



An electrospray ion source for ion-molecule equilibrium studies
by Qiang Wu

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemistry

Montana State University

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Abstract:

Pulsed electron-high ion source pressure mass spectrometry (PHPMS) has proven to be one of the most successful techniques for ion-molecule equilibria measurements. The resulting thermochemical data has had an enormous impact on the development of chemistry.

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A PHPMS has been successfully reinstalled. A new multichannel scaler data acquisition system was installed. Some electronic control units were upgraded. An electrospray ion source with the ability to measure ion-molecule equilibria was designed, built, and installed. Ions produced by electrospray and clustered with water molecules were successfully detected by the existing PHPMS. The operating parameters were optimized. Equilibrium constants of selected ion-molecule reactions were measured. The problems encountered with the electrospray ion source are discussed.

**AN ELECTROSPRAY ION SOURCE FOR ION-MOLECULE
EQUILIBRIUM STUDIES**

by

Qiang Wu

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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Date July 18, 1997

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TABLE OF CONTENTS

	Page
LIST OF TABLES	viii
LIST OF FIGURES	ix
ABSTRACT	xii
INTRODUCTION	1
Background	1
Objectives	3
THEORY	5
Ion-Molecule Equilibrium	5
van't Hoff Plot	6
Source Conditions Required for Reaching Ion-Molecule Equilibrium	6
Mean Free Path of Ions in the Gas Phase	8
Residence Time of Ions Inside the Source	8
Ion Source Sampling Conditions	9
Gas Flow Through Exit Orifice	10
Free Jet Expansion	11
Electrospray Ionization	13
Electrospray Process	13
Mechanism of Gas Phase Ion Formation	17
Ions Transport Through Capillary	19
ESMS Interface	20
Types of Gas Flow Through Capillaries	22

TABLE OF CONTENTS (continued)

	Page
INSTRUMENTATION	24
PHPMS Apparatus	24
Electrospray Ion Source	28
Ion Transport Capillary	30
Pre-Reaction Chamber	30
Reaction Chamber	31
Electrospray Apparatus	33
Gas Handling Plant	35
Ion optic, Mass Analyzer and Detector	37
Quadrupole Power Supply	40
Vacuum System	40
Chemical	44
MEASUREMENTS, RESULTS AND DISCUSSION	45
Operating Parameters	45
Electrospray versus Corona Discharge	45
Ion Transport Capillary	50
Ion Source	50
Ion Optics	55
Quadrupole Mass Filter	55
Flow Rate of the Reaction Gas	58
Ion-Molecule Association Equilibrium	59
Corona Discharge Ionization	60
$\text{Na}^+(\text{H}_2\text{O})_n$ Clusters	63
Protonated Pyridine Water Clusters	69

TABLE OF CONTENTS (continued)

	Page
$K^+(H_2O)_n$ Clusters	73
$K^+(C_6H_6)_n$ Clusters	79
SUMMARY	83
LITERATURE CITED	84

LIST OF TABLES

Table	Page
1. Pump Capacity and Pressure Distribution	43
2. Potential Distribution of Ion Optics Lenses	55

LIST OF FIGURES

Figure	Page
1. Schematic Representation of Processes in Electrospray	15
2. Schematic Diagram of Time History of Parent and Offspring Droplets . . .	18
3. Schematic Diagram of an ESMS apparatus	21
4. Velocity Distribution in Pipe for Laminar Flow and for Turbulent Flow at $N_{Re}=10,000$	23
5. Block Diagram of PHPMS System	25
6. PHPMS Apparatus	27
7. Electrospray High Pressure Ion Source	29
8. A Close look of the Electrospray High Pressure Ion Source	32
9. ES Device	34
10. Gas Handling Plant	36
11. Schematic Diagram of Quadrupole Mass Filter	38
12. Ionization Assembly	39
13. Ion Trajectories Exiting Quadrupole Simulated by SIMION Program . . .	41
14. Signal Intensity at $m/z=73$ and ES Current as a Function of the Potential on the Needle in Corona Discharge Ionization	47
15. Signal Intensity at $m/z=39$ and ES Current as a Function of the Potential on ES Needle in ES Ionization	48
16. Signal Intensity at $m/z=73$ as a Function of the Potential on the Ion Transport Capillary	51

LIST OF FIGURES (continued)

Figure	Page
17. Signal Intensity at $m/z=73$ as a Function of the Potential on the Deflector .	52
18. Signal Intensity at $m/z=73$ as a Function of the Potential on the Interface Plate in Corona Discharge Ionization	53
19. Relationship Between m/z and Sweep Control Voltage	57
20. Mass Spectrum Obtained by Corona Discharge Ionization in Ambient Air .	61
21. Mass Spectrum Obtained by Corona Discharge Ionization in Ambient Air with Added Pyridine Vapor	62
22. Abundance Ratio of $\text{Na}^+(\text{H}_2\text{O})_4$ to $\text{Na}^+(\text{H}_2\text{O})_3$ versus Water Partial Pressure in the Reaction Chamber	65
23. Dependence of the Abundance of $\text{Na}^+(\text{H}_2\text{O})_n$ Clusters on Water Partial Pressure in the Reaction Chamber	66
24. $\ln(K_{3,4})$ versus Water Partial Pressure in the Reaction Chamber	68
25. Mass Spectrum of Protonated Pyridine Obtained by ES Ionization with No Reagent Gas Added to the Reaction Chamber	70
26. Mass Spectrum of Protonated Pyridine Obtained by ES Ionization with Pure Nitrogen Gas Added to the Reaction Chamber	72
27. Mass Spectrum of K^+ Obtained by ES Ionization with 47 mTorr Water Added to the Reaction Chamber	75
28. Mass Spectrum of K^+ Obtained by ES Ionization with No Reagent Gas Added to the Reaction Chamber, Unknown Problem Caused the Intense K^+ Peak	76
29. Mass Spectrum Obtained by Corona Discharge Ionization in Ambient Air .	77
30. Mass Spectrum of K^+ Obtained by ES Ionization with 686 mTorr Water Added to the Reaction Chamber, Unknown Problem Caused the Intense K^+ Peak	78

LIST OF FIGURES (continued)

Figure	Page
31. Schematic Diagram of Cation- π Interaction	80
32. Mass Spectrum of $K^+(C_6H_6)_n$ Obtained by ES Ionization with 2.5 mTorr Benzene Added to the Reaction Chamber, Unknown Problem Caused the Intense K^+ Peak	82

ABSTRACT

Pulsed electron-high ion source pressure mass spectrometry (PHPMS) has proven to be one of the most successful techniques for ion-molecule equilibria measurements. The resulting thermochemical data has had an enormous impact on the development of chemistry.

Electrospray is a technique with which ions present in solution can be transferred to the gas phase. The successful combination of the techniques of electrospray and mass spectrometry opened the door to measure ion-molecule equilibria with many important ions that could not previously be obtained in the gas phase.

A PHPMS has been successfully reinstalled. A new multichannel scaler data acquisition system was installed. Some electronic control units were upgraded. An electrospray ion source with the ability to measure ion-molecule equilibria was designed, built, and installed. Ions produced by electrospray and clustered with water molecules were successfully detected by the existing PHPMS. The operating parameters were optimized. Equilibrium constants of selected ion-molecule reactions were measured. The problems encountered with the electrospray ion source are discussed.

INTRODUCTION

BACKGROUND

Ion-molecule reactions in the gas phase have been studied for a long time. Several different techniques have been used, such as ion cyclotron resonance mass spectrometry, flowing afterglow, and nuclear-decay. Among these techniques, pulsed electron high ion source pressure mass spectrometry (PHPMS) [1-5], also referred as HPMS, has proven to be one of the most successful methods for measurement of ion-molecule equilibria [6] in the gas phase. The resulting thermochemical data has had an enormous impact on the development of chemistry. However, most equilibrium data were obtained before the 90'ies [7]. The reason is that with the traditional type of ion source, only volatile, singly charged molecules could be studied.

In 1984, the electrospray mass spectrometry (ESMS) interface was introduced by Yamashita and Fenn [8]. Electrospray (ES) [8, 9] is a method with which ions present in solution can be transferred to gas phase. With electrospray it is possible to obtain many kinds of gas phase ions [10]: singly charged electrolyte ions such as Na^+ and Cl^- and organic protonated bases BH^+ ; group IIA doubly charged ions as well as doubly and triply charged transition metal and lanthanide ions and complexes thereof; bioorganic ions such as multiply-protonated peptides and proteins of molecular mass as high as 100,000 Da; and multiply-deprotonated, negatively charged nucleic acids.

These ions are of paramount importance in solution chemistry and biochemistry. Thus electrospray opened the door to study gas-phase ion thermochemistry involving many important ions which could not be obtained in the gas-phase prior to the development of the electrospray technique.

Compared to the other two most commonly used ionization methods for non-volatile species, fast atom bombardment (FAB) and laser desorption (LD), electrospray has a great advantage because the ionic solutions used for transferring the ions to the gas phase are the same solutions used in conventional wet chemistry. No unusual liquid matrices like glycerol are required. In electrospray, little if any extra internal energy is imparted to the ions [10], which makes electrospray a very "soft" ionization technique. This propriety is very important because the introduction of unwanted "daughter" ions could much complicate the determinations of ion-molecule equilibrium constants.

A major difficulty with electrospray is the high pressure, about 1 atm, at which the ions are generated. Accurate mass spectrometric determinations of ion equilibrium constants at such a high pressure is difficult because processes occurring at the interface leading to the vacuum of the mass analyzer can cause severe distortion of the ion ratios [11, 12]. A PHPMS ion source usually operates in the pressure range 1-10 torr in order to conform with the normally accepted criteria for perturbation free ion sampling. Therefore, ions produced by electrospray at 1 atm should be first transferred to a torr range ion-molecule reaction region, where the ions are allowed to equilibrate, and then to the mass analyzer. Since the pressure difference between the electrospray

environment and the ion-molecule equilibrium region is about 100 times, ions will enter the ion-molecule reaction region in a supersonic jet. The supersonic jet preserves its integrity over a considerable distance and keeps neutrals away from colliding with ions. Therefore, the jet has to be avoided in order to measure ion-molecule equilibria.

Considerable effort has been put into using electrospray ionization to study ion-molecule reactions [13-16]. However, no equilibria were measured because of the coaxial transport capillary design until 1994 when a new type of electrospray ion source was introduced by Dr. Kebarle and co-workers [17]. Ions produced by electrospray at near 1 atm were transferred via viscous gas flow through a transport capillary to the ion-molecule reaction chamber which was operated in the torr range. The exit tip of the transport capillary was positioned such that the jet was directed at a 90° angle away from the orifice of the ion-molecule reaction chamber. In this way the disturbance of the supersonic jet to the ion-molecule reaction was successfully avoided. The ions were extracted out of the supersonic jet and into the reaction chamber by means of an applied electric field.

