mass spectrometry.
Continuously tunable laser based VUV light sources capable of scanning over a wide frequency range are predominantly based on four wave sum or difference mixing in rare gases or metal vapors. Here three applied frequencies of light are used to produce a fourth based on the non linear response of a gas phase medium. Resonance enhanced four wave mixing increases the VUV output by having two of the applied frequencies set to reach a two-photon resonance in the medium. The third applied frequency is tunable and allows tunable VUV to be generated. This is shown schematically in Figure 5.1.

Figure 5.1 Schematic of resonance enhanced four wave difference mixing in xenon gas

The majority of tunable VUV sources based on four wave mixing use two dye lasers to produce the required frequencies of light. One of the lasers has its output fixed at the wavelength of the two-photon resonance, and the other is scanned to produce tunable VUV. In these systems tuning over a wide range of VUV energies requires frequent dye changes which is time consuming and not suitable for rapid and routine analysis. For example, Hilber et al. used thirteen different dyes to produce VUV light between 127 and 147 nm. Some variations on the two dye laser scheme have been employed. Faris et
al. used a combination of a dye laser and an ArF excimer laser, although dye changes were still required in order to scan over a broad frequency range. Alternatively, Qi and colleagues used two OPOs (optical parametric oscillators) pumped by separate Nd:YAG lasers, a system which overcomes the necessity of frequent dye changes.

A serious concern in analytical applications of VUV generated by four wave mixing is spectral purity. The generated light will contain the residual high intensity UV and visible or IR radiation used for the four wave mixing process, which are typically 6-8 orders of magnitude more intense than the generated VUV radiation. This, particularly in the case of the UV, can lead to unwanted multiphoton ionization. To avoid these effects, the VUV must be separated from the pump frequencies. Traditional grating monochromators typically have only about 10% efficiency in the VUV, and are easily damaged by intense UV pulses. Monochromators based on refractive optics such as prisms or lenses have higher efficiencies and damage thresholds. An off-axis lens monochromator has the advantage of focusing the light and allowing optimal discrimination. This technique has been used quite extensively in experiments where 355 nm light is tripled to produce VUV radiation at 118 nm and was reported in a tunable monochromator by Vondrasek et al. in 1988. However, to our knowledge no design has been presented that is capable of giving a precisely positioned VUV focus while scanning over a broad range of frequencies.

In this chapter a new VUV light source based on four wave difference mixing in xenon gas which incorporates both a dye laser and an OPO is described. The dye laser is used at a fixed frequency to access a two-photon resonance and the OPO provides the tunable wavelength. This has the advantage of allowing wavelength scanning between 122 and 168 nm, while requiring only one dye change. Both the dye laser and OPO produce narrow bandwidth light which allows for high resolution VUV scanning (bandwidth on the order of 0.5 cm\(^{-1}\)). In addition, a custom monochromator based on a single MgF\(_2\) lens has been incorporated into the design to separate the generated VUV from the pump wavelengths, to ensure high spectral purity, and to minimize absorptive losses.

Although this system has other potential applications, it was designed specifically as an ionization source for single particle organic aerosol mass spectrometry. As described
in section 1.2.3, the composition of organic aerosols can be very complex and often consists of large, fragile molecules which present a significant challenge to standard analytical techniques. Single photon ionization is a soft method which can be used to reduce fragmentation of labile compounds. Tripling the third harmonic of an Nd:YAG laser to produce 118 nm light has been used quite extensively in aerosol mass spectrometers. This is a relatively simple technique to undertake and gentle in comparison with many other ionization methods, although it has been shown that even 118 nm light is high enough in energy to cause significant fragmentation of some organics. Other avenues of single photon ionization that have been explored include VUV lamps, use of a synchrotron, and resonance enhanced four wave difference mixing to give VUV light at 142 nm (8.75 eV). Recently developed rare-gas excimer lamps are simple, compact, and have been successfully deployed as photoionization sources for mass spectrometry. The Advanced Light Source in Berkeley California (a synchrotron source) has been used very effectively to characterize the products of heterogeneous reactions involving small organic aerosols. However, the new rare-gas excimer lamps are incoherent, CW, broadband, and not continuously tunable. The synchrotron is also pseudo-CW (it has a very high repetition rate with low pulse energy), and access to such a facility is limited.

The VUV source described here has a high photon flux, which is a prerequisite for aerosol studies, especially for single particle studies (a 1 µm aerosol has ~10⁹ molecules, ~500 fg of material). It is also continuously tunable from 7.4 to 10.2 eV (168 and 122 nm) so that fragmentation can be minimized and compounds can be separated by ionization energies. The custom monochromator maintains a tight and precisely positioned focus even as the VUV wavelength is changed over tens of nanometers. Careful computer control of the pump optics and the monochromator lens also allow a uniformly sized focus to be maintained in the center of the ionization region while scanning. The source is laser based, so pulses are available on demand and mass spectra from individual aerosol particles can be acquired. To the best of our knowledge, this is the first demonstration of a laser based VUV source that is capable of routinely scanning over this wide frequency range while maintaining a tight and precise focus and maintaining a high spectral purity.
In this chapter the development of the continuously tunable VUV source is described in detail and gas phase measurements are shown to illustrate the sensitivity and accuracy of the combined VUV-mass spectrometer. Scanning over a wide frequency range while maintaining a tight and constant focus requires special equipment and carefully designed optical arrangements. This detailed description should allow others to assess the usefulness of such a VUV source for different applications.

The second objective of this work was to demonstrate the performance of the VUV source in analyzing single aerosol particles. Fragment free mass spectra for caffeine particles were acquired and the ionization energy of the aerosol constituent was determined. This is the first measurement of ionization energies of aerosol constituents using a laser based VUV source. The sensitivity of the system for caffeine aerosols was determined and the sensitivity for other types of organic aerosols is discussed.

5.2. Experimental

5.2.1. VUV generation and custom VUV monochromator

In this system vacuum ultraviolet light is generated by resonance enhanced four wave difference mixing in xenon gas. The output of a pulsed Nd:YAG laser (Continuum Powerlite PLUS), which produces 800 mJ per pulse at 355 nm, is split evenly and used to pump both a dye laser (Sirah PrecisionScan SL) and an optical parametric oscillator (OPO) (Continuum Sunlite). The second harmonic of the dye laser is tuned to deliver high intensity pulses (6-12 mJ) at either 249.56 nm or 222.62 nm, each of which corresponds to a separate two-photon resonance in xenon gas. The OPO is used to generate a continuously tunable output between 470 nm and 1250 nm. By focusing one of the two ultraviolet (UV) wavelengths, along with the tunable output of the OPO, into a xenon gas cell, vacuum ultraviolet light is produced by resonance enhanced four wave difference mixing. The four wave mixing process is shown schematically in Figure 5.1 and its particulars have been described extensively.$^{113,114}$ Using a single laser to pump
both the dye laser and the OPO eliminates timing jitter between pulses and increases the stability of the VUV output.

The OPO is capable of producing light between 445 nm and 1750 nm, but for this application the available energy below 470 nm and above 1250 nm was insufficient to produce satisfactory amounts of VUV. These energy boundaries, together with the MgF₂ transmission cutoff at approximately 120 nm, limit our ionization source to photon energies between 7.4 eV (168 nm) and 10.2 eV (122 nm). However, this energy range is well suited for gentle ionization of a wide range of organic molecules.¹¹²,¹³¹,¹³² The vast majority of organic compounds found in aerosols have ionization energies (IEs) in this range, with some notable exceptions. Small acids such as acetic, formic,¹³³ and fumaric acid¹³⁴ have IEs above 10.2 eV. Other molecules such formaldehyde¹³³ and peroxycetyl nitrate (PAN)¹³⁵ are also out of reach with the current setup. Four wave mixing VUV sources which use a jet of rare gas rather than a cell are not limited by the transmission cutoff of the windows and can produce light of up to 20 eV,¹³⁶ albeit at lower intensities and with the necessity of more complex, reflective monochromators.

Figure 5.2 is a schematic of the experimental setup, showing in detail the optical arrangement used to generate vacuum ultraviolet light and the custom monochromator used to separate the VUV from the UV and visible or IR light used to produce it. Also shown is the single particle aerosol mass spectrometer, described in Chapter 4, which is coupled to the VUV source.
Figure 5.2 Schematic of the VUV source and aerosol mass spectrometer. To generate VUV, UV light from a dye laser and visible or IR light from an OPO is focused into a rare gas cell. The UV and visible/IR light are separated from the generated VUV by an off-axis MgF$_2$ lens and blocked by a ceramic beam dump. The VUV light is refocused into the center of an ion trap mass spectrometer by a parabolic mirror. Aerosols are focused into a collimated stream by an aerodynamic lens and detected by scattering from two 532 nm CW Nd:YAG lasers. When a particle reaches the center of the ion trap, a CO$_2$ laser is fired to vaporize it, followed by single photon ionization.
As shown in Figure 5.2, the pulses from the dye laser and OPO are combined using a dichroic mirror and focused together into the xenon gas cell. Because the OPO wavelengths cover such a broad range (470-1250 nm), it is necessary to use two telescopes to maintain focus matching of the UV and visible/IR in the rare gas cell. During a VUV wavelength scan the UV telescope is kept in a fixed position, while the visible/IR telescope is slowly scanned to maintain a good focus overlap and thus maximize the VUV intensity.

At the exit of the xenon gas cell the co-linear UV, visible/IR, and VUV beams are directed off-axis onto a MgF₂ lens which disperses the different wavelengths and allows the UV and visible/IR beams to be blocked by a ceramic plate while the VUV passes through a 3 mm pinhole and is directed into the ion trap mass spectrometer. Due to wavelength dependent changes in the refractive index of MgF₂, VUV beams of different wavelengths are deflected at different angles by the lens. To keep the deflection angle constant as the VUV wavelength is changed, the position of the MgF₂ lens is scanned in a direction shown by arrow 1 in Figure 5.2.

A single lens dispersion system has several advantages over other systems. First, it minimizes absorptive losses by having a single element both disperse the light and act as a vacuum break between the rare gas cell and the high vacuum part of the system. Second, the focusing properties of the lens allow the residual pump wavelengths to be blocked at the focus of the VUV light where discrimination is optimal. The MgF₂ also absorbs any undesired shorter wavelengths generated by four wave sum mixing or tripling of the pump beams.

Once the VUV has been separated from the pump wavelengths, it is refocused and directed into the ion trap mass spectrometer using an off-axis parabolic mirror. For studies of aerosol particles tight focusing of the VUV light is necessary. In aerosol experiments submicron particles enter the mass spectrometer through a hole in the ring electrode and are vaporized by a pulsed CO₂ laser when they reach the center of the ion trap. If the resulting vapor plume is allowed to expand too far, its density and the density of photons in a beam large enough to capture the whole plume are too low to result in good ionization efficiency. On the other hand, if the detection zone becomes too small, irregularities in the position of the particle beam as well as irregularities in the desorption
and ionization beams will significantly decrease reproducibility. A good compromise is using an ionization zone approximately 1 mm in diameter. Assuming a sonic expansion of the vapor plume, this means having the ionization pulse 3-8 µs after the desorption pulse (depending on molecular mass) in order to ensure optimal overlap. Even under these conditions, good reproducibility can only be achieved by a precise control of size and position of the VUV focus. The off-axis parabolic mirror allows for tight focusing; precision positioning is achieved by mounting the vacuum chamber which houses the off-axis parabolic mirror on a precision x-y translation stage allowing micrometer level changes to be made in the horizontal position of the VUV beam. The mirror itself is mounted on a rotational vacuum feedthrough which has been adapted to allow for µrad adjustments in the vertical angle of the beam.

Because of wavelength dependent changes in the refractive index of MgF₂, the VUV focus size in the ion trap will vary as the VUV wavelength is changed. For aerosol experiments it is important that the focus size remain constant as the VUV wavelength changes so that a constant, optimized overlap of the VUV beam with the cloud of molecules from the recently vaporized aerosol particle is maintained. To achieve this, the position of the lens which focuses the pump beams into the xenon gas cell is scanned as function of VUV wavelength. This allows a constant focal volume to be maintained at the position where the VUV beam interacts with the aerosol plume. The VUV light is detected after exiting the ion trap and its intensity is measured using a fast phototube (Hamamatsu, R1328U-54, 270 ps rise time).

The VUV source can be operated in two different modes. The first is a fast scanning mode, where the VUV wavelength is scanned continuously over tens of nanometers. The second is a fixed wavelength mode with the VUV optimized at a single photon energy.

5.2.1.1. Fast VUV scanning mode

The challenge when scanning the VUV photon energy is in maintaining a good overlap between the UV and visible/IR beams in the xenon gas cell while also maintaining a good alignment of the generated VUV through the ion trap. To make this possible in the fast scan mode, the MgF₂ lens, the visible/IR telescope, and the lens which
focuses light into the rare gas cell (Figure 5.2) are all mounted with motorized actuators that can be controlled remotely by a computer. This allows precise control of the VUV beam and makes it easy to scan over large wavelength ranges. The only limitation on scanning speed is the need to change laser dyes when switching between the two xenon resonances. A scan of the full range can be completed in a few hours and, if the UV wavelength is not changed, scans over half of the range can be done in as little as thirty minutes. This quick scanning ability can be very useful for rapid compound identification via ionization energies, and it also allows the VUV wavelength to be easily optimized for any particular compound of interest. If high resolution scans are desired, the various optical elements and the OPO can be scanned very slowly. At the slowest possible scanning speed (0.002 nm/s for the OPO) the scan resolution becomes limited by the bandwidth of the VUV light (less than 0.5 cm$^{-1}$) rather than by the scanning capabilities of the system.

Since the phase matching condition for VUV generation is pressure dependent, careful tuning of the xenon gas pressure in the four wave mixing cell is required for optimum conversion efficiency throughout the spectrum. However, in the current setup the gas pressure is not constantly tuned when scanning quickly across long wavelength ranges. As a compromise between optimum VUV conversion efficiency and ease of scanning, several xenon pressure regimes have been determined that can be used over a range of wavelengths. These pressures are optimized for the pump energies and optical arrangement described here, and may not represent the best conditions for all systems. Table 5.1 shows the range of VUV wavelengths that can be generated using the two xenon resonances and the output of the OPO. Also shown are the xenon pressures used for rapid scans in the different wavelength ranges.
Table 5.1 Wavelength and energy ranges of vacuum UV light generated using different combinations of pump laser wavelength. Also shown are the xenon gas pressures used in the rare gas cell for VUV generation over several broad wavelength ranges.

<table>
<thead>
<tr>
<th>Dye Laser wavelength (nm)</th>
<th>OPO wavelength (nm)</th>
<th>VUV wavelength (nm)</th>
<th>VUV energy (eV)</th>
<th>Xe pressure in the rare gas cell (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>222.56</td>
<td>1250-831 (Idler)</td>
<td>122-128.5</td>
<td>10.16-9.65</td>
<td>35</td>
</tr>
<tr>
<td>831-710 (Idler)</td>
<td>128.5-132</td>
<td>9.65-9.40</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>710-470 (Signal)</td>
<td>132-146</td>
<td>9.40-8.51</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>249.62</td>
<td>1250-1010 (Idler)</td>
<td>139-142</td>
<td>8.94-8.75</td>
<td>45</td>
</tr>
<tr>
<td>1010-710 (Idler)</td>
<td>142-151</td>
<td>8.75-8.19</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>710-470 (Signal)</td>
<td>151-168</td>
<td>8.19-7.40</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

5.2.1.2. Fixed VUV wavelength mode

In addition to operating in a scanning mode, experiments can also be carried out in a fixed VUV wavelength mode. In this case the visible/IR wavelength is fixed, as are the positions of the visible/IR telescope and the lens which focuses light into the rare gas cell. The gas pressure and composition in the cell are optimized to give the best conversion efficiency. The conditions that lead to the best conversion efficiencies are discussed in more detail in section 5.3.1.2. An advantage of this mode is the ability to increase the VUV intensity which can be useful in specific instances. With the fast tunability of the OPO and the motorized actuators on all the stages, it is very easy to jump between VUV wavelengths when operating in this fixed VUV wavelength mode. A jump to a new wavelength tens of nanometers away can be accomplished in just a few minutes.
5.2.2. Gas phase measurements

To introduce the gas phase analytes into the ion trap, a glass bubbler containing a small amount of liquid analyte was coupled to the trap manifold via a 100 µm critical orifice placed off-axis to the ion trap to ensure thermalizing of the compound prior to analysis. Several pump/thaw cycles were undertaken to degas the samples and the analyte was then cooled to a temperature that gave a vapor pressure of 50 to 1000 mTorr above the sample (measured by a capacitance manometer (MKS 622)). The critical orifice between the bubbler and ion trap guaranteed a stable flow into the trap. Typical analyte pressures in the ion trap were between 9-85 µTorr as measured by a cold cathode gauge (MKS 423). The absolute pressure reading of the cold cathode gauge was calibrated using nitrogen gas and a high accuracy absolute capacitance manometer (MKS 120). The cold cathode gauge itself was typically switched off during measurements to avoid ion production from this source.

The ion trap mass spectrometer used for these experiments was described in section 4.3. For these measurements mass scans were performed at a scanning speed of 4000 Da/s, with a mass resolution under these conditions of ~ 500 m/Δm at m/z = 264

5.2.3. Aerosol measurements

A TSI constant output atomizer (TSI Inc., Model 3076) was used to generate aerosol particles from a pure caffeine solution (~1x10⁻³ g/ml in Millipore water (18 MΩ)). The particles were size selected with a TSI differential mobility analyzer (DMA) (TSI Inc., Model 3081) and passed through a ⁸⁵Kr charge neutralizer (TSI Inc., Model 3054) that also acted as drying tube, as well as a 24 inch nafion diffusion dryer (Permapure Inc), to avoid additional drying and size changes prior to analysis.

In these experiments a fixed delay of 3 µs was used between the CO₂ laser desorption and vacuum UV ionization of the aerosol constituents. A delay of 3 µs was chosen because it allowed the cloud of vapor to expand and fill the ionization volume giving the maximum ion signal. The energies of the IR and VUV pulses were measured after they exited the ion trap. For the CO₂ laser a power meter with a thermal detector (Ophir
Model 3A-SH) was used to measure the average IR power. For the VUV, a fast phototube (Hamamatsu, R1328U-54) was used to measure the single-shot energy.