OBJECTIVES

A PHPMS in our lab was donated by Dr. Kerbale, University of Alberta, Canada. This home-build instrument had been standing idle for 3 years when shipped. All electronic controls had been disconnected prior before shipping. The objectives of this research are:

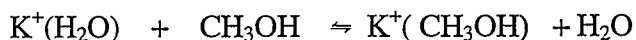
1. Reinstall the PHPMS. Replace or upgrade damaged units and put the PHPMS into operational conditions.
2. Design an electrospray ion source that can be used to measure ion-molecule equilibrium constants. Install and put into operation this ion source as an interface to the existing PHPMS. Investigate the characteristics of the ion source and optimize the operating conditions.
3. Study selected ion-molecule equilibria which had been previously measured. Equilibrium constants, and therefore the free energy change of the reaction will be measured and compared with literature data.

THEORY

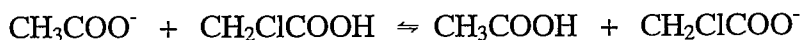
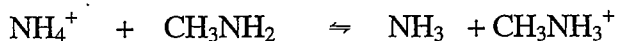
ION-MOLECULE EQUILIBRIUM

The most important types of ion-molecule equilibria to which the PHPMS technique has been applied are listed below with examples:

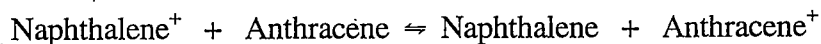
1. Ion-ligand and ion-solvent molecule equilibria:



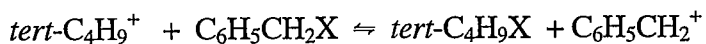
2. Proton transfer: gas phase acidities and basicities



3. Electron transfer: electron affinities and ionization energies



4. Hydride and chloride transfer: hydride and chloride ion affinities, stabilities of carbocations.



The determination of the equilibrium constant of a given ion-molecule reaction is straightforward if the concentrations of all species are known. In practice, the concentrations of neutrals are usually known and are treated as constant since the

neutrals are in vast excess over the ions. The concentrations of the ions are measured by the mass spectrometer using two assumptions:

1. the abundance of a given ion measured by the mass spectrometer is proportional to its concentration in the ion source at that time;
2. the measured intensity ratio of two ions is equal to the ion concentration ratio in the ion source.

When equilibrium constants are measured at different temperatures, not only ΔG° can be obtained but also ΔH° and ΔS° by means of van't Hoff plots.

van't Hoff Plot

From equations 1 and 2,

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (1)$$

$$\ln K = -\Delta G^\circ / RT \quad (2)$$

equation 3 can be derived,

$$\ln K = -\Delta H^\circ / RT + \Delta S^\circ / R \quad (3)$$

when $\ln K$ is plotted against $1/T$, a straight line is expected with a slope equal to $-\Delta H^\circ/R$, and an intercept equal to $\Delta S^\circ/R$.

SOURCE CONDITIONS REQUIRED FOR REACHING ION-MOLECULE EQUILIBRIUM

In order to measure gas phase ion-molecule equilibria, the following thermodynamic and kinetic conditions [18] need to be achieved in the ion source:

1. The reactants and products must be in thermal equilibrium with their common surroundings (carrier gas or walls of the reaction vessel).
2. The path(s) that reactively couple the ions engaged in the equilibrium must be appreciably faster than all other processes affecting the concentration of the ions.
3. Sufficient time must be given for the system to reach equilibrium.

In practice, conditions 2 and 3 require that the kinetics of the reaction system be well understood.

Since the neutral molecules in the ion source are generally stable and in vast concentration excess over the ions, they will be in thermal equilibrium with the gas and walls. However, the ions may be nonthermal because of energy gained due to applied electric potentials, or energy contained in ionic products due to exothermicity of the reaction by which the ions were produced. In practice, the ion-thermalization condition is met by having the ions suffer many collisions with an inert third gas like CH_4 or N_2 before they experience a reactive collision. In order to have sufficient third gas molecules, the ion source should be operated with a much higher pressure than a normal EI or CI source. This is achieved by decreasing the area of the ion exit slit or orifice to reduce gas outflow from the ion source and by increasing the pumping speed at the vacuum housing containing the ion source.

In the situation when an electric field is applied in the ion source, extra energy will be gained by the ions. Castleman et al [19] have observed thermal behavior and measured equilibria at $E/p < 15 \text{ V}/(\text{cmTorr})$.

Mean Free Path of Ions in the Gas Phase

Ions in the gas phase become discharged either on collisions with the walls of the ion source or on collisions with ions or electrons of opposite charge. The mean free path of an ion or molecule depends on the average thermal velocity, v_{ave} , the collision rate, $\gamma_{collision}$, and the number density, n , and can be estimated by equation 4,

$$\lambda = v_{ave} / (\gamma_{collision} \times n) \quad (4)$$

for a given type of gas at a fixed temperature, equation 5, much simplified, is often used:

$$\lambda = k / p \quad (5)$$

where k is a constant depending on the type of gas and p is pressure. For nitrogen (and hence approximately for air), k equals 5×10^{-5} mTorr. As mentioned before in the Introduction part, ion sources used to measure ion-molecule equilibria usually operate in the torr range (1 to 10 torr), which yields a mean free path of 5×10^{-5} to 5×10^{-6} m. The discharge of ions on the wall is slow because the ions have to diffuse through the gas to reach the wall.

Positive ion-negative ion recombination is also slow when low ion densities are used. A high concentration of neutral reactant increases the ion-molecule reaction rate to the point where it may be many orders of magnitude faster than the ion recombination rate [18].

Residence Time of Ions Inside the Source

Ions have to remain in the ion source long enough such that the equilibria are established before the ions are sampled to the mass analyzer. When no electric fields are

applied inside the source, ions react with neutrals and reach equilibrium as they diffuse through the buffer gas and approach the walls of the ion source. Ions diffusing to the vicinity of the exit slit or orifice are carried by gas flow into the vacuum region of the mass spectrometer. When an electric field is applied inside the source, the drift velocity of ions, V_d , is directly proportional to the electric field strength, E ,

$$V_d = \mu E \quad (6)$$

where μ is the ionic mobility, which is a function of pressure, p in torr, and temperature, T in K. The value of μ may be calculated from the reduced mobility constant, μ_0 , by equation 7 [20],

$$\mu = (T/273.16) \times (760/p) \times \mu_0 \quad (7)$$

The residence time, i.e. the reaction time, of ions can easily be calculated by equation 8,

$$t = d / V_d \quad (8)$$

where d is the depth of the ion-molecule reaction region.

ION SOURCE SAMPLING CONDITIONS

Since mass spectrometric methods require well-defined ion trajectories or energies in order to operate properly, mass analysis must occur in a region of comparatively low pressure. When an ion-molecule reaction occurs in the torr pressure range, ions have to be appropriately sampled to the mass spectrometer, which is usually operated under 10^{-5} torr pressure. Sampling is accomplished by the leakage of gas from the high pressure environment through a small exit orifice or slit into the mass spectrometer whose low

pressure is maintained by vacuum pumps. The dimension of the exit opening depends on the following considerations:

1. the upper limit is set by the capacity of the pumps to maintain a sufficiently low pressure in the mass spectrometer;
2. the lower limit is set by the signal detection ability of the detector;
3. the effect which usually sets the upper limit is the sampling of the ions.

In practice, a high capacity pump is used at the housing containing the high pressure ion source in order to handle the gas load flowing from the ion source and maintain a low pressure. An orifice with about 100 μm diameter has been used and proven to be able to provide good mass spectra [17].

Gas Flow Through Exit Orifice

Since ion-molecule reactions occur in a high pressure region, the effect of sampling conditions on ions can be critical. If the size of the sampling orifice is too large, hydrodynamic expansion can lead to additional clustering due to the collisions and the concomitant cooling process. An opposing effect is the dissociation of weakly bound cluster ions due to collisions with neutral molecules, particularly when extraction fields are present that can accelerate the ions [21]. Ideally, molecular effusion from the high pressure region through the exit aperture is desired in order to fulfill the accepted criteria for perturbation-free cluster ion sampling. This condition is attained when the dimensions of the sampling orifice (both hole diameter and thickness) are small compared to the mean free path of the ions.

The Knudson number is an established flow dynamics index for determining if the mass transport of a gas is effusive [22], meaning that no collision occur between gas molecules during the transit through an orifice. It is given by equation 9,

$$K = \lambda / D \quad (9)$$

where λ is the mean free path of the ion or molecule to be sampled, and D is the diameter of the orifice. A Knudson number of less than 0.01 indicates viscous flow through the orifice. A value greater than 0.5 [23] is indicative of molecular flow. The mean free path of nitrogen, as calculated before, is 5×10^{-6} m, or 5 μm in a 10 torr pressure source. The Knudson number is about 0.05 when a 100 μm orifice is used, and near molecular flow will be achieved.

Free Jet Expansion

A free jet expansion embodies the conversion of random motion of gas molecules in a high pressure reservoir into a directed mass flow of gas molecules expanding through a small aperture into a vacuum chamber [24]. The energy required for this process is mainly provided by the internal energy of the gas molecules. A result of free jet expansion is a self cooling effect. Molecular vibrations and rotations can be cooled to temperatures far below the freezing point of the entrained gas molecules and are known to decrease into the low Kelvin range [25]. Therefore, aggregation processes such as clustering may well occur in a supersonic jet.

The extent of cooling in a supersonic jet increases with the pre-expansion pressure and orifice diameter. It is the result of two-body collisions which occur early in a region

of the expansion called the silent zone, in which gas velocities are uniform and have similar trajectories [25]. The number density and local temperature decrease with increasing distance from the sampling aperture. The highest velocities are attained on axis of the direction of flow. Surrounding the silent zone are regions of shock waves. These are the boundaries between the directed flow of the jet and the random motion of the background gas in the expansion chamber. Shock waves are regions of extensive scatter and collisions. The passage of ions and neutrals from the silent zone through a shock wave serves to raise the internal energy of the ion or neutral and may potentially result in collisionally activated dissociation.

The distance from the orifice to the silent zone along the axis of directed flow can be estimated by the empirical equation 10 [26],

$$X_M = 0.67 D_o (P_o / P_1)^{1/2} \quad (10)$$

where D_o is the sampling orifice diameter, P_o is the pre-expansion pressure, and P_1 is the vacuum pressure. The value of X_M is about 1.2 cm in our experiments.

The factors governing in a free jet expansion are:

1. the molecular weight of the expansion gas;
2. the relative percentage of the clustering specie to the expansion gas;
3. the upstream (pre-expansion) pressure;
4. the upstream temperature;
5. the design of the sampling aperture.

Because of the low concentration of ions, essentially all collisions experienced by the ions in the expansion will be with neutral molecules of the expansion gas. The extent of

cooling is dependent on the frequency of collisions, or the relative velocity of the ions and the expansion gas. Usually, the lighter the mass of the expansion gas, such as helium, the smaller the cooling effect. Using an expansion gas with heavier molecules usually increases the residence time of the ions in the silent zone, and therefore ions will experience more collisions, which result in a strong subsequent cooling effect. This in turn results in more extensive clustering.

ELECTROSPRAY IONIZATION

Electrospray had a long history before its application to mass spectrometry [27]. The crucial aspect of electrospray used in mass spectrometric application is the production of gas phase ions from ions in the solution.