After vaporization and ionization, the ions from an aerosol particle were stored in the trap for 10 ms to allow for collisional cooling with the helium bath gas. Mass analysis was conducted with the same scan speed as in the gas phase measurements.

5.2.4. Triggering the laser system; pulses on demand

As described in section 4.2, the Nd:YAG laser which pumps both the dye laser and the OPO operates at 10 Hz, but the timing of each pulse can be shifted by up to 60 ms while still maintaining an average firing rate of 10 Hz. This means that the VUV pulses can be generated on demand to coincide with the arrival of an aerosol particle in the ion trap. The pulsed nature of the VUV source makes it well suited for coupling to an ion trap mass spectrometer, which can obtain discreet mass spectra after every ionization event.

5.2.5. Chemicals

Benzaldehyde (≥99%), ethylbenzene (99.8%), α-pinene (≥99%), and tripropyl amine (99+%) were purchased from Aldrich. Benzene (99.97%) was purchased from OmniSolve, toluene (99.9%) was purchased from Fisher, and chlorobenzene (99+%) was purchased from Acros. Caffeine (≥98.5%) was purchased from Sigma-Aldrich. All chemicals were used without additional purification. Gases were purchased from Praxair. Gases used were xenon (99.999%), argon (99.999%), krypton (99.999%), and helium (99.999%).
5.3. Results and discussion

5.3.1. VUV source characterization

5.3.1.1. Brightness in fast scanning mode

Figure 5.3 shows the number of VUV photons detected as a function of wavelength over the entire 122–168 nm range. Between $10^{10}$ and $10^{13}$ photons are generated per 5 ns pulse. The values in Figure 5.3 were calculated using the absolute photocathode sensitivity at 253.7 nm and a generic (not specific to the particular phototube used) calibration curve from 320 to 115 nm which was provided by the manufacturer of the VUV phototube. A 20% error is estimated to arise from graphical interpolation of this calibration curve. In addition, since the phototube was only calibrated at 253.7 nm, there is some uncertainty in the transmission of the phototube’s MgF$_2$ window at shorter wavelengths. For wavelengths below 130 nm, where MgF$_2$ begins to absorb significantly, it is estimated that the transmission may be up to 50% lower than at the calibration wavelength. Between 130 and 140 nm it is estimated that the MgF$_2$ transmission could be up to 30% lower than at the calibration wavelength. This would lead to an underestimation of the real photon flux in both cases.
Figure 5.3 Number of photons per pulse generated across the full range of the VUV source. The grey traces are UV background shown on the same scale. The dark grey trace is UV light at 222.56 nm and the light grey is light at 249.62 nm. The change in the background at 140 nm reflects the higher UV power available when using 249.62 nm. Estimated uncertainties are listed in Table 5.2.

To prevent saturation of the phototube, the VUV light reflected at 45 degrees off of a MgF₂ window on the exit port is monitored. The amount of reflected light was measured to be (4 ± 1)% at both 148.5 nm and 131 nm leading to a 25% uncertainty in the calculated number of photons. However, due to the increasing absorbance of MgF₂, the reflection may be greater at short wavelengths and for wavelengths below 130 nm it could be up to five times higher. At wavelengths longer than 150 nm the VUV is intense enough that a second MgF₂ reflector has to be used which introduces a further 25% uncertainty at long wavelengths and even with the precaution of a second reflector, it is possible that the phototube is somewhat saturated above 150 nm, which could result in lower than actual photon fluxes being measured. The uncertainties for the numbers reported in Figure 5.3 are summarized in Table 5.2.
Table 5.2: Average photons per pulse available for different VUV ranges. Also included are the estimated upper and lower limits for the photon flux based on the uncertainties discussed in section 5.3.1.1.

<table>
<thead>
<tr>
<th>Dye laser wavelength (nm)</th>
<th>Wavelength range (nm)</th>
<th>Energy range (eV)</th>
<th>Average photons</th>
<th>Upper limit</th>
<th>Lower limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>222.56</td>
<td>122-130</td>
<td>10.16-9.56</td>
<td>$1 \times 10^{10}$</td>
<td>$3 \times 10^{10}$</td>
<td>$1.4 \times 10^9$</td>
</tr>
<tr>
<td></td>
<td>130-140</td>
<td>9.56-8.87</td>
<td>$2 \times 10^{11}$</td>
<td>$4 \times 10^{11}$</td>
<td>$1.1 \times 10^{11}$</td>
</tr>
<tr>
<td>249.62</td>
<td>140-150</td>
<td>8.94-8.28</td>
<td>$4 \times 10^{12}$</td>
<td>$6 \times 10^{12}$</td>
<td>$2.3 \times 10^{12}$</td>
</tr>
<tr>
<td></td>
<td>150-168</td>
<td>8.28-7.40</td>
<td>$1 \times 10^{13}$</td>
<td>$1.8 \times 10^{13}$</td>
<td>$4 \times 10^{12}$</td>
</tr>
</tbody>
</table>

The rapid decline in VUV intensity at wavelengths below 128 nm reflects the increasing absorbance of the MgF$_2$ monochromator lens at short wavelengths as well as the reduced energy of the OPO as it is tuned into the IR. It has also been shown that the efficiency of four wave difference mixing decreases as the generated wavelength decreases.\(^{117}\) Two sharp dropouts which occur at 129.56 nm and 146.96 nm are due to the presence of strong resonance lines in xenon gas. The refractive index of xenon changes rapidly in the vicinity of these resonance lines\(^{139}\) and the phase matching conditions required for generation of VUV by four wave mixing cannot be maintained. Figure 5.3 was made with the VUV system in fast scanning mode, and the xenon pressures used were relatively high (Table 5.1). The width of the energy dropouts around the resonances can be minimized by decreasing the xenon pressure in the rare gas cell, but this comes at the price of reduced energy at wavelengths further away from the resonance lines. The pressures listed in Table 5.1 are compromises which minimize the width of the dropouts without sacrificing too much power over the whole scanning region.

A pulsed VUV source such as this one is very valuable for single particle aerosol experiments. The cloud of molecules from a vaporized particle is only in the ionization region for approximately 10 µs, and with a pulsed source the entire photon flux is delivered during this time, ensuring the maximum photoionization efficiency. With a continuous source the particle is only exposed to a fraction of the total photon flux. For
example, with a synchrotron source which delivers $\sim 10^{16}$ photons per second$^{60}$ a single particle which is in the ionization region for $10 \mu s$ will only see $10^{11}$ photons. It should be kept in mind however, that a continuous source can have other advantages. For instance, a synchrotron source has been used very effectively to study a continuous stream of very small particles which cannot be detected individually.$^{52, 60}$

5.3.1.2. Brightness when optimizing for a single VUV wavelength

In many experiments it is advantageous to fix the VUV at a particular wavelength while other parameters are investigated. For this mode of operation some measures can be taken to increase the VUV output, especially in the vicinity of strong resonance lines. At any wavelength the xenon pressure can be optimized to give the best VUV output. Near resonance lines, low xenon pressures generally give the best conversion efficiency and allow VUV to be generated within 0.5 nm of the resonance. In addition, on the high energy side of the resonances it is possible to achieve increased VUV conversion efficiency by adding a second, positively dispersive gas to the four wave mixing cell. This is possible because xenon shows anomalous dispersion over a short energy range just to the blue of the resonance lines.$^{139}$ The addition of a positively dispersive gas allows the xenon pressure to be increased without destruction of the phase matching conditions required to propagate the generated VUV.$^{112, 140}$ However, since the refractive index changes very rapidly with wavelength in these regions, a particular gas mix will only give enhanced conversion efficiency over a very narrow range of wavelengths, generally much less than one nanometer.$^{112}$

To measure the effectiveness of gas mixing near xenon resonances a series of experiments were done in which the VUV was set to a fixed wavelength and a gas mixture with fixed partial pressures of xenon and argon was slowly leaked into the four wave mixing cell. Typically the maximum VUV output for a given wavelength occurred at a total gas pressure more than twice the optimal pressure seen for pure xenon gas. In Figure 5.4 the compositions of the gas mixtures giving optimal VUV output are shown.

For the longer wavelengths (138 nm to 147 nm) the enhancement in VUV intensity over pure xenon was up to a factor of 3.5. For wavelengths between 126 nm and 129 nm,
and near 125 nm, the enhancement was less, reaching a factor of two at the maximum. It should be noted, however, that this method of testing gas mixtures is rather time consuming since the mixtures must be individually prepared and then leaked into the rare gas cell until a peak in the VUV intensity is seen. This process must be repeated for each gas mixture and at each wavelength to be tested. It is possible that better conversion efficiencies might be attainable with more time spent preparing and testing gas mixtures.

In addition to the xenon resonances, the tuning range of the VUV source includes a resonance in krypton gas at 123.58 nm. By taking advantage of the anomalous dispersion of krypton gas at the high energy side of this resonance, mixtures of krypton and xenon can enhance the conversion efficiency at wavelengths shorter than 123.58 nm. The compositions of the krypton and xenon mixtures that give optimal conversion efficiencies are also shown in Figure 5.4. For these mixtures gains were more modest, with VUV outputs increased by approximately 30% compared to pure xenon.

![Figure 5.4 Composition (in vol %) of the gas mixtures used for four wave mixing throughout the full energy range of the VUV source. On the high energy side of the xenon resonances (at 147.0, 129.6 and 125.0 nm) mixtures of xenon and argon are used. On the high energy side of the krypton resonance (at 123.6 nm) a mixture of krypton and xenon is used. Shaded regions mark areas where gas mixing can be used to enhance the VUV production.](image-url)
5.3.1.3. Spectral purity

The single MgF₂ lens used to disperse the VUV, UV, and visible or IR wavelengths involved in the four wave mixing process gives good separation of the VUV and pump beams with a minimum of optical elements. This allows the UV and visible or IR light to be blocked by a ceramic beam dump while the VUV light passes through a pinhole and is directed into the mass spectrometer.

Figure 5.5 shows calculated edge to edge separations between the UV and VUV beams, based on the $2\sigma$ beam waist of the input UV laser beam (calculations done with OSLO 6.4.4, Lambda Research Corp). Separation is always larger than the blocker pinhole radius (1.5 mm), ensuring proper discrimination at all wavelengths. Also shown in Figure 5.5 is a digital photograph of the ceramic blocker fully inserted into the path of the three laser beams (visible, UV, and VUV). By using the two-photon xenon resonance at 249.62 nm and 355 nm light for the mixing, VUV light at 193 nm was generated. Light at 193 nm not only gives strong fluorescence intensity on the blocker, but also represents the lower limit of achievable separation.
Figure 5.5 Calculated monochromator performance as measured by the separation of the VUV and UV laser beam edges at the ceramic blocker. The photograph in the inset shows the actual fluorescence of the blocker from dispersed 355 nm, 249 nm, and 193 nm light. Even in this worst case scenario, where the dispersion from the MgF2 lens is weakest, good separation of the beams is achieved and experiment and calculation agree fairly well.

Although the wavelength separation of the monochromator is very good, some scattered UV light does enter the ion trap. The scattered UV light can be measured directly by the same phototube as used for the VUV (the sensitivity of the tube in the UV is in fact significantly higher than in the VUV). To correct for this UV background in the measured VUV intensity the light from the OPO is blocked so that no VUV light is produced, but UV light still enters the ion trap and is detected by the phototube. The monochromator is then scanned and the UV background measured as a function of the
lens position. This measured UV background is then used to correct the phototube response when calculating the number of VUV photons at a particular wavelength.

In Figure 5.3 the UV entering the trap is shown as a grey trace. In all cases, measured UV powers were at least eight orders of magnitude lower than the input power, proving the effectiveness of the monochromator. For the UV measurements, the error from interpolation of the phototube calibration curve is negligible, so the total uncertainty of 25% for the UV values in Figure 5.3 stems exclusively from uncertainty in the reflectance of the MgF₂ window.

The presence of the UV background has no discernable effect on single photon ionization. No ions are detected if the light from the OPO is blocked and only the UV background is allowed into the ion trap. This is true even for aromatic compounds which have strong REMPI cross-sections in the UV. Also, for all of the species analyzed, the onset of ionization observed by scanning the VUV energy was very close to the literature value for the ionization threshold, suggesting that the ionized molecules are not absorbing UV photons in addition to VUV photons.

5.3.1.4. Stability

The stability of the VUV source over time is dependent on keeping the dye laser tuned to the two-photon resonance being used. Fortunately broadening of the resonance can virtually eliminate the effects of small drifts in the UV wavelength. With increasing xenon gas pressure, detuning of the UV wavelength away from the resonance reveals broadening which is likely attributable to saturation effects. Figure 5.6 shows the effect of increasing the xenon pressure in the rare gas cell. At pressures between 7 and 38 Torr the resonance becomes considerably broadened. At 17 Torr a small dip appears at the peak of the profile which occurs because phase matching can no longer be maintained at the center of the resonance. At pressures greater than 50 Torr the VUV conversion efficiency begins to decline. However, moderate gas pressures do not reduce the amount of VUV produced, and the broadening of the resonance helps to increase the stability of the system over time allowing the grating in the dye laser to be left for several days before it needs to be re-optimized.
Figure 5.6 Broadening of the 249.62 nm two-photon resonance in xenon gas. For this experiment the tunable wavelength was set at 533 nm (VUV wavelength of 163 nm). Xenon pressures were 2, 7, 10, 17, and 38 Torr. At higher gas pressures phase matching cannot be achieved at the center of the resonance.

In theory the VUV intensity should also be sensitive to drifts in the power of the UV and visible/IR pulses. However, it was observed that increasing the output of either the dye laser or the OPO beyond a certain point had a negligible effect on the VUV production. Although this effectively limits the amount of VUV that can be generated by the system, it does help to give relatively constant VUV intensities over the entire wavelength range since small changes in the intensity of the OPO output as it is scanned do not have an overwhelming impact on the VUV intensity. This also helps explain why the shot-to-shot variability of the VUV power (~10%) is considerably less than the sum of the power variations of the input lasers (~8% per laser).
5.3.2. Ionization of gas phase organics

Seven different organic species were analyzed in the gas phase in order to test the effectiveness of the VUV system as a soft ionization source for mass spectrometry. The linearity of the technique was assessed and both photoionization efficiency curves and mass spectra were collected for all seven organics. Shot to shot variability in the ion signal was approximately 30% with about 10% of this variability arising from fluctuations in the VUV intensity.

The linearity of the instrument’s response was tested with respect to both the VUV intensity and the amount of analyte present. A linear response to changing VUV intensity makes it possible to normalize the ion signal to the VUV photon flux. A linear response to the amount of analyte present means that quantitative studies may be possible. To test the VUV intensity dependence, tripropyl amine was ionized at 8.17 eV (152 nm). At 8.17 eV the photon flux of the VUV source is high, giving a good dynamic range over which to test the response of the system. To test the linearity of the system with respect to the amount of analyte present, benzene was ionized at 10.02 eV (124 nm). In both cases a linear response was seen (Figure 5.7). The larger errors for the benzene number density in Figure 5.7(b) reflect the uncertainty in the reproducibility of the cold cathode gauge (5% is reported by the manufacturer) and the uncertainty in its calibration. The plot of ion signal versus benzene number density can be used to calculate a gas phase detection limit for benzene ionized at 10.02 eV. If a detection limit of three times the standard deviation of the noise is used, the single shot gas detection limit for benzene at this photon energy is $4.2 (\pm 3) \times 10^9$ molecules cm$^{-3}$ [1.3 (± 0.9) x 10$^{7}$ Torr].
Figure 5.7 Total ion signal with respect to (a) VUV intensity and (b) analyte pressure. VUV intensity dependence was measured using tripropyl amine and a photon energy of 8.17 eV (152 nm). Analyte pressure dependence was measured using benzene and a photon energy of 10.02 eV (124 nm).
The ability to obtain photoionization efficiency curves and to observe the appearance energy of ions is a distinct advantage of a tunable VUV system. This information can facilitate the identification of unknown species and can provide a useful tool for determining the composition of a mixture. A group working at the Advanced Light Source at Lawrence Berkeley National Labs has used PIE curves obtained with the tunable VUV light from a synchrotron source to identify components of atmospheric aerosols and to determine their ionization energies. Another group working at the same facility has done considerable work using tunable VUV to study combustion chemistry. They have been able to measure photoionization cross-sections, determine ionization energies, and, by comparison of observed ionization energies with calculated values, identify many of the species involved in combustion chemistry.