Electrospray process

Three major processes are involved in transferring ions from solution to gas phase in electrospray [10]:

1. Charged droplets are produced from electrolyte in a solvent;
2. The charged droplets shrink as the solvent evaporates. The droplets disintegrate (fission) ultimately leading to very small, highly charged droplets that are capable of producing gas phase ions;
3. Gas phase ions are produced.

In secondary processes that occurs after gas phase ions have been formed, the ions are modified in the atmospheric pressure ion source and in the mass spectrometer [10].

These processes are important and complicated but are not essential to this work and will not be discussed here.

Figure 1 shows the sequence of events in electrospray [10]. In order to produce the charged droplets, a high voltage, usually 2-3 kV, is applied to the tip of a narrow metal capillary. The counter electrode is positioned in front of the metal capillary, usually 0.5-3 cm away. In electrospray mass spectrometer (ESMS), this counter electrode has an orifice through which ions pass into the mass spectrometric sampling region. Since the outside diameter of the electrospray capillary is small, the electric field at the tip of the capillary is very high. When the capillary is the positive electrode, the positive ions in the liquid that is flowing out of the capillary will drift toward the surface of the liquid. Under the influence of the positive space charge, the liquid forms a cone (Taylor cone) at the capillary tip, because the positive ions are attracted to the counter electrode. If the electric field is high enough, the cone is not stable, and a liquid filament jet, whose surface is enriched in positive ions, with a diameter of a few micrometers, is emitted from the cone tip. The liquid filament is not stable and breaks into positively charged droplets a short distance from the cone tip.

Droplets of micrometer size or larger are known to maintain their charge; they do not emit gas phase ions [28]. While the charged droplets drift towards the counter electrode, the solvent keeps evaporating, the volume of the droplet is decreasing, but the charge remains constant. Therefore, the charge density is increasing. When the radius of a droplet reaches the Rayleigh radius, where the electrostatic repulsion force

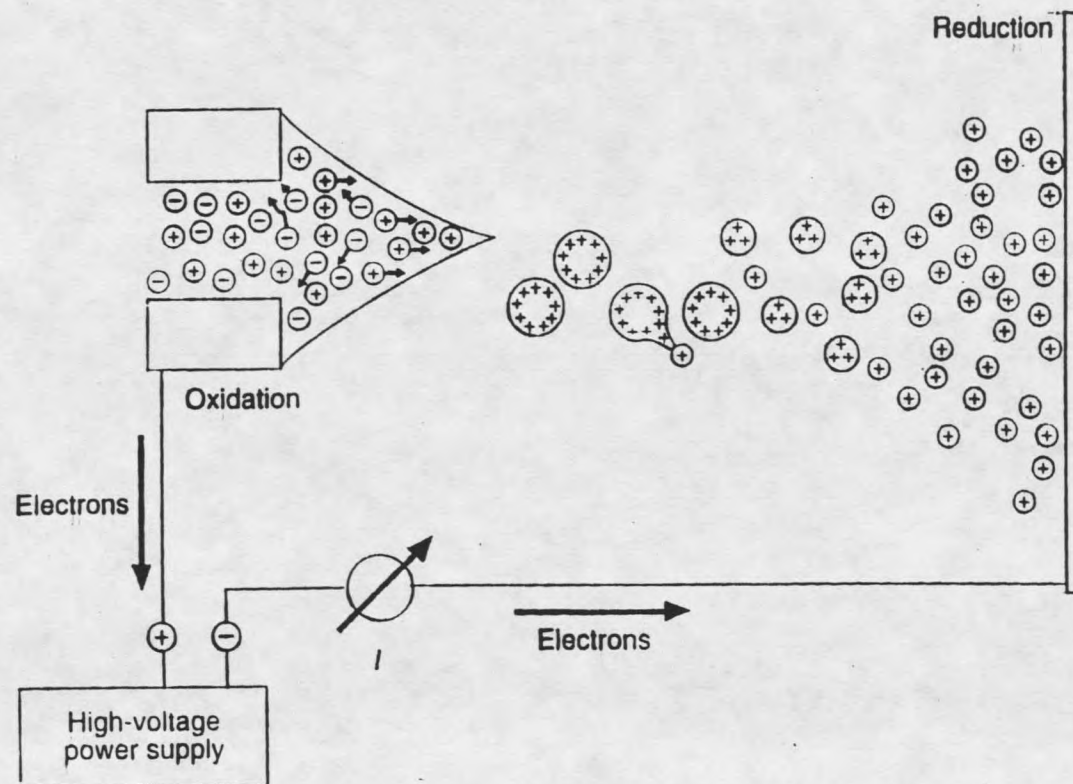


Figure 1. Schematic representation of processes in electrospray. Figure reproduced from reference [10].

inside the droplet is large enough to overcome the surface tension, the droplets undergo fission into smaller droplets.

The Rayleigh equation [29], which gives the condition at which the charge Q becomes just sufficient to overcome the surface tension γ that holds the droplet together, is

$$Q^2 = 64 \pi^2 \epsilon_0 \gamma R^3 \quad (11a)$$

$$Q^2 = 1.25 \times 10^{-10} R^3 \quad (11b)$$

where Q is the charge number, ϵ_0 is the permittivity of vacuum, γ is the surface tension, and R is the radius. Equation 11b gives the condition for methanol, whose $\gamma=0.0226$ N/m²; the numerical factor is for Q in coulombs and R in meters.

It is important to note that a droplet does not split evenly into two smaller droplets of approximately equal mass and charge [28]. The droplets have been observed to vibrate alternately from oblate to prolate shapes. These elastic vibrations stimulate disruptions in which the "parent" droplets emits a tail of much smaller "offspring" droplets [28]. This disruption pattern is similar to the disruption at the tip of the Taylor cone. It has been estimated that the emitted stream of offspring droplets carries off only about 2% of the mass of the parent droplet but about 15% of the parent's charge. Thus the offspring are not only much smaller than the parent but also have a much higher charge-to-mass ratio. Uneven fission separates the droplets into two classes: the small offspring droplets are enriched in charge and are the future gas phase ion emitters; the large parent droplets become the dumps for the unwanted charge-paired

electrolyte ions, like $\text{Na}^+(\text{NaCl})_n$. Figure 2 shows this fission process with time history [10].

Mechanism of Gas Phase Ion Formation

The mechanism of gas phase ion formation from charged droplet is an interesting subject for mass spectrometry users. Basically, two different mechanisms have been proposed and are widely accepted.

The first mechanism was proposed by Dole [30] in 1968 and later supported by Röllgen [31, 32]. It is assumed that the fission processes continues until extremely small droplets, each of which contains only one solute ion are produced. As the last solvent molecule evaporates from these ultimate droplets, gas phase ions are formed.

The second mechanism for electrospray ion formation was proposed by Iribarne and Thomson [33, 34]. They suggested that ions "evaporate" under the influence of the high electric field at the surface of very small but highly charged droplets. It was calculated that ion "evaporation" should become competitive with Rayleigh fission when the radius of a droplet is about 8 nm and the elementary charge number is about 70 [33, 34]. Under these conditions, the droplet should emit gas-phase ions instead of undergoing fission.

The differences between the two electrospray theories are: 1. The Iribarne and Thomson mechanism does not require the production of very small droplets that contain only one ion. Because of the small size of the droplets involved, it is hard to prove whether droplets with a single ion really are formed by the fission process or

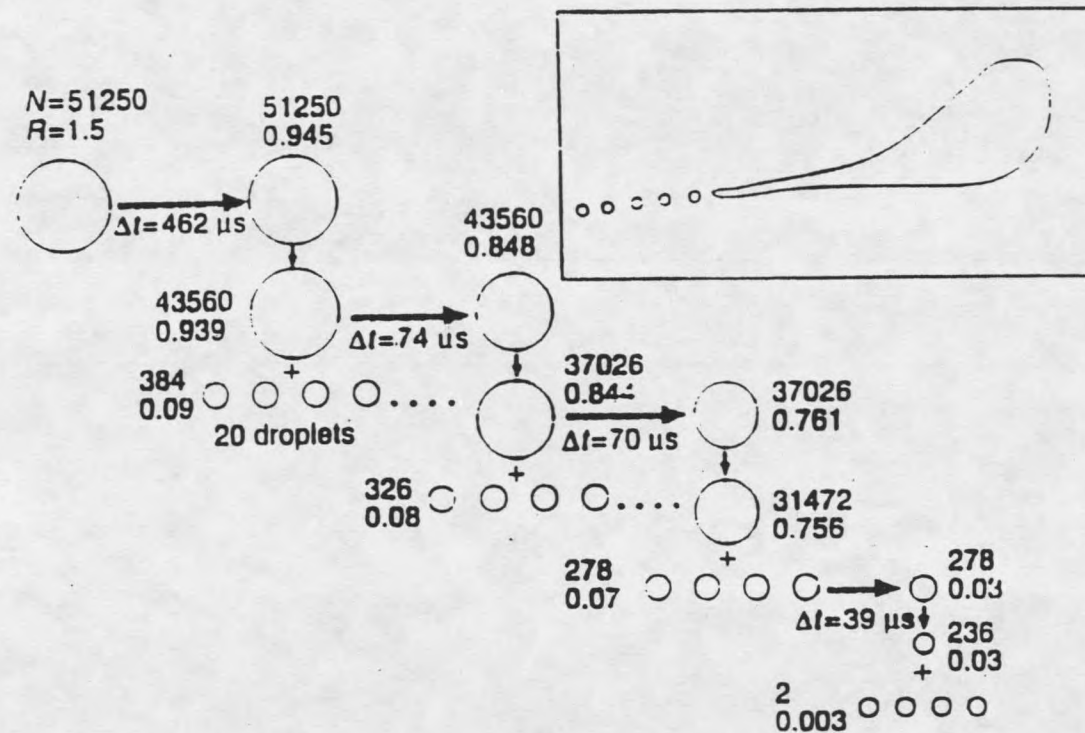


Figure 2. Schematic diagram of time history of parent and offspring droplets. Figure reproduced from reference [10].

not. 2. "Ion evaporation" can occur even when a droplet contains other solutes such as charge-paired electrolytes.

The second difference had been used as an experimental "proof" [35] of the failure of the Dole model before uneven droplet fission had been observed. Since uneven fission provides a mechanism for the formation of single ion in droplet, it is still unclear which mechanism fits better with the experimental evidence.

IONS TRANSPORT THROUGH CAPILLARY

In contrast to other commonly used ionization techniques, electrospray works at atmospheric pressure. This means that ions produced by electrospray have to be separated from ambient gas as they are sampled into the vacuum of the mass spectrometer. This problem had been encountered before with Atmospheric Pressure Ionization (API), which usually uses a corona discharge or a β -emitter like ^{63}Ni as ion generators in atmospheric pressure environment. Basically, there are two designs used for the interfacing of an API source with a mass spectrometer.

One of the designs uses a single pinhole orifice to connect the atmospheric pressure chamber and the vacuum chamber [36]. The gas flow through a $\sim 100\ \mu\text{m}$ diameter orifice is pumped by a very efficient cryopump on the vacuum side. Electric fields are used to extract the ions from the gas jet. The extensive cooling in the supersonic jet may result in unwanted cluster ions, particularly with water molecules. Therefore, a dry nitrogen interface gas is introduced at the high pressure side of the orifice. This design is used in some electrospray sources.