In this study photoionization efficiency curves were obtained for seven gas phase organic molecules with ionization energies spanning the full range of the VUV source (Figure 5.8). To obtain the PIE curves, the VUV wavelength was scanned at a constant speed while the amount of analyte in the ion trap was held steady. A full mass spectrum was obtained for every laser shot, and the scan speed was set so that a mass spectrum was recorded every 0.001-0.002 nm. Literature values for the ionization thresholds of the seven analyzed compounds are listed in Table 5.3 along with the observed ionization thresholds obtained by extrapolating the linear portion of the threshold region of the PIE curves to the baseline. Despite this rather basic approach for determining the ionization threshold from the PIE curves, in almost all cases the observed onset of ionization is within 60 meV of the reported literature value. However, in most cases there is also a low energy tail that does not fall into the linear portion of the threshold, but indicates an onset of ionization at energies below the literature value for the IE. The low energy tails in Figure 5.8 have a width on the order of 2kT (52 meV) at room temperature, and may be attributed to ionization of vibrationally excited neutrals, which can be ionized at lower energy. These PIE curves provide a useful test of the VUV source, and the observed onsets of ionization are close enough to the literature values that the appearance of ions at a particular energy can be used to help identify the molecular ion.
Figure 5.8 Photoionization efficiency curves showing the onset of ionization for (a) benzene [C₆H₆], (b) toluene [C₇H₈], (c) chlorobenzene [C₆H₅Cl], (d) ethylbenzene [C₈H₁₀], (e) benzoic acid [C₇H₆O], (f) α-pinene [C₁₀H₁₆], and (g) tripropyl amine [C₉H₂₁N]. Linear fits were used to extrapolate the experimental onset of ionization from the linear portion of the curve. Onsets of ionization are listed in Table 5.3.
Table 5.3 Neutral molecule masses, literature IE values, and experimental IE values for the seven gas phase organic molecules studied. Also included are the photon energies at which the mass spectra in Figure 5.9 were collected.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Molecular Mass (Da)</th>
<th>Literature IE (eV)</th>
<th>Experimental IE determined by linear extrapolation of the threshold region of the PIE curve (eV)</th>
<th>Photon energy to obtain the mass spectrum in Figure 5.9 (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>78.11</td>
<td>9.24378 ± 0.00007 (^{133})</td>
<td>9.22 ± 0.05</td>
<td>10.12</td>
</tr>
<tr>
<td>Toluene</td>
<td>92.14</td>
<td>8.828 ± 0.001 (^{133})</td>
<td>8.80 ± 0.02</td>
<td>8.84</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>112.56</td>
<td>9.07 ± 0.02 (^{133})</td>
<td>9.04 ± 0.02</td>
<td>9.18</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>106.17</td>
<td>8.77 ± 0.01 (^{133})</td>
<td>8.74 ± 0.02</td>
<td>8.82</td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>106.12</td>
<td>9.50 ± 0.08 (^{133})</td>
<td>9.50 ± 0.02</td>
<td>9.54</td>
</tr>
<tr>
<td>α-pinene</td>
<td>136.23</td>
<td>8.07 (^{152})</td>
<td>8.13 ± 0.10</td>
<td>8.18</td>
</tr>
<tr>
<td>Tripropylamine</td>
<td>143.27</td>
<td>7.23 (^{155})</td>
<td>7.44 ± 0.10</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Figure 5.9 shows the mass spectra obtained by setting the photon energy close to the ionization threshold of each of the seven molecules studied (photon energies used to obtain these spectra are listed in Table 5.3). As expected, most of the mass spectra show a molecular ion and small isotope peak, as is the case for benzene in panel A. Chlorobenzene in panel C shows two sets of peaks in the expected ratio for a compound containing both \(^{35}\)Cl and \(^{37}\)Cl. Toluene, however (panel B), shows a small peak one mass unit below the molecular ion mass. The photon energy used in these experiments is well below the energy need to form the [M-H]\(^+\) ion directly from toluene (based on thermochemical data).\(^{154}\) A possible explanation for the small amount of fragmentation is high energy collisions between [M]\(^+\) and neutral molecules in the trap. During the storage time in the trap, the toluene molecular ion undergoes collisions with the buffer gas, and a small fraction of these collisions may result in enough additional energy transferred to the molecular ion to result in fragmentation. This possibility was
investigated by increasing the RF storage voltage of the ion trap to give a range of $q_z$ values from 0.1 to 0.6. For toluene, increasing the storage voltage over this range gave up to a factor of four increase in the ratio of [M-H]$^+$ ion to molecular ion. For the experiments described here toluene the ions were formed at a $q_z$ value of 0.5 and it seems that collisions are realistic avenue for fragmentation of the gas phase toluene ions at this storage voltage level. The same [M-H]$^+$ fragment can be observed for benzaldehyde (panel E) and tripropylamine (panel G) which were also formed at quite high $q_z$ values. These cases show that post-ionization dissociation in the trap can at times offset some of the benefits gained by near threshold ionization.

Figure 5.9 Single photon ionization mass spectra of (a) benzene, (b) toluene, (c) chlorobenzene, (d) ethylbenzene, (e) benzaldehyde, (f) $\alpha$-pinene, (g) tripropyl amine ionized with with 7.5 eV, and (g') tripropyl amine ionized with 10 eV. The photon energies at which spectra (a) through (g) were collected are listed in Table 5.3

A tunable VUV source has a significant advantage over single photon ionization sources operated at a fixed energy, typically 10.5 eV, since the ability to tune the ionization energy can minimize and, in some cases, completely eliminate fragmentation of the molecular ion. In these experiments tripropyl amine showed no fragmentation near the ionization threshold, but began to show a significant amount of fragmentation.
when the photon energy was increased by as little as 0.5 eV. By the time it was raised 2.5 eV to an energy of 10 eV, the molecular ion made up less than 35% of the total ion signal. This is shown in panels (g) and (g’) of Figure 5.9.

The ability to obtain fragment free, or nearly fragment free, mass spectra has several advantages. For mixtures of compounds it leads to much simpler spectra than those obtained with conventional ionization techniques such as electron impact. In addition, compounds that have very similar fragmentation patterns might be more readily distinguished if only the molecular ion peak is present. On the other hand, electron impact has an advantage in that often the fragmentation pattern gives additional chemical information that is not available from a mass spectrum containing only the molecular ion peak. However, by using a soft ionization source coupled to an ion trap mass spectrometer it is possible to selectively trap a molecular ion of interest and perform MS/MS, thereby regaining the chemical information sacrificed by soft ionization.

5.3.3. Single particle measurements

As a first test of the applicability of the VUV source to organic aerosol mass spectrometry, experiments with caffeine particles were undertaken. Figure 5.10 shows a series of mass spectra from 650 nm particles vaporized at CO2 laser energies of 5, 10, 15, and 20 mJ and ionized 3 µs later by 142 nm (8.75 eV) VUV radiation. The CO2 laser is tunable across 60 rotational lines between 923 cm−1 and 1087 cm−1 (10.8 to 9.2 µm) and for these experiments it was tuned to 978 cm−1 (10.22 µm), which corresponds to an IR absorption band in caffeine.155 The mass spectra show that the molecular ion remains dominant over the full extent of our CO2 energy range; however, fragments begin to appear at energies above ~10 mJ/pulse. The main fragment is at m/z 109 with lower abundance fragments at m/z 193,165, 137, 82, and a very small peak at m/z 94. These peaks are well known from literature caffeine mass spectra obtained using 70 eV electron impact.156 The appearance of fragments with increased heating of the aerosol during vaporization is not surprising and is in agreement with results reported for the vaporization of particles using both pulsed IR lasers and impaction on a heated probe.51, 59, 63, 86 The dynamics of aerosol heating by the CO2 laser pulse will be the focus of
Chapter 7. However, Figure 5.10 does shows that high quality aerosol mass spectra can be obtained with the VUV system. In addition, if the vaporization laser energy is kept reasonably low, fragment free mass spectra can be obtained. Figure 5.11 shows mass spectra from 300 nm caffeine particles which were vaporized with 15 mJ of 978 cm\(^{-1}\) infrared light and ionized by 142 nm (8.75 eV) VUV light after a delay of 3 \(\mu\)s. The top frame is an average of 200 laser shots and the bottom frame is a single particle. Both the averaged and single particle spectra have very good signal to noise ratios. If a detection limit of three times the standard deviation of the noise is used, a minimum detectable particle diameter of 75 nm for caffeine can be calculated from the averaged spectrum. Analyzing particles this small is not possible at present since scattered light cannot be detected from caffeine particles below ~225 nm in the aerosol timing and sizing region, however this limit should allow for detection of low concentration components in larger aerosol particles. With caffeine, for example, detection of as few as \(8 \times 10^5\) molecules which is approximately 1.5% of a 300 nm particle should be possible.

Figure 5.10 Caffeine \([C_8H_{10}N_4O_2]\) aerosol mass spectra as a function of the CO\(_2\) laser energy used to vaporize the particles. The particles used for these experiments were 650 nm in diameter and the vaporization energies were (a) 5 mJ/pulse, (b) 10 mJ/pulse, (c) 15 mJ/pulse, and (d) 20 mJ/pulse.
Figure 5.11 Mass spectra from 300 nm caffeine particles vaporized by 15 mJ of CO$_2$ laser energy (978 cm$^{-1}$) and ionized with 142 nm VUV after 3 µs. The top panel is an average of 200 shots while the bottom is a single particle.

Figure 5.12 is a photoionization efficiency curve for pure caffeine aerosols 550 nm in diameter. The solid line was obtained by continuously scanning the VUV wavelength and recording both the ion signal and the VUV power for each laser shot. Scan speeds were on the order of 0.005 nm/s (0.0003 eV/s at 140 nm) and spectra were recorded 3-4 times per second to give a resolution of ~0.002 nm (0.0001 eV). Fluctuations in the VUV intensity were compensated for by normalizing the ion signal to the recorded VUV intensity for each laser shot. An extrapolation of the linear portion of the PIE curve gives an appearance energy for caffeine of 7.91 ± 0.05 eV. The IE of caffeine has been reported as both 7.95 eV$^{157}$ and 8.50 eV$^{152}$. This is the first measurement of ionization energies of aerosol constituents using a laser based VUV source.
Figure 5.12 Photoionization efficiency curve for caffeine. The extrapolated appearance energy for caffeine is $7.91 \pm 0.05$ eV.

5.3.4. Sensitivity to other aerosol types

The ability of this system to detect various other organic aerosol constituents will be a function of several factors. The degree of vaporization from the CO$_2$ laser will affect the number of molecules that are available in the gas phase for ionization. This has not been explored in this chapter, but the effects of varying the vaporization parameters will be discussed in Chapter 6 and Chapter 7. There are also several factors which will affect the ionization efficiency of the molecules once they are in the gas phase. Obviously the ionization energy must be in the range that is accessible with our VUV source (7.4 to 10.2 eV). For aerosol particles, which are generally composed of larger non-volatile or
semi-volatile molecules, most relevant organics will be accessible. Adam et al. have plotted homologue series of several organic compound classes as a function of ionization energy. In general, the ionization energy decreases as the molecular mass increases. Alkanes with greater than five carbons have ionization energies below 10.2 eV, aldehydes with greater than three carbons have IEs below 10 eV, and alkenes with greater than two carbons have IEs below 9.8 eV, all of which are within the accessible range of our VUV source. Alkynes and alcohols with greater than four carbons tend to have ionization energies below 10.2 eV, but the trend toward lower IEs at higher masses is much weaker for these molecules, which means that shorter VUV wavelengths, where the photon flux is weaker, must be used even for larger molecules. Several larger carboxylic acids, such as oleic, linolenic, and linoleic acid, have IEs in the accessible range (8.52 – 8.69 eV). Hexanoic (≤10.12 eV) and butanoic acid (10.17 eV) are within reach, but small acids such as acetic acid (10.65 eV) and formic acid (11.33 eV) are not accessible. Ketones and aromatics of most sizes should be accessible (IE’s below 10 eV).

Another factor which will affect the ionization efficiency of the gas phase aerosol constituents is the photoionization cross-section. Although SPI is an almost universal ionization method, the photoionization cross-sections for different molecule classes can differ by close to a factor of ten at a given wavelength. For example, the photoionization cross-section of benzene at 118 nm (10.49 eV) is measured as 22 Mb while the cross-section of decane is 3.7 Mb. In addition, the photoionization cross-section increases as the ionizing energy is increased for the first few electron volts beyond the ionization threshold. As a result, a lower detection limit for a particular molecule is possible if a photon energy well above its IE is used for ionization, but this may come at the expense of increased fragmentation.

Arguably the most important factor in determining the detection limit for a particular molecule is the photon flux available at the energy to be used for ionization. For this source, a change in photon flux of over three orders of magnitude between 122 nm and 168 nm will have a significant impact on the detection limit for molecules with high IEs.

As a worst case scenario, one can consider a hypothetical molecule which would be ionized at 123 nm (10.10 eV) where the photon flux is ~8 x 10⁹ photons/pulse, roughly 300 times less than for the caffeine measurements at 142 nm. We will assume that the
molecular mass and density are similar to caffeine, so that a similar number of molecules make up an aerosol particle of any given size. If the photoionization cross-section is the same as that of caffeine, the detection limit would be a pure 500 nm particle, or a 10% component of a 1 µm particle. This instrument has been developed for laboratory studies of heterogeneous chemistry, and a detection limit of 10% of a 1 µm particle is still adequate for many experiments. If we assume a worst case scenario where the photoionization cross-section is an order of magnitude lower, the detection limit would be a pure 1 µm particle. In this case we would be limited to a VUV wavelength of 130 nm to 168 nm (9.56 to 7.40 eV) where the photon flux is high enough.

5.4. Conclusions

A continuously tunable VUV source based on resonance enhanced four wave difference mixing in xenon gas has been constructed and characterized. The source produces narrow bandwidth, high intensity pulses of light between 122 nm (10.2 eV) and 168 nm (7.4 eV), and could readily be applied to a wide variety of mass spectrometry based experiments. Very high spectral purity is achieved with a custom monochromator based around a single MgF₂ lens. Currently, the VUV source is coupled to an ion trap mass spectrometer which has also been fitted with an aerosol interface to conduct single particle mass spectrometric experiments. Aerosol experiments were carried out using caffeine particles. Under appropriate vaporization conditions fragment free mass spectra were collected for single aerosol particles as small as 300 nm in diameter. Excellent signal to noise characteristics for these small particles give a caffeine detection limit of 8 x 10⁵ molecules which is equivalent to a single 75 nm aerosol, or approximately 1.5% of a 300 nm particle. A good photon flux across the full wavelength range of the VUV source should allow the instrument to be used to study the heterogeneous chemistry of many types of organic aerosols of atmospheric relevance. The continuous tunability of the VUV source also allows the components of aerosol particles to be identified by the appearance energies of their ions.
Chapter 6. A study of oleic acid and 2,4-dihydroxybenzoic acid aerosols using an IR-VUV-ion trap mass spectrometer: insights into the strengths and weaknesses of the technique

6.1. Introduction

In Chapter 5 results were shown for the single particle analysis of caffeine aerosols vaporized at several CO$_2$ laser energies and ionized with VUV light at 142 nm (8.75 eV). Caffeine is a robust molecule which has a simple fragmentation pattern with the base peak at the molecular ion mass even under relatively harsh electron impact ionization.$^{155}$

In the caffeine study, fragmentation was negligible at low CO$_2$ energy, although it was observed for energies above ~10 mJ/pulse when using a wavelength on resonance with an absorption band in the caffeine IR spectrum. The single particle detection limits were very good at the VUV wavelength used ($8 \times 10^5$ molecules, approximately 1.5% of a 300 nm particle).

In this chapter the previous work is expanded by looking at two different aerosol types using several VUV photon energies for ionization. Aerosols of 2,4-dihydroxybenzoic acid (DHB) and oleic acid were chosen because they have very different chemical structures and because both have been studied using single particle time-of-flight (TOF) aerosol mass spectrometers, allowing comparisons to be drawn between these instruments and the ion trap device, and to highlight some of the strengths and weaknesses of the VUV-ion trap technique.

Like caffeine, DHB is a cyclic aromatic molecule which forms solid aerosol particles. However, it is slightly less robust than caffeine and with electron impact ionization the base peak corresponds to a water loss fragment.$^{155}$ Oleic acid is a monounsaturated fatty acid with a long carbon chain. It forms liquid aerosol particles and fragments extensively with electron impact ionization.$^{97, 155}$
In this chapter the mass spectra for these two molecules are studied as a function of both the vaporization energy and the ionization wavelength. When using low vaporization energies and near threshold ionization, only the molecular ion is observed for DHB, whereas for oleic acid extensive fragmentation occurs even under the gentlest conditions and only a small amount of the molecular ion is seen. Significant differences between the results from these ion trap experiments and others performed using time-of-flight mass spectrometers are also observed and discussed in detail. In some cases SPI was replaced with resonance enhanced multiphoton ionization (REMPI) to provide a better match with the reference studies and to highlight the differences in the results obtained with single photon ionization. The results of this study demonstrate that the ion trap has advantages over TOF systems when using low CO₂ laser powers to analyze more stable molecules like caffeine and DHB. Even for less stable molecules like oleic acid, the ion trap will give information complementary to that obtained with TOF instruments.

The analytical capabilities of the VUV-ion trap instrument are also further explored in this chapter. Detection limits are calculated for both DHB and oleic acid aerosols at two VUV wavelengths [142 nm (8.75 eV) and 124 nm (10.0 eV)], photoionization efficiency (PIE) curves are shown with both molecular and fragment ion appearance energies measured, and the accuracy in determining appearance energies is discussed.

6.2. Experimental

6.2.1. Particle generation

Aerosols for these experiments were made from solutions of either pure 2,4-dihydroxybenzoic acid (Fluka, ≥98%) or pure oleic acid (Sigma-Aldrich, ≥99%). The DHB solutions were made with filtered Millipore (18 MΩ) water and the oleic acid solutions were made in 2-propanol (Aldrich, 99.9%). In both cases the chemicals were used without further purification. Oleic acid aerosols one micron in diameter were generated from dilute (~1x10⁻⁵ g/ml) solutions using a TSI Vibrating Orifice Aerosol Generator (VOAG, TSI Inc., Model 3450). DHB aerosols 600 nm in diameter were
generated from more concentrated solutions (~1x10^{-3} g/ml) using a TSI constant output atomizer (TSI Inc., Model 3076). Since the constant output atomizer generates aerosols with a very broad size distribution, these particles were size selected with a TSI DMA (TSI Inc., Model 3081) prior to analysis. The Vibrating Orifice Aerosol Generator produces a much narrower size distribution and particles generated using this method were analyzed directly.

All aerosols were passed through an $^{85}$Kr charge neutralizer (TSI Inc., Model 3054) before entering the vacuum region of the aerosol mass spectrometer. This acted as a drying tube and prevented additional drying and size changes in the aerodynamic lens. Those particles made with the constant output atomizer were also passed through a 24” nafion diffusion dryer (Permapure Inc) prior to entering the DMA.

6.2.2. Vaporization and ionization

In this study between 5 and 40 mJ of IR light from a pulsed TEA-CO$_2$ laser (MTL-3G, Edinburgh Instruments) was used to vaporize the particles. The CO$_2$ laser is tunable over 60 lines between 1087 cm$^{-1}$ (9.20 µm) and 926 cm$^{-1}$ (10.80 µm) and for this work was used at 944 cm$^{-1}$ (10.60 µm).

After a variable delay of 0.5 to 30 µs the aerosols were ionized with either vacuum UV light or by REMPI using 249 nm UV light from a pulsed dye laser (Sirah PrecisionScan SL). In two experiments 70 eV electron impact was also used and is described in more detail later in this section.