In the second design, the pressure drop is achieved in two stages. Ions are first transported through an orifice or capillary and enter into an intermediate torr range pressure chamber usually pumped by a mechanical rough pump. Ions are then sampled into the mass spectrometer through a conical skimmer [37]. This design with two pump stages is very common for electrospray interfaces.

ESMS Interface

Figure 3 shows the ESMS interface used by Fenn and co-workers [9, 38]. They used a 0.2 mm i.d., 60 mm long glass capillary in stead of the orifice to connect the electrospray chamber (~ 1 atm) and the intermediate pressure chamber (torr range). The gas throughput in this design was close to that of a 100 μm orifice and equally good mass spectra were obtained. The voltage applied were as follows: ES needle (ground), cylindrical electrode (-3500 V), metalized inlet and exit ends of the transport capillary (-4500 V and +45 V, respectively), skimmer (-20 V). Ions generated are trapped in the gas flow from high pressure to low pressure through the capillary. Most gas is pumped out through a mechanical rough pump but ions are held by applied electric field between the capillary exit and the skimmer in the intermediate pressure chamber. Remaining air is pumped out after the skimmer and ions are sampled into the quadruple mass filter. It is noted that the gas flow can drag positive ions through the capillary, againsting a 4.5 kV "uphill" voltage difference between the two ends of the capillary.

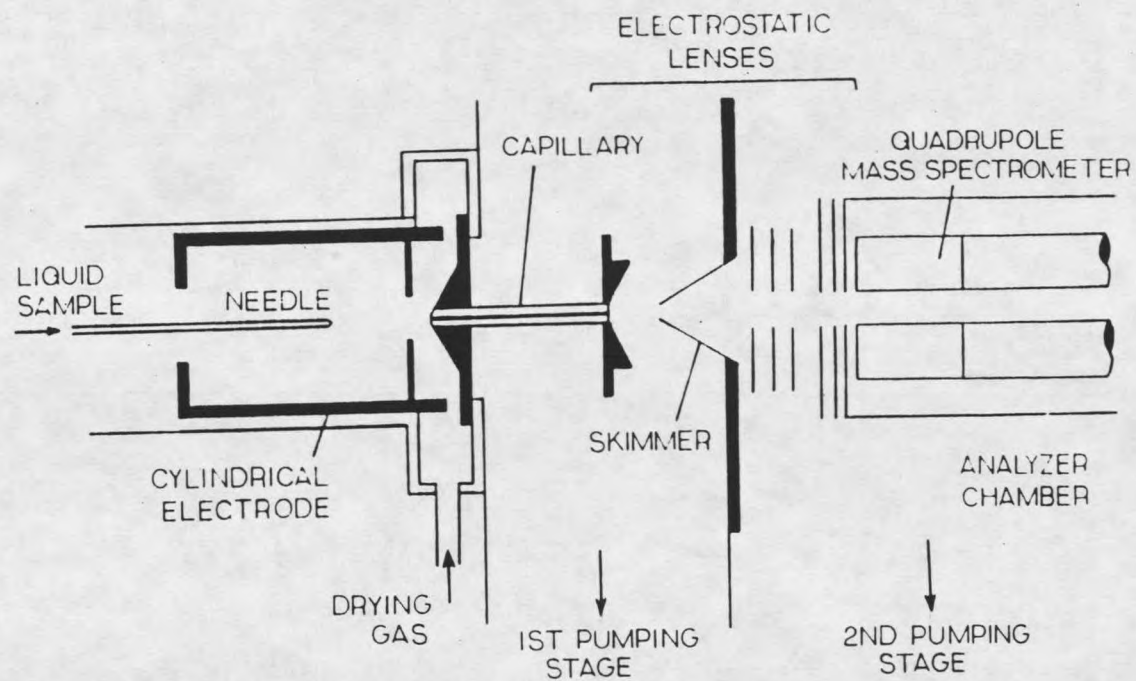


Figure 3. Schematic diagram of an ESMS apparatus. Figure reproduced from reference [9, 38].

That ions can be transported through a narrow capillary was a surprising phenomenon for many mass spectrometrists. It is tempting to assume that with a capillary radius as small as 0.1 mm, very few ions would escape colliding with the wall of capillary. But the research done by Lin and Sunner [39] proved the knowledge among electrospray practitioners has been that ions would pass through even very long capillaries. Since this phenomenon happens in high pressure environment, the gas flow through the capillary plays an important role here.

Types of Gas Flow Through Capillaries

Two types of gas flow are common inside the tubes: laminar flow and turbulent flow. At low flow velocities, fluids tend to flow without lateral mixing, and adjacent layers slide past one another. There are neither cross currents nor eddies. This regime is called laminar flow. At higher velocities, turbulence appears and fluids move erratically in the form of cross currents and eddies. This type of motion is called turbulent flow. The type of flow inside tubes depends on the Reynolds number [32] and the smoothness of tube inner surface.

The Reynold number is defined as

$$N_{Re} = Dvp / \mu \quad (12)$$

where D is inner diameter of tube, v is the average velocity of fluid, ρ is the density of fluid, and μ is viscosity.

Laminar flow is always encountered at Reynolds number below 2100, but it can persist up to several thousands if the tube entrance is well rounded. Typically, when the

Reynold number is above 4000, the flow is turbulent. In the region of the Reynold number between 2100 and 4000, the type of flow may be either laminar or turbulent, depending on the conditions at the entrance of the tube [40]. For a given gas and capillary, the Reynolds number depends on the velocity of the gas since the other three factors are constants. Previous studies [41] have shown that the flow velocities of a fluid inside a tube are not even. Figure 4 shows that the maximum velocity exists at the center of the tube while zero velocity at the wall.

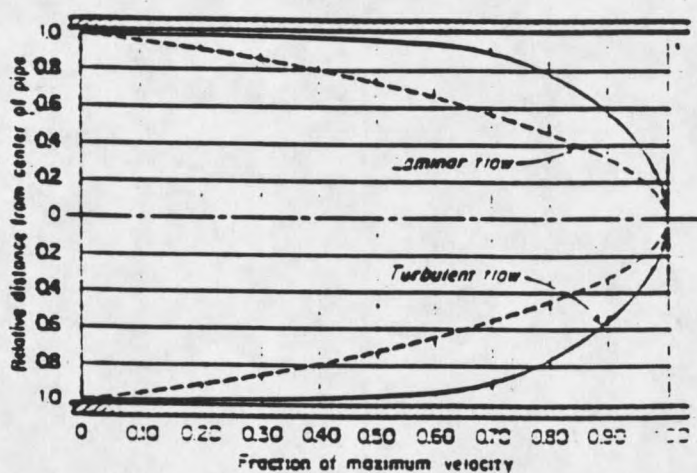


Figure 4. Velocity distribution in pipe for laminar flow and for turbulent flow at $N_{re}=10,000$. Figure reproduced from reference[41] .

It is common to conclude that turbulent flow is being wrapped by laminar flow along the tube. Since there are no cross currents and eddies in laminar flow, most ions are being held in the turbulent flow without colliding the wall while they are transported through the capillary.

INSTRUMENTATION

The mass spectrometer used in this work is a Pulsed High Pressure Mass Spectrometer (PHPMS). The component parts of the mass spectrometer are described below.

PHPMS APPARATUS

The mass spectrometer used for this study was donated by Dr. Kebarle. It was one of several PHPMS home-built in Dr. Kebarle's lab. The technique has been discussed in great detail [6]. Since this study focuses on using the electrospray ion source in PHPMS, only a brief description of PHPMS will be given here. There are several fundamental differences between PHPMS and conventional mass spectrometry. To obtain reliable and reproducible rate constants and equilibrium constants for ion-molecule reactions, the following conditions must be met in a PHPMS: (i) the temperature of the ion source must be accurately known and should be uniform and stable for a prolonged period; (ii) the pressure in the ion source should be accurately known; (iii) a high capacity pumping system is required, because the ion source pressure is several torr and the mass analyzer needs high vacuum. The pressure should be low enough that the mean free path of the ions is greater than the dimension of the apparatus.

A simplified block diagram of the components of the PHPMS system is shown in Figure 5. A detailed description of the essential components of the mass spectrometer is shown in Figure 6, except the existing ion source, which will be replaced by the new designed electrospray ion source, was differently designed.

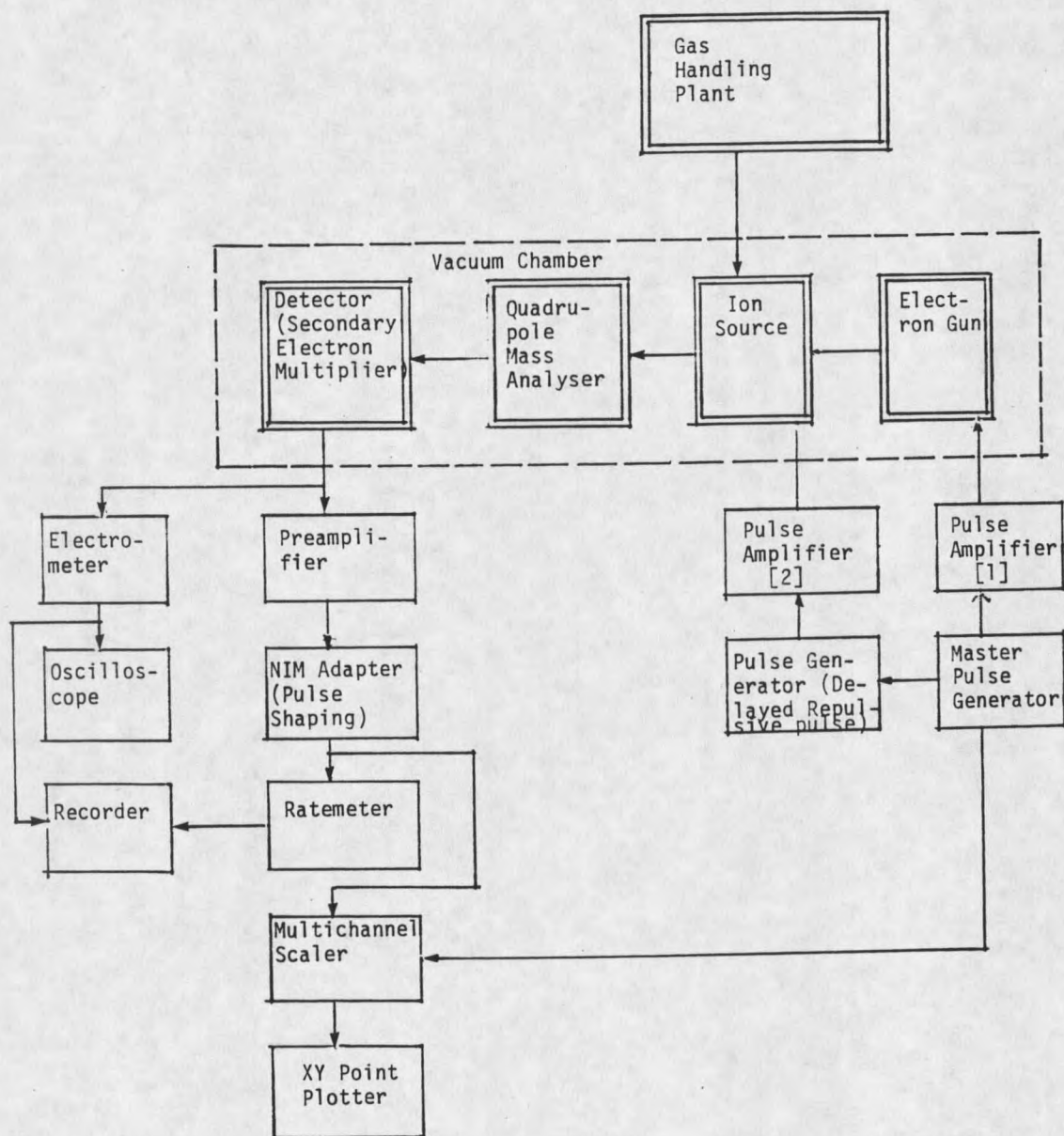


Figure 5. Block diagram of PHPMS system.