In the current setup the paths of the vaporization and ionization lasers and the path of the particle beam do not intersect in the center of the ion trap. Instead the particles first pass through the IR and then the VUV or UV beam as they traverse the trap (Figure 6.1).
The distance that the aerosols travel between the two intersection points is on the order of 2 mm. This was measured by single laser experiments where either the IR or UV laser intensity was increased so that ions were generated by one laser pulse alone. Varying the timing of the firing in these single laser experiments made it possible to determine the location of the two beams relative to the particles. As a result of this distance, there is no ion signal if the ionization pulse is fired immediately after the CO₂ laser. However, if the delay between the two laser pulses is varied, a profile of the expanding plume from the vaporized aerosol can be obtained (Figure 6.2). The shape of this profile is primarily dependent on the translational energy of the vaporized molecules which expand outward from the particle, filling, and then passing beyond the ionization volume. This translational energy is highly dependent on the vaporization energy and, as a result, the time at which the ion signal reaches its peak can vary significantly with the CO₂ laser power (Figure 6.2). In addition, the internal energy of the molecules varies with the delay between the vaporization and ionization pulses. As a result of this change in internal energy, the fraction of the total ion signal that comes from the molecular and fragment ions varies with the ionization delay, with a proportionate increase in molecular ion signal at longer delay times. The dynamics of the plume
expansion and the information that this conveys about the particle heating will be explored in detail in Chapter 7. For the work described in this chapter full scans of the ionization delay time were obtained and the results presented are from an average of several hundred shots at the delay which gave the maximum total ion signal, a strategy similar to that of Nash et al.\textsuperscript{63}

![Graph](image)

**Figure 6.2** The evolution of the total ion signal for oleic acid as a function of the delay between vaporization and ionization at two \textsf{CO}_2 laser energies.

In this instrument there is also the option of ionizing the expanding cloud of gas from the vaporized particle with electron impact.\textsuperscript{97} For this mode of operation an electron gun consisting of a rhenium hairpin filament/cathode held at 0 V and a cathode shield held at −70 V is used. This filament and shield are positioned behind the endcap opposite the ion detector. The endcap is held at 0 V and has a 1 mm hole to admit the electrons to the
trap. When a trigger is sent to electron gun the filament/cathode is pulsed to $-70 \text{ V}$ and a burst of electrons is accelerated into the trap.

6.2.3. Ion trap operation and tandem MS

For most of the experiments described here the ion trap was operated in mass selective instability mode as described in section 4.3. Mass calibration of the ion trap was done using 70 eV electron impact analysis of small amounts of perfluorotributylamine. Mass scans were performed at a scanning speed of 4000 Da/s, with a mass resolution under these conditions of $\sim 500 \text{ m/Da}$ at $m/z = 264$.

In these experiments tandem mass spectrometry of oleic acid was implemented by applying supplemental SWIFT waveforms to the endcaps using custom Labview (National Instruments) software. After ion formation, trapping, and cooling, the selected mass was isolated by applying two rounds of notched broadband waveforms for 5 ms and 3 ms with widths of 15 Da and 2 Da respectively. The isolated ions were stored at $q_x = 0.26$ and underwent collision induced dissociation with He buffer gas using an excitation voltage of 200 mV for 20 ms. The excitation frequency was 84.2 kHz. This was followed by collisional cooling and mass analysis.

6.3. Results and discussion

6.3.1. Mass spectra as a function of vaporization energy (with near-threshold ionization)

Figure 6.3 shows mass spectra from DHB and oleic acid aerosols vaporized with several different CO$_2$ laser energies and ionized using the same, near-threshold, VUV energy of 8.75 eV (142 nm). For DHB the ionization energy is approximately 8.42 ± 0.05 eV and for oleic acid it is approximately 8.65 ± 0.05 eV (section 6.3.3). These mass spectra are presented in the same manner as the previously reported results for caffeine.
aerosols which were also vaporized at several CO₂ pulse energies and ionized at 8.75 eV (section 5.3.3).

Figure 6.3 Mass spectra of (a) oleic acid \([\text{C}_{18}\text{H}_{34}\text{O}_2]\) and (b) DHB \([\text{C}_7\text{H}_6\text{O}_4]\) as a function of CO₂ laser energy. For oleic acid the spectra were taken with 5, 15, 20, and 40 mJ/pulse of CO₂ laser energy at 944 cm\(^{-1}\) and a VUV wavelength of 142 nm (8.75 eV). For DHB the spectra were taken with 10, 15, 20, and 25 mJ/pulse of CO₂ laser energy at 944 cm\(^{-1}\) and a VUV wavelength of 142 nm (8.75 eV).
For any given aerosol type it can be seen that the extent of fragmentation is heavily dependent on the CO$_2$ laser energy used for vaporization, a result consistent with observations by other groups that the degree of fragmentation is a strong function of particle heating, regardless of the soft-ionization method chosen.\textsuperscript{51, 59, 60, 63, 65, 66} It can also be seen that the degree of fragmentation is dependent on the type of molecule being studied. For caffeine, very little fragmentation was seen until quite high vaporization energies were reached (~20 mJ/pulse), whereas for oleic acid an equivalent energy leaves only 5\% of the total signal coming from the molecular ion. DHB is an intermediate case; at low CO$_2$ laser energy only the molecular ion is observed, but at higher energies it is reduced to a minor component of the mass spectrum.

Preliminary results were also obtained for linolenic acid aerosols. Like oleic acid, linolenic acid is a long chain fatty acid with 18 carbon atoms, however, it contains three double bonds in contrast to oleic acid’s one. For linolenic acid aerosols vaporized with low energy CO$_2$ pulses (5 mJ/pulse), only ~2\% of the total ion signal is from the molecular ion. To some extent the differences in fragmentation of the species studied here may be a result of the differences in IR absorption cross-sections of the molecules. For example, at 944 cm$^{-1}$ linolenic acid has an IR absorption cross-section almost twice that of oleic acid (estimated from literature spectra with absorbance normalized to the C=O band)\textsuperscript{160} which could result in the much lower abundance of the molecular ion that was observed.

Although it causes increased fragmentation, the benefit of high CO$_2$ energy is that a higher fraction of the aerosol is being vaporized. This results in a higher total ion signal which can in turn give lower detection limits by improving the signal to noise.

At low CO$_2$ laser energy it is unlikely that the entire particle is being vaporized, but the combination of low vaporization energy and near-threshold ionization gives the benefit of relatively simple mass spectra. For caffeine and DHB only the molecular ion is observed and in cases like these tandem MS can be used to positively identify organics even in complex mixtures.

Oleic and linolenic acids, on the other hand, have very little molecular ion remaining even at low vaporization energies. Nevertheless, the fragmentation patterns for oleic and linolenic acid at low vaporization energies are biased towards a few large, high m/z
fragments. These high m/z fragments could be used as markers and targets for tandem MS (see section 6.3.4). Reduced fragmentation, and thus increased ease of molecular identification, is also expected for systems containing other aromatics and shorter chain n-alkanes, n-alkenes, ketones, and carboxylic acids. These classes of molecule have been shown to have higher stability with 10.5 eV SPI\textsuperscript{131,132} and shorter chain lengths mean that less CO\textsubscript{2} energy will be required to vaporize the particles.

The fragmentation observed in the aerosol mass spectra for oleic acid is more than initially expected based on previous aerosol studies that incorporated an IR laser for vaporization, soft photoionization, and TOF-MS for mass analysis.\textsuperscript{63} The differences between the ion trap results and previous TOF-MS results are discussed in detail in section 6.3.4.

### 6.3.2. Mass spectra as a function of VUV photon energy

One of the strengths of this approach is that the tunable VUV source allows the photon energy to be set very close to the ionization threshold of a molecule of interest. This near-threshold technique should reduce the amount of fragmentation by depositing very little excess energy in the molecule during ionization. This strategy has been successful in other aerosol experiments using TOF mass spectrometers,\textsuperscript{52,63} but it has not been previously demonstrated for a VUV ion trap combination. The mass spectra in Figure 6.3 show that molecular ion signal is seen for both DHB and oleic acid, but they do not demonstrate the effectiveness of near-threshold ionization in reducing the amount of fragmentation.

In Figure 6.4 and Figure 6.5 mass spectra from DHB and oleic acid aerosols that were vaporized at two different CO\textsubscript{2} pulse energies and ionized with two different VUV wavelengths are shown. The impact of changing the VUV photon energy at both low and high CO\textsubscript{2} laser energies is discussed below.
Figure 6.4 DHB mass spectra as a function of vaporization energy and ionization wavelength. In all cases the spectra were normalized to the most abundant ion peak and therefore care should be taken when comparing the peak intensities for different experimental conditions.
Figure 6.5 Oleic acid mass spectra as a function of vaporization energy and ionization wavelength. As for DHB, the spectra were normalized to the most abundant ion peak and therefore care should be taken when comparing the peak intensities for different experimental conditions.

6.3.2.1. Low CO$_2$ laser energy.

At low vaporization energy the benefit of near threshold ionization can be clearly seen for both DHB and oleic acid. For DHB at low CO$_2$ energy (10 mJ/pulse) and with near-threshold ionization (8.75 eV, 142 nm) only the molecular ion is seen. In contrast, if the VUV photon energy is raised to 10.0 eV (124 nm), the molecular ion accounts for only 70% of the total ion signal, with the remaining 30% coming from the water loss peak (at m/z 136). This higher photon energy is typical of many VUV sources which employ 10.5 eV radiation produced by tripling the third harmonic of an Nd:YAG laser.
For oleic acid vaporized with low CO$_2$ energy (7 mJ/pulse) there is some fragmentation at both VUV wavelengths, but the near-threshold spectrum is considerably less complicated. At 8.75 eV there are no fragments below m/z 100 and most of the ion signal comes from only a few prominent species. The largest peak is from the water loss fragment at m/z 264, and some molecular ion is seen at m/z 282. When the VUV energy is raised to 10.0 eV the molecular ion signal is virtually eliminated and the abundance of fragment peaks is considerably increased.

When compared to electron impact ionization, the benefits of near-threshold ionization are obvious for both DHB and oleic acid. For DHB, electron impact ionization even at low CO$_2$ energies results in extensive fragmentation, with only 4% of the total ion signal coming from the molecular ion (this is without considering the possibility of very low mass fragments below the mass range used in these experiments). For oleic acid, electron impact ionization with relatively low CO$_2$ energy also results in extensive fragmentation, with no molecular ion signal, and almost no ion signal at all above m/z 100.

### 6.3.2.2. High CO$_2$ laser energy

For oleic acid the benefit of near-threshold ionization even at high CO$_2$ energy (25 mJ/pulse) is fairly clear. At 8.75 eV there is a prominent peak at m/z 264 and few fragments below m/z 75. At 10.0 eV there is virtually no signal above m/z 175 and considerable signal below m/z 75. For DHB the benefit of near-threshold ionization is less clear at high CO$_2$ energies. At 25 mJ/pulse the molecular ion accounts for 10% and 12% of the total ion signal at 8.75 and 10.0 eV respectively. However, with 10.0 eV ionization the lower mass fragments (108 and 80 m/z) become more prominent.

### 6.3.3. Determining ionization energies

Another benefit of a tunable VUV source is the ability to obtain photoionization efficiency curves which can be used to identify compounds by their appearance energies as described in Chapter 5. Figure 6.6 shows the photoionization efficiency curves for
DHB and oleic acid. These were obtained by continuously scanning the VUV wavelength and recording both the ion signal and the VUV power for each laser shot. Scan speeds were on the order of 0.005 nm/s (0.0003 eV/s at 140 nm) and spectra were recorded 3-4 times per second to give a resolution of ~0.002 nm (0.0001 eV). Any fluctuations in the VUV intensity were compensated for by normalizing the ion signal to the recorded VUV power. The ability to measure an appearance energy for caffeine was demonstrated in section 5.3.3. Here we measure appearance energies for DHB and oleic acid molecular and fragment ions. The measured appearance energies for the molecular ions of DHB and oleic acid are 8.42 ± 0.05 eV and 8.65 ± 0.05 eV respectively (black traces in Figure 6.6). The uncertainty in these measurements arises mainly from the uncertainty in fitting a line to the linear portion of the PIE curve. The ionization energy for oleic acid has been previously measured as 8.68 eV\textsuperscript{52} and the appearance energy measured here agrees well with this value.

Although the ability to identify compounds by their appearance energy can be quite useful in determining aerosol constituents,\textsuperscript{60} it should be noted that for small particles or low abundance components, signal to noise issues may make collection and interpretation of PIE curves more difficult. In such cases many spectra can be collected and averaged at discreet VUV wavelengths to construct PIE curves, although this will of course be time consuming. In addition, uncertainty in fitting the linear portion of the PIE curves can be reduced by acquiring points over a broader VUV wavelength range.
Figure 6.6  Photoionization efficiency curves for (a) DHB and (b) oleic acid. The molecular ion peaks are at m/z 154 for DHB and m/z 282 for oleic acid. The break in the DHB curve from 8.42 to 8.48 eV occurs because a strong xenon resonance prevents VUV generation in this region.
An interesting feature of the PIE curves is that the individual fragment ions all show roughly the same appearance energies as the molecular ion for both DHB and oleic acid (Figure 6.6). For DHB a low vaporization energy was used and only a single fragment at m/z 136 was observed. This fragment had an appearance energy of 8.50 eV, 0.08 eV higher than the molecular ion. It is possible that the appearance energy for this fragment is in fact slightly higher than that of the molecular ion, but since both measurements have an uncertainty of 0.05 eV, we cannot conclusively say that it is different. For oleic acid the molecular and fragment ions all appear at the same VUV photon energy. Figure 6.6 shows representative traces for high and low mass oleic acid fragments at m/z 264 and m/z 127.

An interesting question that arises for these systems is whether fragmentation occurs before or after ionization. Two scenarios are possible; in the first scenario the molecule is fragmented during vaporization and the neutral fragments are then ionized by the VUV light. In the second scenario the neutral molecule is produced during vaporization, is subsequently ionized by the VUV light, and then decays to give fragments post-ionization. The fact that we observe the same appearance energies for the molecular and fragment ions supports the case of fragmentation occurring post-ionization, a reasonable possibility given the generally lower dissociation energies of ionic species. If a series of neutral fragments were being independently ionized, their appearance energies would almost certainly be different. One would expect this to be especially true in the case of oleic acid where the m/z 282 and m/z 127 ions are likely to have quite different structures, although for DHB the m/z 136 fragment is similar enough in structure to the molecular ion that this interpretation might not apply. In addition to the appearance energies, a comparison of the mass spectra obtained with the VUV-ion trap system and a VUV-TOF system also supports fragmentation occurring post-ionization. This is discussed in detail in section 6.3.4.

The most probable scenario regarding fragmentation seems to be that the vaporization step imparts enough internal energy to the neutral molecule to let it dissociate after ionization even with very low VUV photon energies, making the appearance energies of the fragments the same as that of the molecular ion. Such a shift to lower fragment appearance energies with particle heating was observed by Wilson et al. in a study of
tryptophan aerosols using a heater for vaporization. However, although high internal energy can shift the appearance energy of fragments arising from an ionized molecule, it has only a small effect on the ionization cross-sections of polyatomic neutral molecules and very little change in the molecular ion appearance energy is expected. This makes identification of molecules using appearance energies possible even with considerable heating.

6.3.4. Comparison with results from TOF mass spectrometers

Both DHB and oleic acid have been studied previously in other single particle aerosol mass spectrometers, allowing a comparison of the results from this study with the results from time-of-flight systems.

Nash et al. studied 3-4 µm oleic acid particles using a CO₂ laser for vaporization and VUV generated by pulsed lasers for single-photon ionization. The mass analysis in their system was done using a TOF mass spectrometer, but the conditions for vaporization and ionization were very similar to those used in this study.

Nash et al. reported the ratio of the molecular ion to total ion signal as a function of the CO₂ laser energy. Their data is re-plotted in Figure 6.7 along with the data from this study. It can be seen that fragmentation is much more extensive in these experiments than in the work of Nash et al. We believe that this disparity occurs because of the type of mass spectrometer used and the resulting difference in the time that the ions are stored prior to mass analysis.
This Study - VUV
Nash et al

Figure 6.7  A comparison of this study with the study of Nash et al.63 The ratio of the molecular ion to total ion signal is plotted as a function of the vaporization pulse energy. In our experiments a pulsed TEA CO₂ laser was used at 944 cm⁻¹ (10.6 µm). The laser focus has a Gaussian spatial profile with a FWHM of 0.9 mm and a total pulse duration of ~1 µs with a sharp 140 ns wide spike at the beginning of the pulse accounting for approximately 50% of the total energy. Based on a different study from the same group91 we assume that for Nash et al. the CO₂ laser spot was 0.9 mm and the pulse duration was 140 ns. Given the similarity of the two pulses, the points in the above figure are not corrected for any differences in beam profile or pulse duration. The dotted line shows a lower limit for the values of Nash et al. if a correction is made for differences in the dependence of total ion signal on CO₂ laser energy (see text).

In their study Nash et al. noted that if the extraction pulse in the TOF mass spectrometer was delayed by 3 µs, the ratio of the molecular ion to the water loss fragment decreased from 1.72 to 1.27, an effect which they attributed to the decay of a metastable oleic acid molecular ion with a low dissociation rate constant. Using these ratios we can calculate an approximate rate constant for the decay of the metastable oleic acid ion which gives a half-life on the order of several tens of microseconds. In the ion
trap, residence times for the ions are on the order of tens of milliseconds. Helium gas is introduced to cool the ions and collisions with helium should thermalize and therefore stabilize the metastable ions. However, at the 1 mTorr pressure used in the trap, the collision rate with helium is on the order of 1 per 120 µs. Even considering the upper limit for cooling in which only a single collision with helium is required to quench the excited oleic acid ion, there is still ample time for the metastable ions to dissociate. The fact that we calculate an approximate half-life on the order of several tens of microseconds from the Nash data means that one would expect to see almost no molecular ion after 120 µs, which is indeed the case for the collected spectra.

It should also be noted that in general Nash et al. used much higher CO₂ pulse energies than were used in this study. This discrepancy might be due to the much higher mass of the particles used by Nash et al. or it might be due to differences in the CO₂ beam profiles of the two lasers used. Despite some uncertainty in comparing the CO₂ pulse energies from the two experiments directly, we have attempted to scale the two sets of data to account for some of the possible discrepancies. In the study of Nash et al. a plateau starting around 150 mJ/pulse was observed in the plot of total ion signal versus vaporization energy. This could indicate the onset of complete vaporization of the particles. In the ion trap experiments the dependence of the total ion signal on CO₂ pulse energy became less steep after an energy of approximately 25 mJ/pulse was reached, although a true leveling was never observed. In Figure 6.7 we have plotted a line that shows where the values of Nash et al. would fall if we scaled their energies so that the leveling seen in the ion trap signal overlapped the beginning of the plateau in their data. Even with this adjustment made, the fragmentation is much more extensive in the ion trap experiments.

An interesting consequence of the different degree of fragmentation seen for the ion trap and TOF systems is that it gives some insight into when the decomposition of oleic acid occurs. In the previous section we discussed how the observed appearance energies for oleic acid fragments support the idea that fragmentation is occurring after ionization rather than as a result of vaporization alone. The large differences between the mass spectra from this study and those of Nash et al. give additional evidence that fragmentation of oleic acid is occurring post-ionization. Since the time between
vaporization and ionization is very similar in the two systems, one would expect to see similar ratios of the molecular ion to total ion signal if the fragmentation was occurring during this interval. The fact that much more fragmentation is seen in the ion trap system argues for a primarily post-ionization mechanism.

To further explore the differences between ion trap and TOF systems, we can compare the DHB results from the ion trap with results obtained by Morrical et al. using a TOF MS. Morrical et al. used a pulsed CO$_2$ laser to vaporize 1 µm DHB particles followed by resonance enhanced multiphoton ionization (REMPI) using a 266 nm UV laser pulse. The data from the work of Morrical et al. has been re-plotted in Figure 6.8 alongside the results from this study.

![Figure 6.8 A comparison of this work with the study of Morrical et al.](image)

The ratio of the molecular ion to total ion signal is plotted as a function of the vaporization power density to allow a better comparison with the data of Morrical et al. For the work of Morrical et al. we know only the total CO$_2$ focal area, which is given as $3.2 \times 10^{-2}$ cm$^2$. Since we do not know the spatial profile of the laser used by Morrical and colleagues, we can consider a worst case scenario in which their laser spot has a top-hat profile with a uniform energy distribution across the whole profile. This would result in the aerosols being exposed to only 40% of the energy that they are exposed to in the Gaussian profile case. The data point shown for the Morrical data in the above figure does not account for any differences in laser profile; however, we have added a horizontal arrow which shows where the point would fall with relation to our data if this correction for a top-hat beam profile was made.
In the ion trap study low energy single photon ionization was used (142 nm, 8.75 eV) and decreased fragmentation compared to Morrical and co-workers was expected. This was indeed the case for low IR fluences (5 x 10⁶ W/cm², 10mJ/pulse) where the ratio of the molecular ion to total ion signal was close to 1, however, when the power density was raised to 1.6 x 10⁷ W/cm² (30 mJ/pulse) the ratio of the molecular ion to total ion signal dropped to only 0.15. Morrical et al. had a ratio of approximately 0.6 at an IR fluence of 5 x 10⁷ W/cm².49 Even when we introduce a correction factor to account for possible differences in CO₂ beam profile (horizontal line in Figure 6.8) the fragmentation in the ion trap experiments is considerably higher for lower IR power densities.

To obtain a better comparison with Morrical’s work, we also carried out a series of experiments using resonance enhanced multiphoton ionization (REMPI) with a UV laser pulse at 249 nm. Even with the lowest possible CO₂ laser intensity, the ratio of the molecular ion to total ion signal in these REMPI experiments was only 0.26, considerably lower than the value of 0.6 obtained by Morrical et al. Of interest is the fact that although REMPI is a soft ionization technique, it still deposits considerably more excess energy in the ions than is the case for near-threshold single photon ionization. At low vaporization energy close to 100% of the total ion signal comes from the molecular ion when SPI is used, however, when REMPI is used a maximum of 26% of the total ion signal comes from the molecular ion.

One major difference between this study and those of both Morrical et al. and Nash et al. is the size of the particles used. Morrical et al. used 1 µm DHB particles whereas in this work 600 nm particles were used. Nash et al. used 3-4 µm oleic acid particles whereas 1 µm particles were used in this work.

In order to test the effect of particle size on the degree of fragmentation, mass spectra were collected from DHB particles ranging in diameter from 300 nm to 700 nm, close to a factor of thirteen change in particle volume. This change in particle size did not reveal any clear trend towards more or less fragmentation and suggests that the higher degree of fragmentation observed in this study is, as with oleic acid, due to the decay of metastable ions during the long storage interval of the ion trap.

The conclusion that the fragmentation observed in our studies is related to the type of mass spectrometer used and the long storage time in the ion trap is consistent with very
recent observations by J. D. Smith and K. R. Wilson (Personal communication). These researchers studied stearic acid aerosols using TOF mass analysis and observed a single peak at the molecular ion mass. When an ion trap was used in lieu of the TOF mass analyzer (with storage times from 10 to 100 ms) only fragment ions were observed.

Metastable ion decay is a well known phenomenon in MALDI. It can be either beneficial or detrimental depending on the application. Post-source decay can be used to gain structural information from large biomolecules, but it can also result in complicated mass spectra, especially for mixed samples of unknown compounds. Several groups using MALDI coupled to ion traps have experimented with high pressure pulses immediately after ionization to control fragmentation by quickly thermalizing and stabilizing the metastable ions. This high pressure pulse approach has worked well for large biomolecules in MALDI systems, and may be an option in our instrument as well.

As shown above, aerosol mass spectrometers with time-of-flight mass analyzers have an advantage over ion trap systems in that less fragmentation is observed when dealing with labile molecules. One may ask, based on this data, if a TOF mass analyzer would be more useful in an aerosol instrument. The answer to this depends on the type of compound to be studied. The ion trap system works particularly well when using low CO$_2$ energies and studying more stable compounds like caffeine and DHB. In these cases only the molecular ion is observed and tandem MS can be used for positive identification. For labile molecules like oleic acid, the time-of-flight instruments have an advantage in that they give considerably less fragmentation, although even these systems do not give mass spectra consisting exclusively of a molecular ion. However, even for a compound like oleic acid, the tandem MS capabilities of the ion trap can be used to determine structural information from fragments that appear in the mass spectrum. In addition to giving structural information, MS/MS spectra from these fragments could be used as markers for specific organic molecules and for product identification. In Figure 6.9 the MS/MS spectrum for the main fragment ion (m/z 264) observed in the oleic acid mass spectrum is shown. The fragmentation pattern from this ion can be used to help identify oleic acid in a mixture of compounds. The MS/MS efficiency of the ion trap is also high enough that tandem mass spectra can be collected for individual particles,
although for oleic acid the signal to noise ratio for individual particles is not exceptional. More work is needed to determine if the tandem mass spectra for individual particles will be sensitive enough for quantitative studies of complex aerosol particles.

Figure 6.9 Tandem MS of oleic acid. Spectra (a) – (c) are the average of 300 laser shots. (a) Aerosol mass spectrum of oleic acid vaporized with a CO₂ energy of 7 mJ/pulse and ionized with 8.75 eV VUV photons, (b) isolation of water-loss fragment at m/z 264, (c) MS/MS spectrum of m/z 264 (trapped at qₑ of 0.26, excitation amplitude of 200 mV for 20 ms), and (d) single particle MS/MS spectrum of m/z 264.
It seems reasonable to suggest that the ion trap will provide information complementary to that obtained with TOF systems, even for less stable molecules like oleic acid. Perhaps the best mass analyzer for this instrument would be a quadrupole time-of-flight (Q-TOF). This would allow both analysis of metastable ions and MS/MS experiments. Another option is to operate the ion trap at high pressures using a pulsed gas source as mentioned above. Experiments in either of these directions would be interesting.

6.3.5. Ion trap chemistry

In order to better understand the effect of ion storage time on the extent of fragmentation, experiments were done in which the trapping time was increased from the minimum of ~25 ms to a maximum of 830 ms. For oleic acid this increase in trapping time had no discernable effect on the extent of fragmentation, a result consistent with the decay of metastable ions on a microsecond timescale resulting in a stable distribution of ions. For DHB, however, an interesting phenomenon was observed. As the storage interval was increased to very long times, there was an increase in the fraction of ion signal at the molecular ion mass (m/z 154).

Figure 6.10 shows the relative abundances of the DHB molecular ion and main fragment ion (m/z 136) as a function of trapping time and helium bath gas pressure. Extending the trapping time to several hundred milliseconds revealed an almost total conversion of the m/z 136 progeny to generate ions at m/z 154. Since ion cooling doesn’t result in recombination of an already fragmented ion, the most plausible explanation is a reaction with background species, in this case water. In the ion trap a significant part of the background pressure comes from water vapor (based on EI mass spectra) and this water vapor could provide an ample supply for reaction. An ion-molecule reaction of this kind is expected to be heavily pressure dependent, a fact that can be easily confirmed by varying the helium pressure (Figure 6.10b). The mono-exponential dependence suggests that at the pressures used here the reaction rate is exclusively limited by the He gas pressure (Lindeman’s low pressure limit for a three-body reaction). The fact that almost identical recombination yields are obtained at 34 ms cooling time with 4.4 mTorr Helium
and 100 ms cooling time with 1.4 mTorr helium further supports the idea of a recombination mechanism.

![Graph](image_url)

**Figure 6.10** DHB molecular and main fragment ion contributions to the total ion signal at 6 µs ionization delay as a function of (a) trapping time and (b) helium pressure.
The observation that stored ions can undergo reactions is another effect that arises from the long storage time of ions in the trap. Reactions with a background neutral, as shown here, are a distinct possibility. Since there is no expected benefit from longer storage times, cooling times should always be kept at a minimum (1 ms).

The fact that long storage times lead to an increased abundance of ions at the molecular ion mass seems to suggest that we should actually see a higher fraction of molecular ions in our mass spectra when compared with the results of Morrical et al. since the time between ionization and mass analysis is orders of magnitude longer in our system. This would indeed be the case if our storage time was several hundred milliseconds rather than tens of milliseconds. However, we believe that two different processes are occurring and that the combined effect gives us low molecular ion abundances at shorter storage times. The first process is a fast decay of metastable ions that occurs on a timescale shorter than the minimum extraction time of ~30 ms and leaves us with low molecular ion abundance under normal operating conditions. The second is the much slower recombination process described above that regenerates ions of m/z 154 on long timescales. Based on the extrapolated ratios from Figure 6.10a, the nascent molecular ion ratios at 0 ms storage time should be probably 25% less than those reported in Figure 6.8, at 34 ms effective storage time.

6.3.6. Detection limits

In section 5.3.3 a caffeine detection limit of $8 \times 10^5$ molecules (3.5% of a pure 225 nm aerosol) with ionization at 8.75 eV (142 nm) was calculated. In the caffeine data, and the results presented in this chapter, the reported detection limits are predicated on a negligible background at the mass peak used for detection. While our pulsed technique guarantees that there will be virtually no gas background, in a complex mixed aerosol there might be an increased background from fragmentation of other components.

In addition to the caffeine data, some tentative estimates as to what the detection limits would be for other aerosol types using shorter VUV wavelengths for ionization were also made in the previous chapter. In this section DHB and oleic acid mass spectra
at both 8.75 eV (142 nm) and 10.0 eV (124 nm) are presented and detection limits for these particles at these two VUV photon energies can be calculated.

The intensity of the ion signal at a particular VUV photon energy is determined by two factors. As the VUV wavelength is shifted from 8.75 eV to 10.0 eV the number of photons per pulse is reduced by two orders of magnitude (Figure 5.3). The resulting signal reduction is compensated for by the increase of the molecular ionization cross section as the VUV wavelength is shifted towards the blue away from the ionization threshold. As a result, the detection limit at a particular wavelength can vary considerably from molecule to molecule.

To calculate a detection limit we average several hundred mass spectra and set a detection limit of three times the standard deviation of the baseline noise at the most intense peak. The signal to noise ratio at this most intense peak is used to determine the detection limit. Because higher vaporization energies result in more fragmentation, it is often the case that the best detection limit is achieved for a low to intermediate CO2 laser energy where only a few peaks are very prominent.

For DHB the detection limit at 8.75 eV is \(~7.0 \times 10^5\) molecules. At 10.0 eV the detection limit is \(~1.2 \times 10^7\) molecules. These are equivalent to \(~2.5\)% and \(~40\)% of a 225 nm particle respectively (assuming that the other compounds present do not increase the background signal level), which is relevant for these studies since the scattering detection limit in the sizing region of the aerosol mass spectrometer is \(~225\) nm.

For oleic acid the detection limit at 8.75 eV is \(~2.6 \times 10^7\) molecules (equivalent to a pure particle diameter of \(~300\) nm). At 10.0 eV it is \(~5.2 \times 10^7\) molecules (equivalent to a pure particle diameter of \(~375\) nm). For oleic acid the minimum detectable particle sizes are larger than the scattering detection limit of the instrument, but are equivalent to \(~2.6\)% and \(~5.2\)% of a 1 µm particle respectively.

These detection limits are more than adequate for heterogeneous studies and it is anticipated that a realignment of the system to bring the CO2, VUV, and particle beams on top of each other in the center of the ion trap will give approximately an order of magnitude increase in the ion signal (assuming instantaneous evaporation) which should substantially decrease the detection limit. If the particle is vaporized within the ionization volume, there is no need to wait for the vaporized molecules to reach the
ionization region and the VUV laser can be fired at an earlier time when the vapor plume is much denser and more of the molecules are contained within the ionization zone.

6.4. Conclusions

In this work DHB and oleic acid aerosols were studied using a pulsed CO₂ laser for vaporization, single photon ionization with vacuum UV, and an ion trap for mass analysis. The extent of fragmentation seen in the mass spectra was heavily dependent on both the vaporization energy and the type of molecule being studied. For DHB, a low vaporization energy gave mass spectra in which only the molecular ion was observed. In contrast, oleic acid aerosols showed quite extensive fragmentation even at low vaporization energy and the base peak was the water-loss fragment at m/z 264. Tandem MS was performed on this fragment and could provide a means for identifying oleic acid in mixtures.

Mass spectra from DHB and oleic acid aerosols were also collected as a function of the VUV photon energy used for ionization. Near-threshold ionization was seen to result in reduced fragmentation.

Photoionization efficiency curves were collected by continuously scanning the VUV wavelength. The appearance energies for the DHB and oleic acid molecular ions were measured and for oleic acid were found to agree well with the literature value. A literature value could not be found for DHB. The ability to determine molecular ion appearance energies together with the ability to identify organic analytes using tandem MS, should make this technique well suited for studying the reactivity of organic particles in the laboratory.¹⁶⁷–¹⁶⁹

Appearance energies for the fragment ions of DHB and oleic acid were also measured and found to be the same as those of the molecular ions within the uncertainty limits of the technique. This indicates considerable heating of the particle and offers evidence for a post-ionization fragmentation mechanism. A post-ionization fragmentation mechanism was further supported by large differences in the extent of fragmentation when comparing
the ion trap results to those from aerosol mass spectrometers with time-of-flight mass analyzers.

The degree of fragmentation observed in this study, particularly for oleic acid, was considerably higher than in comparable experiments using TOF mass analyzers. This is attributed to the long storage interval in the ion trap which allows ample time for metastable ions to decay. Because of this, those aerosol mass spectrometers with TOF analyzers have an advantage over ion trap systems in that less fragmentation is observed when dealing with labile molecules, although even the TOF mass analyzers do not give exclusively the molecular ion for oleic acid under similar experimental conditions. It is also not possible to perform tandem MS, a potentially important tool for unraveling the composition of mixtures, with the single TOF systems currently employed in aerosol mass spectrometers. Although not undertaken in these experiments, in an ion trap it is also possible to set the trapping level so as to immediately eject low mass ions, increasing sensitivity at higher masses, and resonant ejection can be used to improve mass resolution. Recent MALDI experiments suggest that the increased fragmentation observed in these ion trap studies could be overcome by using high pressure pulses to quickly stabilize the metastable ions.

In addition to allowing time for the decay of metastable ions, the long storage time of the ion trap can also provide opportunity for reactions to occur with background gases, as was seen for DHB ions held in the trap for several hundred milliseconds. The implications of long ion storage times need to be considered when carrying out aerosol studies with ion traps in order to avoid any experimental artifacts.

The detection limits for DHB and oleic acid aerosols were calculated at two VUV wavelengths. For DHB the detection limit at 8.75 eV is ~65 nm (~7.0 x 10^5 molecules, ~2.5% of a 225 nm particle) and the detection limit at 10.0 eV is ~165 nm (~1.2 x 10^7 molecules, 40% of a 225 nm particle). For oleic acid the detection limit at 8.75 eV is ~300 nm (~2.6 x 10^7 molecules, ~2.6% of a 1 µm particle) and at 10.0 eV the detection limit is ~375 nm (~5.2 x 10^7 molecules, ~5.2% of a 1 µm particle). These detection limits should be sufficient for studying organic reactions in the laboratory.
Chapter 7. Insights into the vaporization of aerosols with a pulsed CO$_2$ laser – A comparative study of 2,4-dihydroxybenzoic acid, caffeine, and oleic acid aerosol particles

7.1. Introduction

Aerosol mass spectrometers with separate vaporization and ionization stages need to transfer the particles from the liquid or solid phase into the gas phase before ionization and mass analysis can take place. While this can be done using either a heated surface or a pulsed laser, those instruments that perform single particle analyses typically use pulsed lasers for the vaporization stage.\textsuperscript{44, 45, 49, 50, 67}

For these single particle instruments understanding the impact of various experimental parameters related to the desorption step is necessary for both maximizing the total ion signal obtained from each particle and for interpretation of the mass spectra. The laser pulse intensity, the delay between vaporization and ionization, and the particle composition will all have an impact on the results.