Figure 6. PHPMS Apparatus [6].

A. Electron Gun

1. Filament
2. Filament support and electron reflector plate
3. Draw out electrode
4. Pulsing electrode
5. Acceleration
6. Collimation electrode
7. Solenoid providing axial magnetic field for electron collimation
8. TV yoke for X and Y deflection of beam
9. Deflection plates, not in use

B. Ion Source

10. Fluorescent beam focusing screen
11. Electron entrance slit carrying flange
12. Ion exit slit carrying flange
13. Ion source block with heaters
14. Electron trap
15. Wire mesh electrical shield

C. Ion Acceleration and focusing

16-20: Electrodes

D. Mass Analysis and Detection

21. Quadrupole
22. Electron multiplier

E. Others

- 23, 24. Reactant gas circulation glass tube for inflow and outflow
25. To 6 inch diffusion pump
26. Differential pumping lid
27. To 4 inch diffusion pump

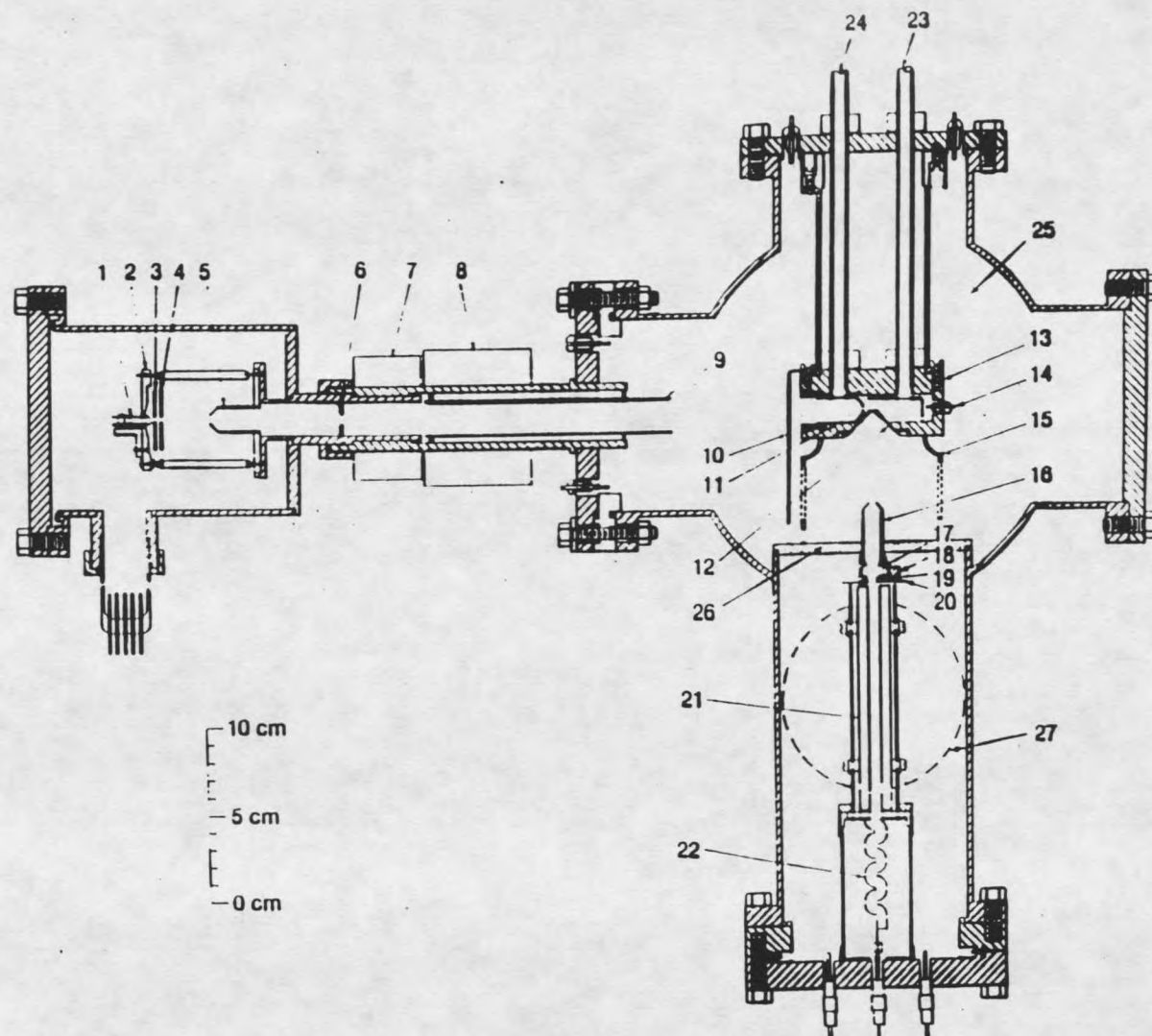


Figure 6. PHPMS apparatus. Figure reproduced from reference [6].

ELECTROSPRAY ION SOURCE

The electrospray ion source designed and built as part of this work is shown in Figure 7. The source follows the basic design used by Kebarle and coworkers [17]. It is constructed from stainless steel. It was designed to fit the ion source flange and the vacuum manifold of the existing PHPMS. The source consists of electrospray chamber, transport capillary, pre-reaction chamber, reaction chamber, reagent gas supply line, vacuum pumping line and pressure measuring line.

The electrospray chamber is situated outside the vacuum chamber, in ambient room air. The pressure is typically 640 torr for the 5,000 ft elevation of Bozeman, Montana. A stainless steel "transport" capillary connects the electrospray chamber and the pre-reaction chamber that is operated at a pressure of about 10 torr. The exit tip of the transport capillary is bent 90° so that the gas jet exiting the capillary is directed parallel to the interface plate at the bottom of pre-reaction chamber. This is necessary in order to minimize the disturbance to the reaction chamber by the supersonic jet. Ions entrained in the jet are induced to drift towards the interface plate, and through an orifice in the interface plate into the reaction chamber by means of an applied electric field. In the reaction chamber, ions, while undergoing ion-molecule reactions, drift towards the exit orifice at the bottom of the reaction chamber due to a weak applied electric field. They enter the vacuum of the mass spectrometer through a small circular sampling orifice.

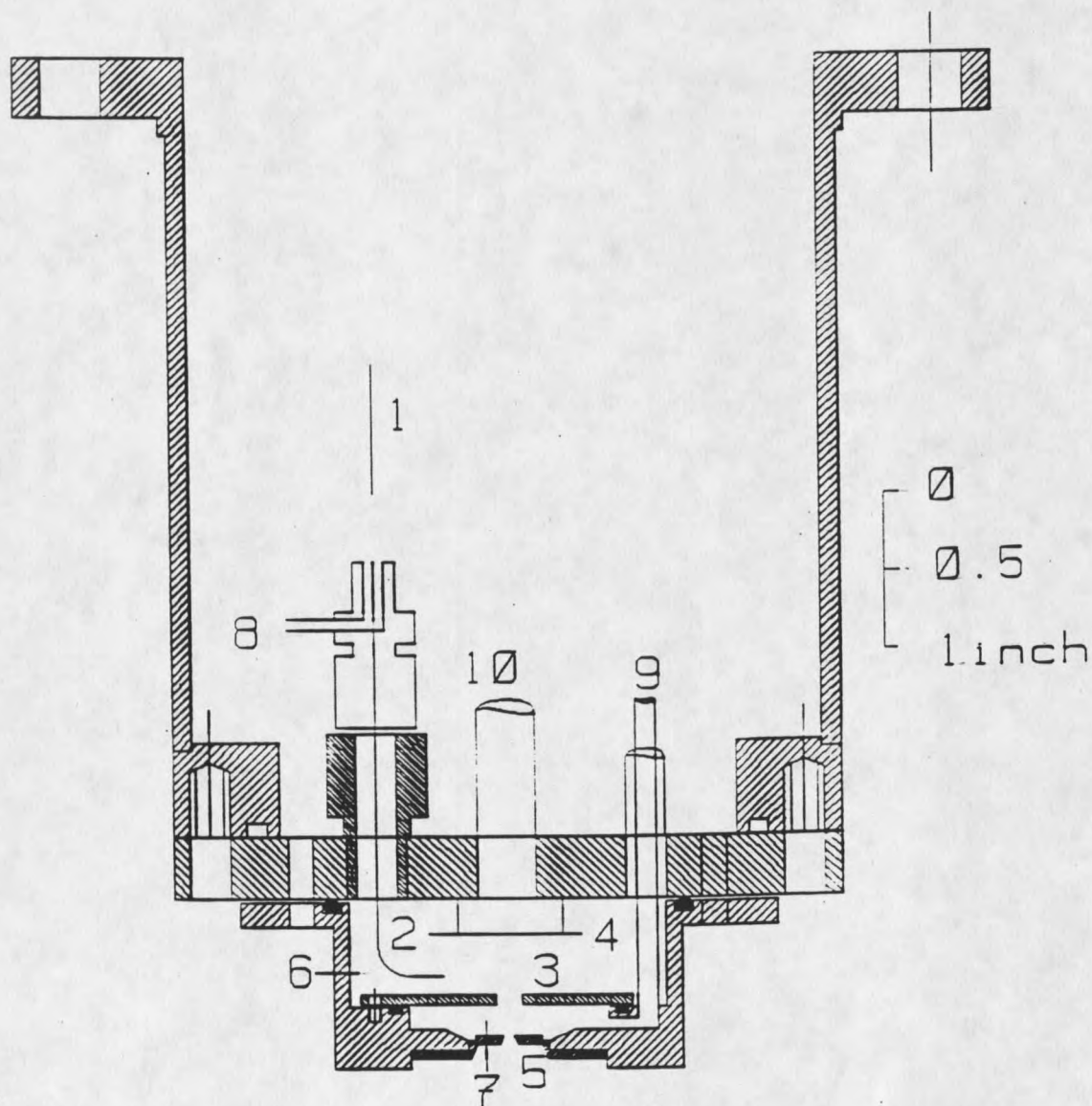


Figure 7. Electrospray high pressure ion source.

1. ES capillary; 2. ion transport capillary; 3. interface plate; 4. deflector; 5. ion exit flange; 6. pre-reaction chamber; 7. reaction chamber; 8. purge gas line; 9. reagent gas inlet line; 10. pressure measurement line.

Note: pumping line is not shown in the figure.

Ion Transport Capillary

The ion transport capillary is made of stainless steel, 1.6 mm o.d., 0.4 mm i.d. and about 8 cm long. The ion transport capillary entered the vacuum through a 6.1 mm o.d. and 33 mm long glass tube. The capillary was glued and sealed to the glass tube by epoxy glue, and the glass tube was held by a 0.25 inch i.d. Cajon Fitting. The glass tube also served as electric insulation when voltage was applied to the transport capillary.

The position of the ion transport capillary is 20 mm off the axis of the ion sampling orifice. The exit tip of the capillary, which is at right angle to the ion source axis, is 3 mm above the interface plate and 1 cm away from the enter axis. The distance between the exit tip and the deflector is 7 mm.

Pre-Reaction Chamber

The pre-reaction chamber is cylindrical in shape, with inside diameter 4.9 cm and height 17 mm. The deflector, a round stainless steel plate used to establish the electric extraction field that pushes ions out of the supersonic jet, is in the middle of the chamber, 10 mm away from the bottom of the chamber. An opening behind the deflector leads to a 0~10 torr capacitance manometer (Validyne DP15) used to measure the pressure in the source. The pumping line out of the chamber leads to a 500 l/min mechanical rough pump (Welch 1297). The diameter of the orifice that connects the pre-reaction chamber and reaction chamber is 4 mm. The air flow through the ion transport capillary maintains a pressure in the pre-reaction chamber as well as the reaction chamber of about 7.2 torr when no additional reagent gas is added. A four-pin electric

feed-through provides electrical connections between the atmospheric chamber and the pre-reaction chamber. Three pins are used to apply voltages to the ion transport capillary, the deflector, and the interface plate, respectively. A springloaded contact is used for the voltage supply to the interface plate so that the ion source can be easily assembled.

Reaction Chamber

The reaction chamber has a cylindrical geometry, with inside diameter 3.1 cm. The distance between the interface plate and the exit orifice is about 5 mm. A 36.6 mm o.d., 33.0 mm i.d. rubber O ring and nylon screws were used to seal and electrically insulate the interface plate. A voltage difference of about 10 V was typically applied between the interface plate and the body of the reaction chamber. A hole in a side wall of the reaction chamber connects the reagent gas inlet line, a 3.2 mm o.d. stainless steel tubing. The tube passes through the upper pre-reaction chamber to connect to the gas handling plant where a given concentration of reagent gas is mixed with buffer gas. The reaction chamber exit orifice is a $70 \times 80 \mu\text{m}$ ellipse in a thin metal foil spot-welded to a stainless steel flange. A gold ring is used for sealing the exit flange. A potential of 10 V was usually applied to the exit flange and the walls of the reaction chamber through the reaction gas inlet line. Figure 8 is a close look of the ion source with normal potentials applied to each electrode.

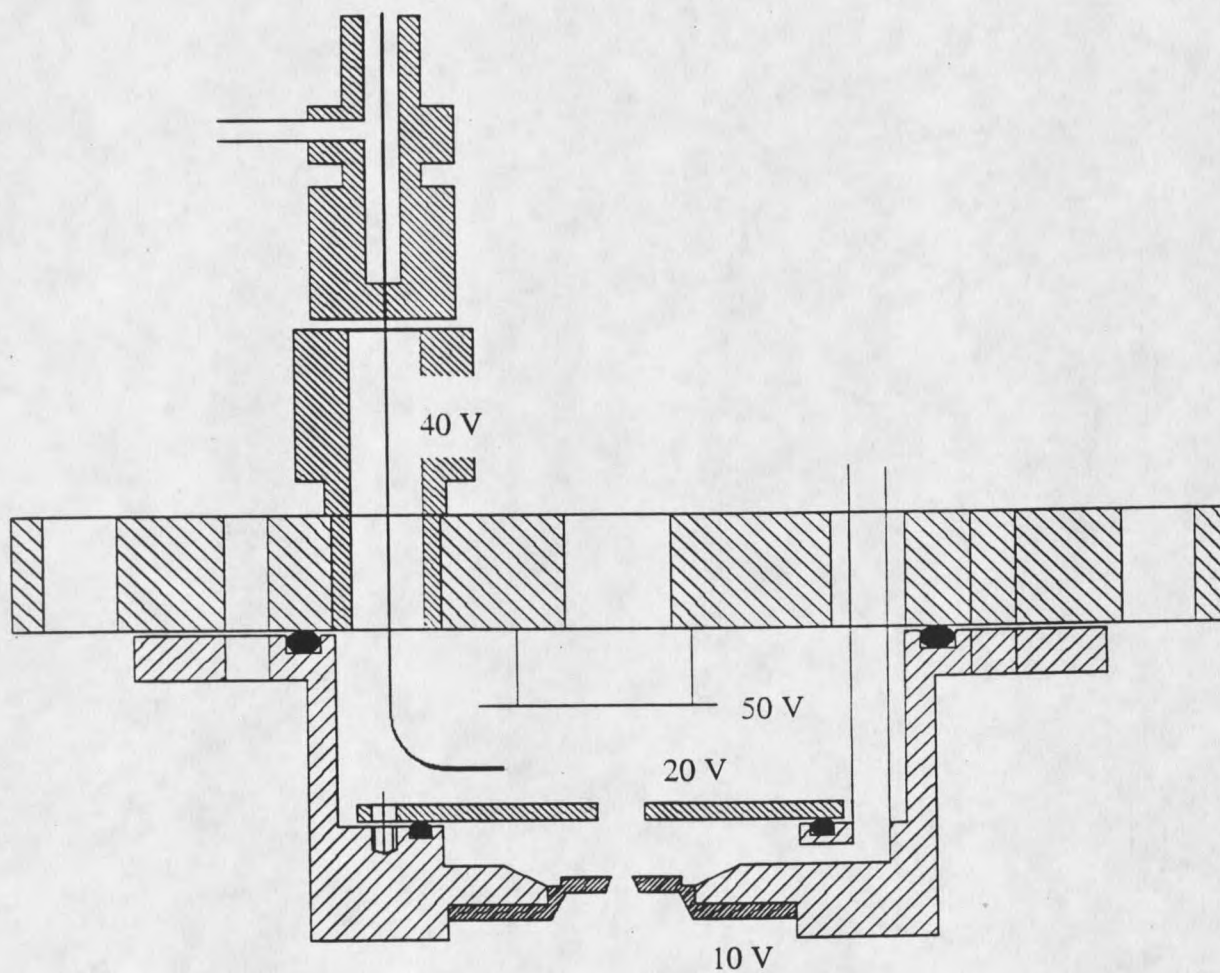


Figure 8. A close look of the ES ion source.

Ion transport capillary: 40 V; deflector: 50 V; interface plate: 20 V; exit: 10 V.

ELECTROSPRAY APPARATUS

There are two major components of the electrospray apparatus: the syringe pump and the spray needle. A 25 μ l syringe was loaded the electrospray analyte solutions. The solution was supplied to the spray needle at a constant flow rate through a fused silica capillary by a motor-drive syringe pump (SAGE 355). The joint was made using union fitting and ferrules.

Two different electrospray needles were used for this study. The first needle is very simple and similar to the one used in the Mass Spectrometry Facility in Montana State University. It consisted of a fused silica capillary, 50 μ m i.d and 146 μ m o.d., which also served as solution supply tubing. The tip of the silica capillary was gold coated by vapor deposition in a sputter coater (International Scientific Instruments PS-2 Coating Unit) in order to be able to supply a potential and current to the tip. No discharge-suppression gas like SF_6 was used with this tip. The second needle design is similar to the one used in Dr. Kebarle's lab, which is shown in Figure 9 [42]. The main assembly used in our lab consisted of an HPLC union and a swagelock union tee, both are 1/16 inch i.d. and are made of stainless steel. A 0.11 mm i.d. and 0.24 mm o.d. stainless steel capillary is used as the spray needle. An outer tube, which is also made of stainless steel with 1.6 mm o.d. and 0.4 mm i.d., is used to supply a SF_6 gas flow to the spray needle tip in order to suppress corona discharge.

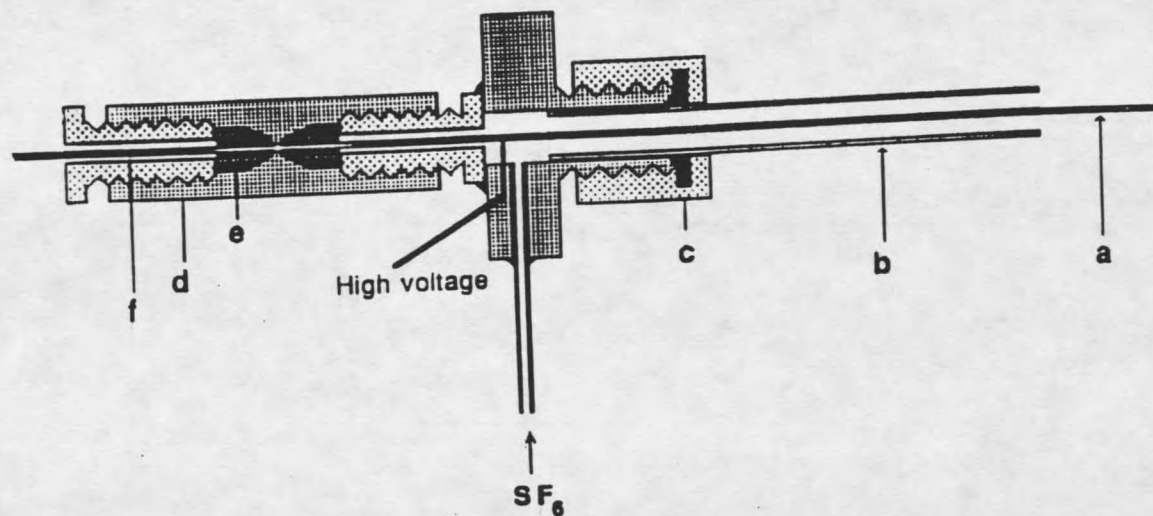


Figure 9. ES device. Figure reproduced from reference [42].
 a. Inner ss capillary. b. Outside ss tube. c. 1/16 in. ss swagelock union. d. 1/16 in. ss union. e. ferrule. f. Silica tubing.

The high voltage required for electrospray was supplied to the metal part of the capillary assemblies. The distance between the capillary tip and the opposing electrode, i.e. the entrance to the ion transport capillary, was about 5 mm.