The desorption pulse intensity will affect both the translational and internal energy of the vaporized molecules.\textsuperscript{63, 79, 86, 90, 91} If the translational energy of the expanding plume is high, then the molecules will leave the ionization region quickly, requiring either very precise timing and/or using a larger detection volume, which typically lowers the signal to noise ratio. For instruments that operate with the vaporization and ionization regions slightly offset from one another (as in the single particle instruments first described by Zelenyuk et al.,\textsuperscript{44} and Woods et al.,\textsuperscript{67} and this work) the time after vaporization at which the maximum signal intensity is obtained will change as the translational energy of the plume changes. This will require a change in the delay between the vaporization and ionization pulses in order to maximize signal for plumes with different translational energy distributions. If the internal energy of the vaporized molecules is high, then increased fragmentation is expected which can complicate interpretation of the results.\textsuperscript{51, 59, 60, 63, 65, 66} In addition, if there is cooling of the particle or the vaporized plume during
desorption and/or expansion, the distribution of fragments in the mass spectra might be expected to change as a function of the ionization delay. Very few studies have looked at the effect of the IR laser intensity and the ionization delay on the mass spectra and all of the existing work has been done using liquid particles with diameters on the order of a micron or larger. A brief summary of this pioneering work is given below.

One of the first studies to examine this issue was that of Cabalo et al. In their experiments 5 µm liquid aniline aerosol particles were vaporized with a pulsed CO2 laser very similar to the one used in this work. They observed an increase in translational energy of the expanding plume as a function of laser intensity, and were able fit their data to a model using a modified Maxwell-Boltzmann distribution which included a stream velocity for higher laser intensities. A decrease in the molecular ion intensity was observed as the ionization delay was increased and Cabalo et al. concluded that collisional cooling was effective early in the plume development. In addition they observed a leveling of the total ion signal with laser intensity which could indicate complete vaporization of the particle.

Woods et al. conducted several investigations into liquid aerosol particles vaporized with a pulsed CO2 laser and ionized using vacuum UV at 118.5 nm. In a study of 2 µm glycerol particles coated with oleic acid they were able to observe a transition as the CO2 laser intensity was increased from a more surface specific vaporization to a shattering mechanism which produced signal preferentially from the core of the particle at early ionization delays. In a study of the internal energy of molecules from 2 µm ethylene glycol particles they observed an increase in the translational energy of the plume as a function of CO2 laser energy. They also observed an increase in internal energy as a function of CO2 laser energy and a sudden transition in internal energy which was attributed to a transition from slow, layer-by-layer evaporation to an explosive mechanism. The internal energy of the molecules was found to be greatest at short ionization delays, a result in contrast to that of Cabalo et al.

Nash et al. studied 3-4 µm oleic acid particles vaporized with a CO2 laser and ionized with vacuum UV light. In their work increased fragmentation was also observed at short ionization delay times indicating a high internal energy early in the plume.
expansion. In addition, a leveling of the total ion signal as a function of CO\textsubscript{2} laser intensity was seen that could indicate complete evaporation.

Deforest, Qian, and Miller also studied the vaporization dynamics of micron sized organic liquid particles.\textsuperscript{90} In their work formamide aerosols were seen to undergo an initial shattering event followed by a slower evaporation. The extent of shattering was seen to be correlated with increased CO\textsubscript{2} laser intensity.

Due to the relatively small number of studies investigating the CO\textsubscript{2} laser vaporization of organic aerosol particles, the work presented here was undertaken to observe the effect of CO\textsubscript{2} laser intensity and ionization delay on the mass spectra and total ion signal of three different particle types. Since the same instrument was used for all three, some insight can be gained into the impact of particle type on the mass spectra. This work also involves small solid particles which have not been investigated in the past and as a result this study provides additional data necessary for understanding the vaporization of aerosol particles by CO\textsubscript{2} lasers.

In the first part of this work the total ion signal was measured as a function of laser intensity for both single laser desorption/ionization (CO\textsubscript{2} laser only) and for the two-laser process (CO\textsubscript{2} + VUV). This investigation showed that the threshold energies for generating ions with the CO\textsubscript{2} laser alone are strongly dependent on the aerosol type.

In the second part of this work the expansion of the vapor plume was followed by varying the delay between the vaporization and ionization pulses. This showed that the delay giving maximum ion signal is strongly dependent on both the CO\textsubscript{2} laser intensity and the particle type, a result which has important implications for analytical measurements.

From the measurements of signal as a function of ionization delay, expansion speeds for the vaporized plume were calculated and a translational temperature for the expanding plume was determined. This was carried out to observe how much translational energy is imparted to the particles by the vaporization process and to try to understand how this translational energy varies with CO\textsubscript{2} power and particle type.

In the last part of this work, the degree of fragmentation (which is used as a proxy for vibrational temperature) was measured as a function of both laser intensity and ionization
delay. This has some important implications for analytical applications of the instrument and provides some insight into the plume expansion dynamics.

7.2. Experimental

7.2.1. Particle generation

Particles for these experiments were generated as described in Chapter 5 and Chapter 6. DHB (Fluka, ≥98%) and caffeine (Sigma-Aldrich ≥98.5%) solutions were made with filtered Millipore (18 MΩ) water. Oleic acid (Sigma-Aldrich, ≥99%) solutions were made with 2-propanol (Aldrich, 99.9%). All chemicals were used without further purification. For DHB and caffeine, 600 nm particles were generated using the TSI constant output atomizer. For oleic acid 1 µm particles were generated using the vibrating orifice aerosol generator. In all cases the particles were passed through an 85Kr charge neutralizer (TSI Inc., Model 3054) before entering the vacuum region of the aerosol mass spectrometer.

7.2.2. CO2 laser characteristics

The CO2 laser used in these experiments was described briefly in the preceding chapters. Here a more detailed description of the laser pulse characteristics is given, since this has an important impact on particle heating.

The laser used is a pulsed TEA-CO2 laser (MTL-3G Edinburgh Instruments Ltd) with a single mode output which is focused into the ion trap with a 25 cm ZnSe lens. The spatial profile of the CO2 laser was measured at the point where it intersects the aerosol stream by increasing the energy until ions were generated with the CO2 laser alone. This was done with ammonium bisulfate aerosols since IR only ions can be readily generated from these particles. To measure the laser beam geometry, the timing of the laser pulse was then varied so that particles were vaporized/ionized at different points in the CO2
laser beam. By recording the particle hit rate as a function of this timing, a profile of the laser spot can be obtained (Figure 7.1). The recorded profile can be fit with a Gaussian function which gives a FWHM of ~0.9 mm.

The temporal profile of the CO\textsubscript{2} laser pulse was provided by the manufacturer, Edinburgh Instruments Ltd. It consists of an initial sharp spike with a width of ~140 ns followed by a long tail of ~1 \( \mu \)s duration. Approximately 50\% of the total pulse energy is contained in the initial spike. The temporal profile and cumulative energy of the laser pulse is shown in Figure 7.2.

**Figure 7.1 Spatial profile of the CO\textsubscript{2} laser spot in the ion trap.** This was generated by recording the aerosol hit rate while the timing of the CO\textsubscript{2} pulse was varied. The profile shown here is corrected for the 35 degree angle between the laser beam and the incoming aerosol stream.
For these experiments the CO$_2$ laser was tuned so as to be on resonance with IR absorption bands in the compounds studied. By using an on-resonance CO$_2$ wavelength, a higher degree of particle heating could be achieved due to the stronger absorbance of the IR radiation. This gave a larger dynamic range over which the effects of aerosol heating could be observed.

To confirm that the particles were being heated on-resonance, IR absorption spectra were collected for the pure compounds. This also allowed the IR absorption cross-sections to be measured for the three compounds in the bulk phase and these cross-sections are used to help in understanding differences in the vaporization processes for the three aerosol types.

For DHB and caffeine the solid phase absorption spectra were collected by making KBr discs containing the compound of interest. To obtain quantitative results a precise amount of analyte and KBr was weighed out and pulverized for 60 s in an automatic
sample grinder (Pike Technologies). The resulting powder was pressed into a disc and the disc weighed and measured. A series of concentrations was made for each compound to test the effectiveness of the technique. For oleic acid a neat liquid sample was used.

In all cases IR absorption spectra were obtained with an FTIR spectrometer (Bruker Equinox 55). The IR absorption spectra for the three compounds are shown in Figure 7.3. The vertical lines indicate the CO$_2$ laser wavelength used for vaporization of the aerosols in these experiments.

![Figure 7.3 Absorption spectra for (a) oleic acid (b) DHB and (c) caffeine. Vertical lines indicate the CO$_2$ laser wavelengths used in these experiments.](image-url)
The results for the absorption cross-section measurements are given in Table 7.1. From the measured absorption cross-sections and a simple Beer’s Law calculation we can determine that all three of oleic acid, DHB, and caffeine aerosols are optically thin media, absorbing no more than ~2.5% of the incident IR radiation. As a result the particle is likely to be uniformly heated by the IR pulse, ruling out front side ablation as described by Schoolcraft et al.\textsuperscript{87,88} In addition the particle diameters are small compared to the wavelength of the CO\textsubscript{2} laser, so there is no internal focusing of the light which can cause ablation of the shadow side of the particle.\textsuperscript{170} This same conclusion was reached by Woods et al. in a similar study of oleic acid particles vaporized with a CO\textsubscript{2} laser.\textsuperscript{79}

Table 7.1 Measured IR absorption cross sections for the molecules studied. Error limits are 95% confidence intervals

<table>
<thead>
<tr>
<th></th>
<th>IR Absorption Cross-section (cm\textsuperscript{2}/molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic acid at 944 cm\textsuperscript{-1}</td>
<td>(1.05 ± 0.07) x 10\textsuperscript{-19}</td>
</tr>
<tr>
<td>DHB at 978 cm\textsuperscript{-1}</td>
<td>(2.1 ± 0.4) x 10\textsuperscript{-19}</td>
</tr>
<tr>
<td>Caffeine at 978 cm\textsuperscript{-1}</td>
<td>(8.8 ± 1.0) x 10\textsuperscript{-20}</td>
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7.3. Background and theory on pulsed laser heating of particles

Pulsed laser heating of aerosol particles is a complex phenomenon, the exact mechanism of which depends on the intensity of the laser, the duration of the laser pulse, and the composition of the particle. In order to provide some framework for understanding the results presented in this chapter, a brief summary of the relevant theory and experimental evidence regarding pulsed laser heating of small particles is presented in this section.

For heating with laser pulses two different regimes can be identified. In the first, the thermal energy is deposited in the particle on a time scale shorter than that required for thermal diffusion\textsuperscript{89,171,172} and in this case the particle may become superheated.\textsuperscript{173,174} In the second case, thermal energy is deposited in the particle on a time scale so short that
mechanical relaxation is not possible and the resulting near-constant volume heating can lead to a large pressure buildup which causes mechanical breakdown of the particle.172, 173, 175

Thresholds for these two regimes can be defined with respect to the laser pulse duration and the particle characteristics. For the first case, known as the thermal confinement regime, the laser pulse duration ($\tau_L$) must be shorter than the thermal relaxation ($\tau_{th}$) time of the material being heated.86, 172 The thermal relaxation time is defined in equation 7.1 and is a function of the particle density ($\rho$), the heat capacity ($C$), the penetration depth ($d$), and the thermal conductivity of the material ($\lambda$).

$$\tau_{th} = \rho \cdot C \cdot \frac{d^2}{\lambda}$$  \hspace{1cm} 7.1

For the second regime, known as the stress confinement regime, the laser pulse duration ($\tau_L$) must be shorter than the time required for an acoustic wave to traverse the irradiated region ($\tau_{ac}$). The time for an acoustic wave to traverse the region can be calculated from the speed of sound in the material as shown in equation 7.2 (where $v_s$ is the local speed of sound and $d$ is the penetration depth as defined above).172, 173, 175

$$\tau_{ac} = \frac{d}{v_s}$$  \hspace{1cm} 7.2

For the laser characteristics and particle types used in this study, heating occurs within the thermal confinement regime, but not within the stress confinement regime (see appendix). Because of this, the thermal confinement regime will be the focus of the remainder of this section.

Within the thermal confinement regime the vaporization process can differ depending on the intensity of the laser irradiation. Molecular dynamics simulations have shown that at low laser fluences the vaporization is characterized by a gentle evaporation of molecules from the surface with the desorption yield following an Arrhenius type dependence on the laser fluence.89, 176
At higher laser intensities within the thermal confinement regime the particle can be heated well beyond its normal boiling temperature. Because the time scale of the heating is short, normal vaporization and boiling are ineffective at dissipating the thermal energy deposited in the particle. Instead, at a temperature of approximately 0.8*T_c (where T_c is the critical temperature) small bubbles will homogeneously nucleate within the material and an explosive vaporization occurs.\textsuperscript{177} This explosive vaporization results in a distribution of free molecules and small clusters or droplets.\textsuperscript{87, 176} These droplets may continue to evaporate for a short time after ejection\textsuperscript{176} although it has been proposed that in the case of CO_2 laser vaporization the long tail of the laser pulse may cause significant evaporation to continue for some time after the passage of the initial laser pulse.\textsuperscript{86} For water droplets on the order of a micron in diameter, the CO_2 laser irradiation threshold for explosive vaporization is on the order of 10^4 W/cm^2.\textsuperscript{90}

At very high laser fluences (on the order of >10^8 W/cm^2) plasma formation can occur and lead to optical breakdown of the material.\textsuperscript{90}

For the experiments described in this work the laser fluence is on the order of 10^6 - 10^7 W/cm^2 and explosive vaporization is a distinct possibility. Unfortunately, due to the constraints of the experimental technique, small droplets or clusters generated during an explosive vaporization process cannot be detected; only free molecules can be ionized and identified. Molecular dynamics simulations have shown that yield of monomers increases smoothly as a function of laser fluence with no discernable change at the threshold for explosive vaporization.\textsuperscript{176}

### 7.4. Results and discussion

#### 7.4.1. Total ion signal as a function of CO_2 laser energy and observations of ions from the CO_2 laser alone

The total ion signal for 1.2 um oleic acid particles, 600 nm DHB particles, and 600 nm caffeine particles is shown in Figure 7.4 as a function of the vaporization pulse energy.
Figure 7.4 Total ion signal as a function of the CO₂ laser pulse energy for (a) oleic acid (b) DHB and (c) caffeine. The black closed points indicate ions generated in the two-laser process at the delay between vaporization and ionization giving the maximum signal. The red open points indicate ions generated by the CO₂ laser alone. The caffeine and DHB values for the CO₂ only ions are scaled to be comparable with one another. All values are calculated from an average of 300 particle spectra and the VUV wavelength was 142 nm (8.75 eV) in all cases.
For oleic acid the total ion signal from the two-laser process (CO$_2$ + VUV) rises steadily as a function of the CO$_2$ pulse energy with an indication of some leveling at higher laser intensities. No oleic acid ions were observed at any energy with the CO$_2$ laser alone. The observed trend in total ion signal from the two-laser process is consistent with experiments conducted by Nash et al$^{63}$ who studied 3-4 µm oleic acid aerosols in a similar instrument and saw a leveling of the ion signal as a function of CO$_2$ laser fluence.$^{63}$ This effect could indicate complete evaporation of the particle.$^{67}$ For the experiments conducted by Nash et al. the signal leveled off at much higher energies than were used in this work. This may be a result of the larger particles used or of differences in the CO$_2$ beam profile. In this study the oleic acid signal did not completely level off, but the slope of the rise in ion signal as a function of CO$_2$ pulse energy does decrease and may indicate that leveling would occur at higher energies.

For DHB we see a near-linear rise in the total ion signal from the two-laser process as a function of the CO$_2$ energy up to approximately 10 mJ/pulse. At this point the ion signal starts to drop off and we see a concurrent rise in ions generated during the desorption pulse alone. For caffeine we see a similar pattern with a near linear rise in ion signal from the two-laser process for CO$_2$ energies up to ~ 20 mJ/pulse followed by a leveling and a rise in ions generated by the desorption pulse alone. Once the single laser process begins, there is no further increase in the two-laser ion signal as a function of IR energy for either DHB or caffeine. In fact for DHB the signal begins to drop slightly. Once the CO$_2$ pulse energy is high enough to generate ions directly, particles hit in the center of the laser beam are desorbed and ionized in a single step and are no longer available for the two-laser process. This causes the total two-laser ion signal to level and even decrease as a function of CO$_2$ laser energy.

For two of the three compounds studied here ions are produced directly by the CO$_2$ laser pulse (Figure 7.4). This occurs at relatively low laser energies which are on par with what would be used in laboratory or field experiments. Because of this effect, the CO$_2$ laser power will have to be maintained below a certain threshold to monitor different aerosol types with the two-laser experiment. Since the total ion signal is proportional to the CO$_2$ laser energy, this will result in a higher detection limit for some types of particle. In field measurements the CO$_2$ laser energy will likely remain fixed for routine
measurements, and a high laser power will probably be necessary to have adequate signals for most aerosol types. In this case the mass spectra could contain a mixture of ions from the one and two-laser processes. These two processes produce ions at different m/z ratios which will complicate data analysis. These potential complications need to be considered when designing and carrying out two-laser experiments in both the laboratory and field.

The single laser desorption/ionization mechanism observed in these experiments may be analogous to the process occurring in IR-MALDI, where a single laser pulse both desorbs and ionizes a condensed phase sample. The exact mechanism of ion generation in IR-MALDI is not fully understood, but in general there is thought to be two stages which define the final ion distribution. In the first stage ions are generated from neutral sample molecules, typically from matrix molecules rather than the imbedded analyte. In the second stage many of the ions will undergo collisions and secondary ion-molecule reactions will occur. The final distribution of matrix and analyte ions will reflect both the primary and secondary ion generation processes.

The primary ions are formed in the initial stages of the plume expansion which is a bath of moderately hot neutral molecules and clusters. For IR-MALDI there are several theories about the mechanism for primary ion formation. Zenobi et al. proposed four possible processes, the most likely of which they determined to be desorption of preformed ions, a mechanism most applicable to samples that contain ionic species. In addition to liberation of pre-existing ions, Zenobi et al. proposed primary ionization by spallation if the desorption is occurring in a stress confinement regime, or by thermal ionization if a high enough temperature can be reached. In addition Zenobi discussed ionization by energy pooling between excited molecules. In all cases the ions are generated during the energetic process of the explosive phase transition and the plume expansion provides enough energy to complete the separation of charges necessary to produce ions.

Regardless of the specific ionization mechanism, a threshold is typically observed in IR-MALDI above which ions are detected, but below which a large number of neutral molecules are desorbed but not ionized. For DHB and caffeine we see ionization
thresholds for the one laser process at approximately 10 and 15 mJ/pulse respectively, but for oleic acid a threshold is not observed.

It has been noted in several MALDI studies that ionization thresholds can differ from analyte to analyte and possibly for different phases as well. Feldhaus et al. measured IR-MALDI thresholds for several matrices including three solids and a liquid. Although the three solids had quite similar thresholds, the liquid matrix (glycerol) had a much higher threshold despite also having the highest absorption cross-section. These differences have led the same group to propose that different desorption/ionization mechanisms may be operative for solid and liquid matrices. This interesting difference for MALDI matrices of different phases may also be reflected in our results for solid and liquid aerosol particles, and illustrates that thresholds for desorption/ionization can vary significantly from species to species.

Based on the above discussion, the fact that ions can be generated by the CO₂ laser alone for the DHB and caffeine aerosols, but not for the oleic acid aerosols could be due to several factors. It is possible that there are ions present in the caffeine and DHB aerosols which are liberated by the CO₂ pulse once a certain threshold is reached. It seems unlikely, but these ions may be incorporated during preparation of the solutions from which the aerosols are generated. Another possibility involves differences in the heating of the particles. As discussed in more detail below, oleic acid aerosols do not appear to reach the same high temperatures as DHB and caffeine aerosols upon irradiation with the CO₂ laser pulse. The lower temperature of the oleic acid vaporization may provide less energy for a thermal ionization mechanism and the less energetic plume expansion may not be as efficient at charge separation. Finally, the fact that DHB and caffeine are solids while oleic acid aerosols are liquid, may play a role in the desorption/ionization mechanism. Further work will be required to determine what processes are occurring in the different aerosol types.

For the remainder of this chapter the focus will be on the case where ions are produced by the two-laser process. Hence for DHB and caffeine particles the discussion is limited to vaporization energies of 15 mJ/pulse or less, since in these cases the occurrence of ions from the CO₂ laser alone was minor.
7.4.2. Expansion of the vapor plume – optimal ionization delay and translational energy

The expansion of the vaporized aerosol plume can be followed if the delay between the CO₂ and VUV pulses is varied. Figure 7.5 shows the evolution of the total ion signal for the three aerosol types studied as a function of the VUV pulse delay. It can be seen that the plume expansion speed increases with increasing CO₂ laser energy for all three species. It can also be seen that there are considerable differences between the smaller, solid DHB and caffeine aerosols and the larger, liquid oleic acid particles.

In the current instrument configuration the paths of the vaporization and ionization lasers and the path of the particle beam do not intersect in the center of the ion trap. Instead the particles pass first through the IR and then the VUV laser spot as they traverse the ion trap (Figure 6.1). For the data shown in Figure 7.5 the size of the CO₂ and VUV laser spots, and the distance between them, remained the same in all experiments. Therefore the reason that the ion signal profile changes with CO₂ energy (or compound), is due to changes in the kinetic energy of the vaporized molecules. In cases where the molecules have higher kinetic energy, they will enter and leave the ionization region quickly, whereas at lower energies the molecules will take longer to pass through the ionization zone.

These differences in ionization delay profile have important implications for analytical applications of CO₂ lasers to particle desorption. For field work, and in many lab studies, a single fixed delay is the ideal analytical situation. This simplifies both data collection and analysis. However, because of the changes in the delay profiles for different species and CO₂ laser energies, instrument parameters optimized for one kind of particle may be far from ideal for an aerosol with a different chemical composition. For example, if an IR energy of 15 mJ/pulse is used and the delay is optimized for oleic acid particles, the maximum signal for DHB and caffeine particles will be missed by a significant margin. In this hypothetical configuration, the sensitivity of the instrument will be biased toward oleic acid aerosols.
Figure 7.5 Total ion signal as a function of the VUV delay is shown for (a) oleic acid (b) DHB and (c) caffeine. Each trace is for a different IR pulse energy as indicated in the legends. All traces have been normalized to make comparison easier for different signal intensities. The VUV wavelength was 142 nm (8.75 eV) in all cases.
The expansion profiles in Figure 7.5 can be used to estimate the translational temperature of the vapor from the desorbed particles via a modified Maxwell-Boltzmann distribution of speeds (equation 7.3).

\[ F(v)dv = A4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} (v - s_{aero})^2 \exp \left( -\frac{m(v - s_{aero})^2}{2kT} \right) dv \]

Where \( m \) is the mass of the molecules, \( k \) is the Boltzmann constant, \( T \) is the temperature of the expansion, \( v \) is the speed of the gas phase molecules, \( s_{aero} \) is the speed of the aerosol particle as it enters the ion trap (between 70 and 80 m/s for these experiments), and \( A \) is a normalization factor. To fit the experimental data equation 7.3 was transformed to a distribution of arrival times (equation 7.4) using the relationship \( dv = -x t^{-2} dt \) where \( x \) is the distance that the molecules travel between the vaporization and ionization events, and \( t \) is time.

\[ F(t)dt = A4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \left( \frac{x}{t} - s_{aero} \right)^2 \exp \left( -\frac{m\left( \frac{x}{t} - s_{aero} \right)^2}{2kT} \right) \left( -\frac{x}{t^2} \right) dt \]

It should be noted that, although useful for estimating the average translational energy of the vapor plume, the single temperature Maxwell-Boltzmann model shown above is not likely to provide an accurate description of the true vaporization process. At low laser fluences the actual vaporization process is likely a thermal, layer-by-layer, vaporization. In this scenario the particle would cool during evaporation which would continuously change the temperature of the vaporized molecules resulting in a
poor match with the single temperature Maxwell-Boltzmann distribution, particularly for long delay times. At higher CO₂ laser intensities the particle may shatter into a number of smaller droplets and vapor. These small droplets can continue to evaporate over time and experience the same changing temperature as in the layer-by-layer vaporization case. In both scenarios the long tail of the CO₂ laser pulse (Figure 7.2) can continue to heat the particle (or microdroplets) for some time after the passage of the initial laser pulse (~140 ns) potentially providing a longer time scale source of vapor. However, despite the fact that the single temperature Maxwell-Boltzmann model is unlikely to be an accurate description of the true vaporization physics, it does provide a very useful tool for obtaining information about the average translational energy of the expanding vapor plume and it allows us to make some comparisons between the three systems studied. A more thorough discussion of the possible vaporization mechanisms, and of the limitations of the single temperature model, is given in section 7.4.3.2.

Examples of the Maxwell-Boltzmann fit are shown below for the three particle types studied (Figure 7.6). It can be seen that for high and intermediate CO₂ laser energies the Maxwell-Boltzmann distribution fits the profiles well. However, for the very slow oleic acid expansions, the Maxwell-Boltzmann fit does a poor job of capturing the shape of the expansion profile. In addition the tails of the profiles at long delay times are not captured well for any CO₂ pulse energies with the exception of oleic acid aerosols vaporized with a high CO₂ pulse energy (40 mJ/pulse).
Figure 7.6 Maxwell-Boltzmann fits for the expansion profiles of (a) oleic acid (b) DHB and (c) caffeine aerosols each vaporized at three different CO$_2$ laser energies.
One of the shortcomings of a simple Maxwell-Boltzmann fit is that there is no account taken of the shape or size of the ionization and detection volumes. In an attempt to correct for this weakness, a more complex model which includes both the Maxwell-Boltzmann distribution and a contribution from the ionization volume was developed and the results compared with the simple fitting procedure.

A schematic of this model is shown in Figure 7.7 and a brief overview is given here. First, an ionization/detection volume (shown in green in Figure 7.7. Not to scale) is defined using the VUV laser parameters and an estimate of the trapping volume. The height and width of the detection zone are defined from the VUV beam parameters (estimated to have FWHM of 0.25 mm in the x axis and 0.5 mm in the y axis, shown in the inset of Figure 7.7) and the detection efficiency is weighted by a Gaussian distribution to approximate the photon density in the laser beam. The length of the detection zone is variable, but for these simulations was set to 2 mm, approximately the diameter of the apertures in the endcap through which the ions are ejected. The expanding plume from a vaporized particle is modeled using the Maxwell-Boltzmann distribution of speeds described in equation 7.3. In order to model the expansion numerically, the molecules in the expanding plume are assigned to velocity bins weighted by the Maxwell-Boltzmann distribution. The number of bins is variable and high resolution simulations can be run by increasing their quantity. In addition to the Maxwell-Boltzmann distribution of velocities, a stream velocity can be added to the simulation if required. The angles of the IR and VUV beams and the position of the aerosols stream are set according to known ion trap parameters and the single laser ionization measurements described in section 6.2.2. When the model is run the position and volume of each bin of the expanding vapor plume is calculated for a series of time intervals. At each time interval the overlap between the expanding plume and the detection volume is calculated and used to determine the relative ion signal for that particular time increment. For the results presented here the model was run for each aerosol type using a series of Maxwell-Boltzmann distributions and no stream velocity. All other parameters of the model were fixed at the same values as used for the simple fitting procedure. The results of the model were then compared with the data and with the results of the simple fits.
Figure 7.7 A schematic of the model used to estimate translational temperatures of the expanding plume from a vaporized aerosol particle. The inset shows the VUV beam profile which was used to define the ionization/detection volume in the horizontal and vertical axes.

Examples of the simulations which gave the best fit to the data are shown in Figure 7.8. The model does a better job than the simple fit of capturing the tails of the profiles at long delay times, although it still does not achieve a perfect match. It also does a slightly better job of capturing the very slow oleic acid expansions. However, it does a somewhat poorer job with the fastest oleic acid profiles. Adding a stream velocity did not significantly improve the fit in any case.
Figure 7.8 Best fit simulation results for the expansion profiles of (a) oleic acid (b) DHB and (c) caffeine particles vaporized at three different CO$_2$ laser energies. The experimental data are the same as shown in Figure 7.6. Most probable velocities and translational temperatures obtained from these fits are shown in Figure 7.9 and Figure 7.10.
For these experiments the most probable velocities and translational temperatures of the expanding vapor plume were calculated with both the simple fit and the simulations. The agreement between the two was quite good, although the simulation gave slightly lower velocities and temperatures in all cases. The simulated velocities were approximately 10% lower and the simulated temperatures were approximately 8% lower than the results from the fits.

Figure 7.9 and Figure 7.10 show the most probable velocities and the translational temperatures of the expanding vapor plume as a function of the CO$_2$ laser pulse energy for all three aerosol types as calculated with the simulation. The uncertainties are the resolution of the temperature intervals at which the simulation was run. It should be noted that the systems are not at thermal equilibrium and the temperatures obtained are not definitive values, rather they are fitting parameters that let us make some comparisons between the three systems studied.

For both the fitting and the modeling cases, an important consideration when determining the translational temperature is accurately knowing the distance that the desorbed neutrals travel prior to entering the ionization region. This distance was measured using a UV pulse in lieu of the VUV pulse. With this arrangement the approximate distance can be found by increasing both the CO$_2$ and UV laser fluences until each generates ions independently of the other. One of the lasers is then shut off and the timing of the firing of a single laser is varied relative to the arrival time of an aerosol in the ion trap. In this manner it is possible to map out both the position and width of the two laser spots relative to the aerosol beam. This type of measurement gives the exact position of the CO$_2$ and UV lasers relative to one another; however, for the experiments performed here, the UV laser was replaced with the VUV laser which cannot be located in the same manner because of its much lower intensity. Because of this, only the approximate distance between the CO$_2$ and VUV laser spots can be known and as a result the uncertainties for the temperatures calculated from the Maxwell-Boltzmann fits are considerable. The VUV beam is confined by the 2 mm slit between the endcap and ring electrodes and it can be assumed that the alignment procedure is good enough to keep the beam within a 1 mm wide region at the center of the slit. However, even with this constraint, the uncertainty in the temperature calculated by the Maxwell-Boltzmann
fit can be up to a factor of two depending on the exact position of the VUV beam. This is not shown in Figure 7.9 and Figure 7.10. However, despite this considerable uncertainty in the temperature, valid comparisons between the three aerosol types can still be made since the changes in temperature affect all three particle types equally and the trends are robust no matter what distance is used in the calculations.

An interesting feature of the plots in Figure 7.9 and Figure 7.10 is the notable differences between the smaller, solid DHB and caffeine particles and the larger liquid oleic acid particles. Although similar CO₂ laser energies are used, the vapor plumes from the DHB and caffeine particles expand faster and have higher translational temperatures than the plumes from oleic acid. This is especially evident at low laser fluences and can also be clearly seen in the plots showing the expansion profile as a function of VUV delay (Figure 7.5).

The trend observed in Figure 7.9 and Figure 7.10 is likely due in part to the difference in the IR absorption cross sections and heat capacities of the three materials studied. The IR absorption cross-sections will determine how much of the incident light is absorbed by the particles while the heat capacity will determine how much of the absorbed energy goes into raising the particle’s temperature. There may also be an impact from the differences in particle size. However, experiments with DHB particles ranging in diameter from 300 to 700 nm did not show any clear dependence of the expansion profile on the particle size.
Figure 7.9 Most probable velocity of the expanding plume as a function of the CO$_2$ laser pulse energy for (a) oleic acid (b) DHB and (c) caffeine. Results are from the simulation.
Figure 7.10 Translational temperature of the expanding plume as a function of the CO$_2$ laser pulse energy for (a) oleic acid (b) DHB and (c) caffeine. Results are from the simulation.
Shown in Table 7.1 are the absorption cross-sections of oleic acid, DHB, and caffeine measured at room temperature. For oleic acid, pure liquid was used in the measurements. For DHB and caffeine, KBr pellets were utilized. The trend from these measurements is the following: \( \sigma_{\text{DHB}} > \sigma_{\text{oleic acid}} > \sigma_{\text{caffeine}} \), where \( \sigma \) is the absorption cross-section. However, these cross-sections were determined at room temperature and the absorption cross-sections can vary with temperature during the heating process. Also, the absorption cross-sections determined for bulk solutions do not necessarily apply directly to the aerosol particles. In addition, the phase of the DHB and caffeine aerosol particles may be different than in the bulk measurements, an effect which can change the absorption cross-sections. As a result there is uncertainty when applying this trend directly to the aerosol measurements.

In Figure 7.11 the results from four studies measuring heat capacity as a function of temperature have been re-plotted on the same set of axes. Since data for DHB could not be found, data for p-hydroxybenzoic acid is shown. It is immediately evident that the heat capacity of oleic acid is considerably greater than that of either p-hydroxybenzoic acid or caffeine meaning that in order to raise the temperature by an equivalent amount more energy has to be absorbed by oleic acid than by the other two species. This may offer, at least in part, an explanation for the lower oleic acid translational temperatures reached for the same laser pulse intensities as DHB or caffeine. Another possible contributing factor could be differences in the heat of vaporization of the three particle types studied.
7.4.3. Fragmentation – internal energy

7.4.3.1. Fragmentation as a function of vaporization energy

Fragmentation likely occurs post-ionization (Chapter 6) but it does reflect the internal temperature of the neutral molecules desorbed from the aerosol. As a result, the extent of fragmentation might be expected to increase with increasing vaporization energy. This is in fact true for this study and is shown in Figure 7.12 for all three particle types analyzed. This is in good agreement with observations by other researchers using aerosol mass spectrometers.\textsuperscript{51, 59, 60, 63, 65, 66}
For oleic acid the amount of molecular ion observed is quite low and drops steadily as the CO₂ pulse energy is increased. For DHB the amount of molecular ion decreases initially but then levels off at about 12 mJ/pulse and is approximately 10% of the total ion signal at all energies above this point. In Chapter 6 it was shown that ions at the DHB molecular ion mass can also be generated from a reaction of the water-loss fragment with background gases, likely water. Over the storage time of the water-loss fragment in the ion trap (34 ms), the amount of signal at the molecular ion mass increases by approximately 10% (Chapter 6). For this reason it seems likely that the 10% molecular ion we see for DHB at high plume velocities is not present because fragmentation has leveled off, but rather because a certain quantity of ion at the molecular mass is being regenerated by reactions in the trap during storage. For caffeine there is very little fragmentation until an energy of approximately 10mJ/pulse is reached.

![Graph showing the fraction of total ion signal as a function of CO₂ laser energy for oleic acid, DHB, and caffeine.](image)

Figure 7.12 The fraction of the total ion signal (integrated over the full VUV delay scan) attributable to the molecular ion as a function of the CO₂ laser energy for all three compounds studied.
This increase in fragmentation with increasing vaporization energy has important implications for analytical applications since extensive fragmentation can make it difficult to determine the identity of a compound, particularly in a mixture. In addition, extensive fragmentation can decrease detection limits by spreading the ion signal across many peaks which are less readily distinguished from background noise. This is the case for oleic acid where increasing the CO₂ pulse energy not only decreases the amount of molecular ion seen, but also greatly increases the number of fragment peaks. As a result there is a trade-off between increasing ion signal by increasing the vaporization energy (Figure 7.4) and decreasing fragmentation by lowering it (Figure 7.12). For oleic acid the lowest detection limit was achieved for a pulse energy of ~10-15 mJ. For DHB the lowest detection limit was achieved for a pulse energy of ~15-20 mJ. For caffeine there was very little fragmentation at any energy and the lowest detection limit was at ~20-25 mJ/pulse.