GAS HANDLING PLANT

A gas mixture containing known concentration of a reagent gas in an inert buffer gas (nitrogen was used as the buffer gas in this study) must be supplied to the reaction chamber of the ion source. A convenient device for the preparation of the gas mixture is the gas handling plant, shown in Figure 10. The gas handling plant is contained in a box that is temperature controlled. The temperature used for the study was $\sim 110^{\circ}\text{C}$. The valves in the manifold are all-metal valves in order to minimize outgasing and impurities from previous gas mixtures. The gas mixture is prepared in a 5 liter glass bulb with a glass extension fitted with a rubber septum. The procedure is as follows. The bulb is first evacuated via valves 1 and 2 (Figure 10). Valve 2 is closed and the bulb is filled with nitrogen gas, usually to ~ 640 torr, from a high-pressure gas storage cylinder attached to gas inlet valve 3. The pressure in the bulb is measured with an automotive Vacuum and Pressure Tester (KAL Equip 2512) through valve 4. Valve 1 is closed and the reagent, usually a liquid, is injected through the septum into the bulb. After allowing about 1 hour for mixing, valve 1 is opened and the gas mixture fills the previously evacuated manifold. The gas flow to the reaction chamber is controlled through valve 7, which was adjusted to achieve a pressure increase of ~ 0.5 torr in the ion source. The gas phase composition, in particular the percentage of the reactant, in the reaction chamber would

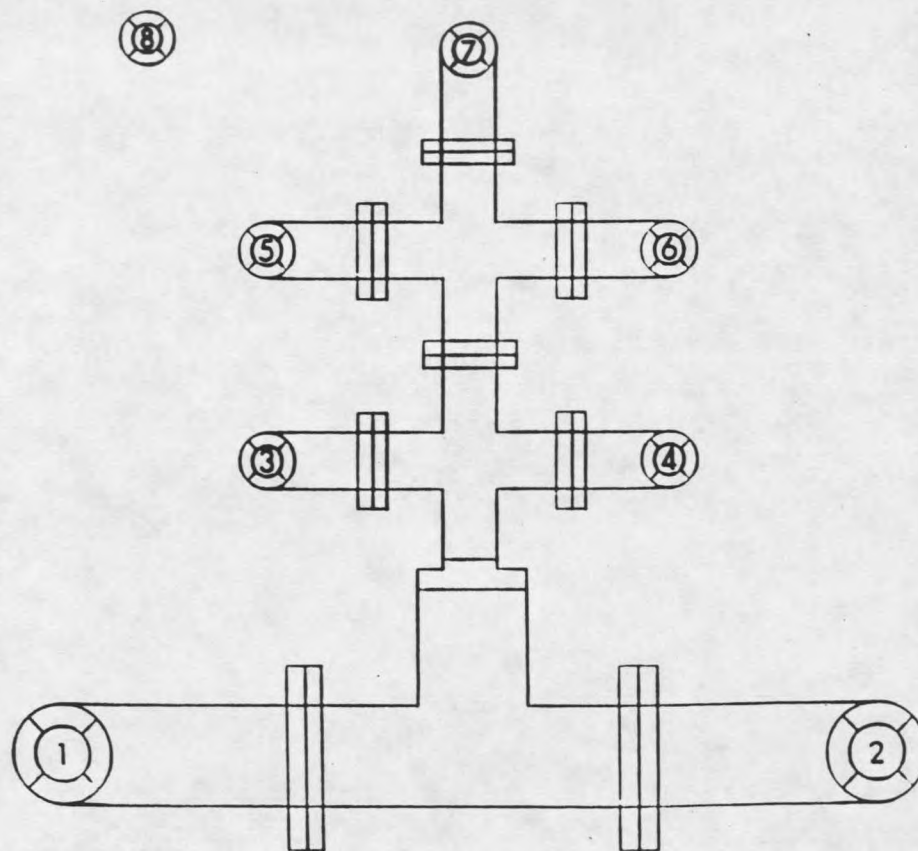


Figure 10. Gas handling plant. Figure reproduced from reference [6].

1 and 2 valves with 1 inch port, 3-8 valves with $\frac{1}{2}$ inch port. Valve 1, to 5 L storage bulb; valve 2, to rough pump; valve 3, gas inlet; valve 4, to vacuum & pressure tester; valve 5, no use; valve 6, to manometer; valve 7, to ion source; valve 8, no use.

be the same as that in the 5 L bulb. The partial pressure of the reactant is therefore easily determined from the total pressure of the ion source.

ION OPTICS, MASS ANALYZER AND DETECTOR

The mass analyzer used in this work is a quadrupole mass filter (Extranuclear Laboratories Inc., Model 4-162-8). A schematic of this instrument is shown in Figure 11. An ionization assembly in front of the entrance to the quadrupole can be used as an EI source. This assembly is shown in Figure 12. The EI source is controlled by an EAI Ionizer Controller. It has been used to analyze background gas (air) in order to determine the conditions of the quadrupole and secondary electron multiplier (SEM) after the PHPMS had been reassembled in Bozeman. The ionization assembly functions as ion optics when analyzing ions from the high pressure source. Most of the electrodes are grounded, only the potentials to lens #2 and lens #3 could be adjusted.

Ions that pass through the quadrupole filter are detected by a secondary electron multiplier (Gallileo Electric Optics) . In single ion mode the pulses were amplified and counted with an amplifier/discriminator photon counter (Princeton Applied Research, Model 1120) and collected in a multiscaler (EG&G ORTEC, MCS-plus PC plug-in card) and dedicated computer (Digital PC) . In analog mode, the signal was measured with a high speed picoammeter (Keithley Instruments, Model 416) and displayed on a oscilloscope (Hewlett Packard 130 C) .

A new secondary electron multiplier (SEM) was installed to replace the previously damaged one. The new SEM was not of the same type as the old and a new support base

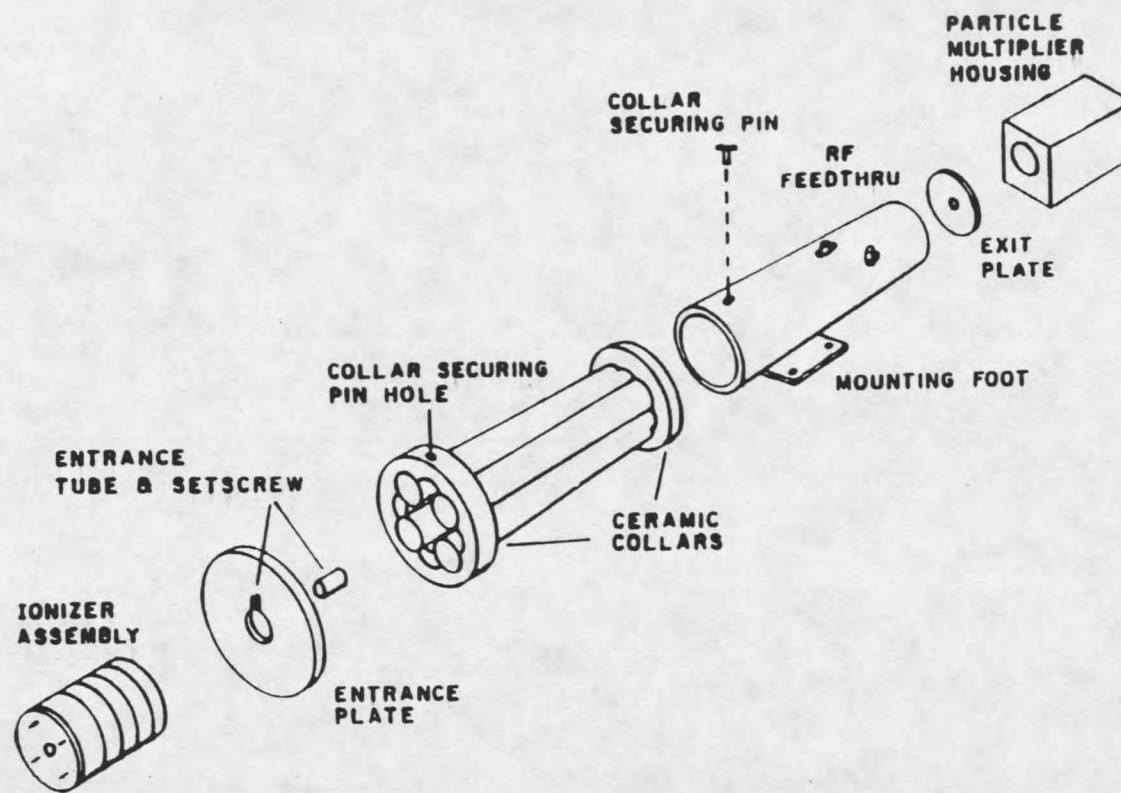


Figure 11. Schematic diagram of quadrupole mass filter. Figure reproduced from instruction manual of Extranuclear Laboratories, Inc.

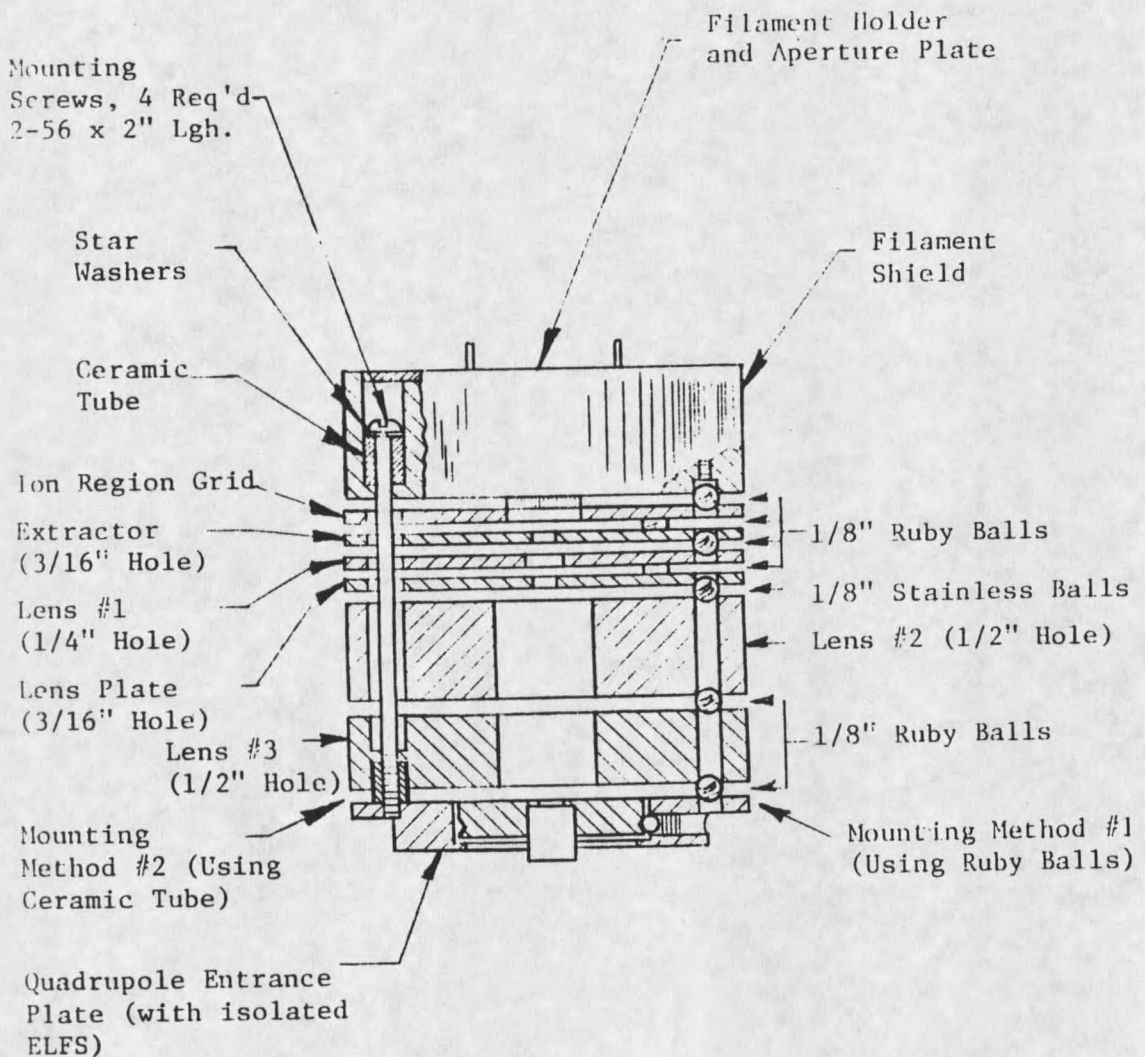


Figure 12. Ionization assembly. Figure reproduced from instruction manual of Extranuclear Laboratories, Inc.

for the SEM was made. Trajectories of ions exiting the quadrupole mass filter were simulated with the SIMION program [43] to ensure that ions were efficiently collected on the entrance funnel of the SEM. The appropriate potential distributions and the SEM dimensions used are shown in Figure 13.