**7.4.3.2. Fragmentation as a function of ionization delay**

If mass spectra are collected at different times during the expansion, different ion distributions are observed. This is shown in Figure 7.13, Figure 7.15, and Figure 7.17 where the fraction of the total ion signal coming from the molecular ion and major fragment ions is plotted as a function of VUV delay for oleic acid, DHB, and caffeine respectively. An alternative presentation of the same data is given in Figure 7.14, Figure 7.16, and Figure 7.18 where the normalized absolute ion signal from the molecular ion and main fragment ions is plotted as a function of VUV delay. For oleic acid only the major fragments at m/z 264 and m/z 97 are shown in both cases.
Figure 7.13 The fraction of the total ion signal arising from two different fragments of oleic acid as a function of the VUV delay. Data are shown for (a) 12 mJ/pulse (b) 30 mJ/pulse and (c) 40 mJ/pulse in the IR.
Figure 7.14 The normalized absolute ion signal arising from two different fragments of oleic acid as a function of the VUV delay. Data are shown for (a) 12 mJ/pulse (b) 30 mJ/pulse and (c) 40 mJ/pulse in the IR.
Figure 7.15 The fraction of the total ion signal arising from the molecular ion and two major fragment ions of DHB as a function of the VUV delay. Data are shown for (a) 6 mJ/pulse and (b) 15 mJ/pulse in the IR.
Figure 7.16 The normalized absolute ion signal arising from the molecular ion and two major fragment ions of DHB as a function of the VUV delay. Data are shown for (a) 6 mJ/pulse and (b) 15 mJ/pulse in the IR. In figure (b) the noise in the data points for m/z 154 is a result of very low ion signal at this mass to charge ratio.
Figure 7.17 The fraction of the total ion signal arising from the molecular ion and the major fragment of caffeine as a function of the VUV delay. Data are shown for (a) 10 mJ/pulse and (b) 15 mJ/pulse in the IR.
Figure 7.18 The normalized absolute ion signal arising from the molecular ion and the major fragment of caffeine as a function of the VUV delay. Data are shown for (a) 10 mJ/pulse and (b) 15 mJ/pulse in the IR.

In general the fragment ions dominate the mass spectra at early delay times and the molecular ions become more prominent at long delay times. This effect has been observed in a number of experiments with both aerosol and surface desorption.63, 186, 187

There are a number of possible explanations for these trends. The first involves a thermal, layer-by-layer, evaporation of the particle. As discussed above, this mechanism is most likely operative at lower CO₂ laser energies. In this scenario the laser pulse heats
the particle to a maximum temperature determined by the laser intensity. This is still within the thermal confinement regime, but the heating is not sufficient to cause an explosive vaporization. Neutrals evaporated from the hot particle have high internal energies and produce ions that fragment readily. However, as the particle gives off vapor its temperature falls due to evaporative cooling. Neutrals that leave the particle at later times have lower temperatures that reflect this cooling and they produce ions that fragment to a lesser extent.

A second possible explanation for the trends observed in the fragmentation as a function of VUV delay involves explosive evaporation of the particles. Since these experiments are carried out in the thermal confinement regime the evaporation dynamics can change from a surface process to an explosive evaporation if the laser intensity is high enough. As described earlier, this explosive evaporation results in a mixture of small droplets and gas phase molecules. The gas phase neutrals from the initial explosion have high internal energies and produce ions that fragment readily. Slow evaporation and cooling of the microdroplets will give progressively colder gas phase neutrals that produce ions which fragment to a lesser extent.

Although explosive vaporization is a possibility in these experiments, work done by Woods et al. provides some evidence that this mechanism may not be operative for the particle types and IR pulse energies used in this work. In the work of Woods et al. a transition from a layer-by-layer evaporation to an explosive process was indicated by a sharp change in the dependence of ion internal energy on the vaporization laser intensity. Although in the experiments done here we do not have a means to measure internal energy directly, we can use the extent of fragmentation as an indicator of the degree of vibrational excitation of the ions. The fragmentation as a function of vaporization energy is shown in Figure 7.12. This plot shows a smooth dependence of fragmentation on vaporization pulse energy for all three aerosol types studied and it argues against a transition between vaporization regimes for the range of IR pulse energies used. In another set of experiments Woods et al. studied particles with a core of glycerol coated with oleic acid. A transition from a layer-by-layer to an explosive vaporization was observed by noting when ions from the core began to be detected in large excess. An
experiment such as this latter one would be an interesting means to determine whether explosive vaporization is occurring in the systems studied here.

A third possible process that could result in reduced fragmentation at longer delay times is collisional cooling of the expanding vapor plume. In the fast expansion from an exploding particle neutrals originating from below the aerosol surface might experience many collisions which could lead to vibrational cooling. Neutrals coming from the outer layers of the particle, however, would be removed with fewer collisions and these hot neutrals could produce ions that fragment easily. This would result in a higher degree of fragmentation in the early part of the expansion profile. Woods et al. observed such an effect in their study of ethylene glycol aerosols.86 In their work a rapid drop in internal energy was seen in the first few microseconds of the plume expansion for particles vaporized with higher energy CO₂ laser pulses. This rapid drop was taken as a possible indication of collisional cooling.

All of the mechanisms discussed above argue against a single-temperature model for particle vaporization. Evidence against a single temperature model is also given by Figure 7.19. Here we have re-plotted one panel from each of Figure 7.14, Figure 7.16, and Figure 7.18 in which the normalized absolute ion signal as a function of VUV delay is followed independently for the molecular and main fragment ions of the compounds studied. An attempt was made to fit each of these independent profiles with a Maxwell-Boltzmann distribution of arrival times. By fitting the data in this manner, two different temperatures for the expansion could be found.

As can be seen in Figure 7.19 two-temperature model is as effective as the single temperature model in fitting the data. It also has the added benefit that, unlike the single temperature model, it can offer an explanation for the observed changes in fragmentation as a function of delay time. However, based on the above discussion, a purely two temperature process is as unlikely as a single temperature one and the most realistic scenario would involve a continuum of temperatures as the particle, or particle fragments, evaporate. The discrepancies between the data and the Maxwell-Boltzmann fits seen in Figure 7.19 support this. Increased molecular, or large fragment, ion signal at long delay times might arise from a particle that is cooling by evaporation and giving off vapor in which the molecules have lower and lower translational energies. This lower
translational energy is correlated with a lower internal energy and thus the molecular, or larger fragment, ions are enhanced at long delay times.

Figure 7.19 Maxwell-Boltzmann fits to the normalized expansion profiles of the molecular ion and main fragment ion of (a) oleic acid particles vaporized with 12 mJ/pulse of IR, (b) DHB particles vaporized with 6 mJ/pulse of IR, and (c) caffeine particles vaporized with 15 mJ/pulse of IR.
7.5. Conclusions

In these experiments the vaporization mechanisms of three different aerosol types were studied under the same experimental conditions. This direct comparison gives some insight into how parameters such as chemical composition, phase, and heat capacity affect the vaporization process.

For two of the three compounds studied ions were observed from the vaporization pulse alone at relatively low laser intensities. This single-laser desorption/ionization process might also occur for other atmospherically relevant compounds and has implications for aerosol studies. The single-laser desorption/ionization process is discussed in the context of MALDI and some possible explanations are proposed.

The expansion of the vaporized aerosol plume was followed by varying the delay between the vaporization and ionization events. These delay profiles showed large differences in the vaporization dynamics for different particle types and CO2 laser energies.

Translational temperatures and most probable velocities of the expanding plumes were determined using a simulation that models translational temperature with a Maxwell-Boltzmann distribution. Plumes from vaporized oleic acid aerosols were seen to have much lower translational temperatures than those from DHB and caffeine particles, a result which may be due to differences in their respective heat capacities.

The Maxwell-Boltzmann model for determining translational temperature was less effective for low energies and long delay times. This may be due in part to continued evaporation and evaporative cooling of the aerosol particles after the initial laser pulse. It also might be due in part to continued evaporation of the particle during the long tail of the CO2 laser pulse (Figure 7.2). Monitoring the plume expansion after altering the laser gas mixture to reduce the intensity of the pulse tail might provide additional insight into the impact of the pulse duration.

A strong dependence of fragmentation on the CO2 laser energy was also seen for all three systems. In addition, a strong dependence of fragmentation on VUV delay was
observed. The fact that different fragmentation ratios are observed for different delay
times may indicate that some cooling of the vapor plume is occurring during evaporation.
Chapter 8. Concluding remarks

8.1. General conclusions

This thesis focused on the development and characterization of a single particle mass spectrometer which can be applied to laboratory-based studies of organic aerosols. A unique, tunable VUV source and monochromator were developed to give soft, near-threshold ionization of organic molecules and provide an additional means of compound identification though measurement of appearance energies. When coupled with an ion trap mass spectrometer this provides a powerful tool for identifying the components of aerosol particles. Detailed studies were carried out on three different aerosol particle types to investigate the impact of the vaporization and ionization conditions on the mass spectra and to investigate the process of pulsed laser heating in aerosol particles.

In Chapter 4 a summary of the instrument components was given. Here a brief overview of the particle inlet and sizing region was provided, while the remainder of the thesis focused on the vaporization, ionization, and mass analysis of detected particles. In the particle inlet a collimated stream of particles ranging from 0.2 to 1 µm is generated and individual aerosol particles are detected downstream of the inlet by light scattering. The efficiency of the detection is greater than 90% for particles with diameters of 400 nm and above. Particles detected and sized by the light scattering system can be vaporized and ionized in the center of an ion trap mass spectrometer. Custom software controls the timing of the vaporization and ionization laser pulses and manages the acquisition of mass spectra.

In Chapter 5 the development of a novel, pulsed VUV source and a custom monochromator was described in detail. A high photon flux ($10^{10}$ to $10^{13}$ photons/pulse) for VUV wavelengths ranging from 122 nm (10.2 eV) to 168 nm (7.4 eV) was measured. The monochromator was found to give excellent separation of the pump and generated wavelengths, reducing the UV light by eight orders of magnitude in the ionization region. Initial characterization of the source and monochromator was carried out with gas phase
species. In these experiments appearance energies were measured that agreed well with literature values for the ionization energies. In addition the mass spectra from the gas phase species showed minimal fragmentation. Initial experiments using caffeine aerosols were also described in Chapter 5. In these preliminary investigations the appearance energy of caffeine from aerosol particles was found to be $7.91 \pm 0.05$ eV. Near-threshold ionization of caffeine molecules showed minimal fragmentation for vaporization energies below approximately 20 mJ/pulse. In addition, single particle mass spectra with excellent signal to noise characteristics were obtained.

In Chapter 6 a more detailed study of 2,4-dihydroxybenzoic acid and oleic acid aerosols was undertaken. Increased fragmentation was seen for both high vaporization intensity and ionization photon energy. In addition, an increased degree of fragmentation was observed in comparison with studies done by other research groups using time of flight mass analyzers. This was attributed to the decay of metastable ions during the long storage time in the ion trap. This observation, together with measurements of fragment ion appearance energies, implies that a large degree of the fragmentation seen in single particle aerosol studies with decoupled vaporization and ionization occurs after ionization rather than after vaporization alone.

In Chapter 7 the vaporization of oleic, DHB, and caffeine particles was investigated. By studying these three different aerosol types with the same instrument and under the same experimental conditions, some important differences in the vaporization mechanisms could be observed. For DHB and caffeine particles, ions were generated by the vaporization pulse alone at high CO$_2$ laser energies, whereas for oleic acid ions from the IR pulse alone were never seen. This has some important implications for the use of pulsed IR lasers in particle vaporization. Studies of the plume expansion from the vaporized particles, undertaken by varying the delay between the vaporization and ionization pulses, showed considerably different vaporization dynamics for the small, solid DHB and caffeine aerosols and the larger, liquid oleic acid particles. Modeling the expansions profiles with a Maxwell-Boltzmann distribution showed that the DHB and caffeine plumes had much higher translational temperatures than the oleic acid plumes. These higher temperatures may be part of the reason that ions can be generated for these compounds from the CO$_2$ laser pulse alone. In addition to studying the translational
temperature of the vaporized plumes, the internal energy was monitored by observing the
degree of fragmentation of the vaporized and ionized molecules. Although fragmentation
likely occurs post-ionization, the extent of fragmentation still reflects the initial
desorption temperature of the molecules. In the investigations described in Chapter 7, a
higher degree of fragmentation is seen early in the plume expansion, hinting at some
cooling of the particle as it evaporates.

8.2. Considerations for future work

Future work with the aerosol mass spectrometer described in this thesis can focus on
a number of different avenues. In one, a more in depth understanding of particle
vaporization could be sought. In another, the instrument could be applied to studying
questions of relevance to atmospheric chemistry.

A more in depth understanding of particle vaporization could be obtained with some
modification of the instrument setup. The addition of a third scattering laser downstream
of the ion trap could be used to determine whether or not particles are being fully
vaporized by the CO₂ laser pulse. In addition, the vaporization dynamics of a wider
range of particle sizes and types could be studied to determine the effect of morphology,
phase, and chemical composition on the desorption process. More detailed modeling of
the vaporization process could also lead to a better understanding of the mechanism of
particle desorption. Molecular dynamics simulations such as the ones carried out by
Zhigilei and Garrison⁸⁹ and Schoolcraft and coworkers⁸⁷, ⁸⁸ could be extended to consider
liquid particles with IR laser vaporization.

There are also a wide variety of topics in atmospheric chemistry to which this
instrument could be applied. Determining the composition of particles emitted from
specific sources is important in understanding the complex chemistry of urban pollution.
Particles from sources such as diesel engines, meat cooking, and cigarette smoking have
been detected in polluted urban environments¹⁵, ¹⁸, ¹⁹ and may have an adverse impact on
human health. Laboratory studies can look at specific sources in isolation and the
knowledge gained from these experiments can be used in field work to trace particles emitted by a particular process.

One particle source that may be particularly well suited for study with this instrument is the combustion engine. Studies of combustion engine emissions have revealed a variety of particle compositions, including, but not limited to carbonaceous particles, particles containing inorganic components, and particles containing polycyclic aromatic hydrocarbons (PAHs). For this instrument particles which may contain PAHs are an attractive target for study since PAHs were shown to fragment to a lesser extent in the ion trap.

In addition to helping understand the complex composition of atmospheric particles, laboratory based instruments can study the aging processes that particles undergo in the atmosphere. A major focus of laboratory based aerosol studies has been the determination of products and mechanisms from reactions of aerosols with gas-phase species.

The uptake of atmospheric oxidants by organic surfaces has been an active area of research in our group. In particular, considerable work has been done to determine the uptake coefficients of nitrogen containing oxidants such the nitrate radical (NO₃), nitrogen dioxide (NO₂), and dinitrogen pentoxide (N₂O₅) by organic surfaces. In these measurements the loss of the gas phase species as it flows across an organic surface is monitored by chemical ionization mass spectrometry. The aerosol mass spectrometer described in this thesis offers a nice complement to these types of measurements since it can be used to determine what products are formed when the gas phase species are taken up by the organic surface. The two techniques can be used side by side to measure the quantitative uptake coefficients and elucidate reaction mechanisms from the identified products. Currently work is underway to construct an aerosol flow tube which can be coupled to the aerosol mass spectrometer for these types of measurements.

A number of different research groups have studied heterogeneous chemistry involving aerosol particles. In recent years oleic acid aerosols have been widely studied as a model system for these reactions. Oleic acid has been found in atmospheric particles and is prominent in aerosols arising from meat cooking operations.
products, mechanisms, and kinetics of the reaction between oleic acid and ozone have been studied by several research groups using aerosol mass spectrometers. Since pure oleic acid particles have already been studied quite extensively with the instrument described in this thesis, they offer a potential starting point for experiments involving heterogeneous chemistry. However, given the extensive fragmentation seen for oleic acid particles, initial results might be easier to obtain for PAH particles or shorter chain olefins. The reactions of species such as NO₃, NO₂, and N₂O₅ with any of these particle types would be a new and interesting area of research.

Another interesting area of atmospheric particle research is the formation of secondary organic aerosols (SOA) from the condensation of precursor gases. Volatile organic compounds (VOC) are emitted to the atmosphere from both natural and anthropogenic sources in amounts estimated to be up to 1150 Tg of carbon per year. Once in the atmosphere these compounds can react with oxidants such as O₃, NO₃, and OH to form a wide variety of oxygenated compounds some of which are less volatile that the precursor molecules. These can either condense onto existing particles or nucleate homogeneously to form new particles. Studies with smog chambers have been undertaken to determine the mechanisms and products involved in SOA formation (see Odum et al. and references therein). In this area single particle aerosol mass spectrometry with soft ionization could help differentiate the many compounds observed in these particles. In addition the inclusion of an ion trap gives a further tool for compound identification through MS/MS.
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Appendix

Thermal confinement regime.

The condition for thermal confinement is $\tau_L << \tau_{th}$, where $\tau_L$ = laser pulse duration, $\tau_{th}$ = thermal relaxation (or thermal equilibration) time of the material being heated.\textsuperscript{86, 172}

With $\tau_{th}$ defined as:

$$\tau_{th} = \rho \cdot C \cdot \frac{d^2}{\lambda}$$

where $\rho$ is the particle density, $C$ is the heat capacity, $d$ is the penetration depth (in this case the particle diameter), and $\lambda$ is the thermal conductivity of the material.

For the materials studied here the heat capacities at ~300 K were taken from the study of Cendeno et al. for oleic acid,\textsuperscript{182} Parks et al. for p-hydroxybenzoic acid,\textsuperscript{183} and Dong et al. for caffeine\textsuperscript{184} as presented in Figure 7.11.

Thermal conductivity values are less readily available. For oleic acid the value for olive oil measured by Kaye and Higgins at 298 K was used (0.17 W m\(^{-1}\) K\(^{-1}\)).\textsuperscript{190} For DHB the values measured by Sun and Teja for benzoic acid were extrapolated to 300 K (0.13 W m\(^{-1}\) K\(^{-1}\)).\textsuperscript{191} For caffeine a thermal conductivity value could not be found, so the benzoic acid value of 0.13 W m\(^{-1}\) K\(^{-1}\) from Sun and Teja was also used in this calculation.

The calculated thermal relaxation times are listed below.

<table>
<thead>
<tr>
<th></th>
<th>Thermal relaxation time (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic acid</td>
<td>~ 4.0</td>
</tr>
<tr>
<td>DHB</td>
<td>~ 2.9</td>
</tr>
<tr>
<td>Caffeine</td>
<td>~ 2.5</td>
</tr>
</tbody>
</table>
**Stress confinement regime**

The condition for stress confinement is $\tau_L \ll \tau_{ac}$, where $\tau_L = \text{laser pulse duration}$, $\tau_{ac} = \text{time for an acoustic wave to traverse the irradiated region}$ \(^{172, 173, 175}\)

With $\tau_{ac}$ defined as:

$$\tau_{ac} = \frac{d}{v_s}$$

Where $v_s$ is the speed of sound in the sample and $d$ is the penetration depth as defined above.

For materials similar to the ones used in this study, the speed of sound in the condensed phase is on the order of $10^3 \text{ m/s}$ \(^{172}\). For this order of magnitude $\tau_{ac}$ would be on the less than 1 ns for all particles studied.