Quadrupole Power Supply

The DC and RF voltages of the quadrupole mass filter are controlled by a quadrupole power supply (Extranuclear Laboratories, Inc., Model 011-1). The quadrupole power supply is divided into three major units: the Quadrupole Control, the Radio Frequency Power Source, and the High-Q Head. The Radio Frequency Power Source produces the RF voltage. A High-Q tuned transformer steps up the RF voltage to a level suitable for driving a mass filter. This tuned transformer is called the High-Q Head. The Quadrupole Control unit is the central unit used for controlling and monitoring the operation of the quadrupole. It regulates the DC and RF voltages to desired values and allows the voltages to be swept over a chosen range. This unit also indicates the m/z number to which the filter is tuned and the balance of the DC and RF outputs. Resolution is varied by knobs marked "Resolution" and " ΔM ".

VACUUM SYSTEM

The first requirement for any mass spectrometer is a good vacuum system. This ensures that ions traveling through the instrument will not undergo any collisions with gas molecules that will cause the ions to be scattered, to lose energy, to change their

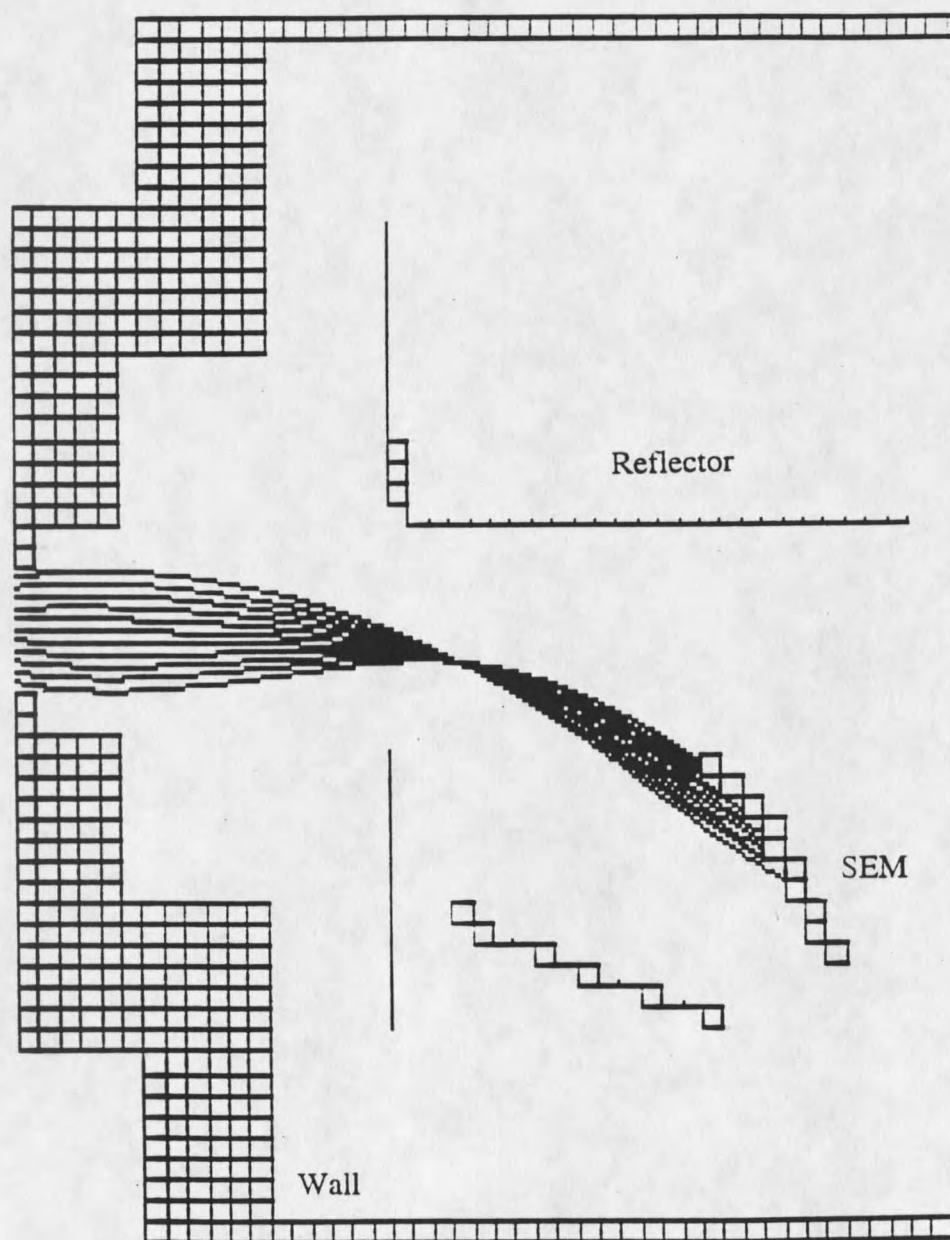


Figure 13. Ion trajectories exiting quadrupole simulated by Simion program.
Ion energy: 15 eV; reflector: 0 V; SEM: -2000 V; walls: 0V.

charge state or to fragment. To ensure this, the mean free path of the ions at the pressure within the vacuum system must be long compared with the path length.

The gas throughput Q of the ion transport capillary and the exit orifice can be calculated using the following equations:

for capillary:
$$Q = (\pi d^4 / 128 \eta L) P_{ave} \Delta P \quad (13)$$

where η : the viscosity of the gas

d : the inner diameter of the capillary

L : the length of the capillary

P_{ave} : the average of the pressures at the entrance and exit of the capillary

ΔP : the pressure drop across the capillary

for orifice:
$$Q = (2\pi RT / M_r)^{1/2} (d^2 / 8) \Delta p \quad (14)$$

where M_r : the molecular weight of the gas molecules

ΔP : the pressure difference between chambers

d : the diameter of the orifice

R : constant

T : the temperature

Equation 13 can be used to calculate the gas throughput through the ion transport capillary. The ion transport capillary used in this work had an i.d. of 0.4 mm and was ~8 cm long. The atmospheric pressure is about 640 torr in Bozeman and the ion source pressure was ~7.5 torr. Under this conditions, the gas throughput Q is calculated to be 12 torr L sec⁻¹.

Equation 10 can be used to calculate the gas throughput through the sampling orifice. For the 80 μm diameter exit orifice, gas throughput Q is calculated to be about 0.01 torr L sec⁻¹ at 300 K for nitrogen (and hence approximately for air). To handle the gas load resulting from gas outflow from the ion source, a 6 inch oil diffusion pump, providing a pumping speed of ~ 400 L/s, is used to pump the ion source manifold. With a gas throughput of 0.01 torr L sec⁻¹, the manifold pressure is calculated to be 2.5×10^{-5} torr. The quadrupole housing is differentially pumped by a 4 inch oil diffusion pump with pumping speed of ~ 100 L/s. A mechanical rough pump (Welch 1298) with pumping speed of 500 L/min is used to back up the diffusion pumps. The pump capacities and pressure distribution in each part of the system are shown in Table 1.

Table 1: Pump capacity and pressure distribution.

Section	Type	Pump Model	Capacity	Pressure
Spray Chamber	-----	Ambient Air	-----	640 torr
Ion Source	Rotary Pump	Welch 1298	500 L/min	7 torr
Ion Source Housing	Rotary Backing Pump	Welch 1297	500 L/min	2.5×10^{-5} torr
	6" Diffusion Pump	NRC Equipment Type 0162	400 L/s	
Mass Analyzer Housing	Rotary Backing Pump	Welch 1297	500 L/min	$< 5 \times 10^{-6}$ torr
	4" Diffusion Pump	NRC	100 L/s	

CHEMICALS

The chemicals used in this study were obtained from commercial suppliers and used with no further purification. HPLC grade methanol used as the solvent for the electrospray solutions.

MEASUREMENTS, RESULTS AND DISCUSSION

OPERATING PARAMETERS

Electrospray versus Corona Discharge

As mentioned in the instrumentation part, two different electrospray needle designs were used. The single fused silica capillary, 50 μm i.d. and 146 μm o.d., had a gold coated outer surface for electric conductivity. Producing electrospray spectra without a concurrent corona discharge proved to be a problem with this design.

The second electrospray needle design used a stainless steel capillary, 0.11 mm i.d. and 0.24 mm o.d., as the spray needle. In both cases, the needle tip was about 0.5 cm away from the entrance tip of the ion transport capillary.

Mass spectra were obtained with both needle designs under corona discharge conditions, with no solutions supplied to the needle and no reaction gas added to the reaction chamber. These corona spectra were dominated by $\text{H}^+(\text{H}_2\text{O})_n$ clusters, where $n=2$ to 5, and $\text{H}^+(\text{H}_2\text{O})_4$ ($m/z=73$) was the highest intensity peak. The voltage required to produce a corona discharge was studied by gradually increasing the voltage applied to the spray needle while other parameters were kept the same. The quadrupole mass filter was tuned at $m/z=73$ for the highest signal intensity. The ion signal intensity as well as the electrospray current were measured as a function of the voltage applied to the needle.

Figure 14 shows the corona discharge was initiated when the voltage applied to the spray needle was higher than 2.5 kV. The corona current was over 11 μA at 2.5 kV. The current increased with the voltage but the ion signal intensity changed little.

The voltage required for electrospray was also studied. A potassium acetate solution, 10^{-3} M in pure methanol, was pumped by the syringe pump at speed of 10 $\mu\text{L}/\text{min}$. Other conditions were the same as for the corona discharge study above. The mass spectrum was dominated by the K^+ peak, of $m/z=39$, but no $\text{K}^+(\text{H}_2\text{O})_n$ clusters were observed. Figure 15 shows the ion signal intensity and the electrospray current as a function of the voltage applied to the spray needle.

The highest electrospray ion signal was obtained when the electrospray current was in the range of 0.15 to 0.25 μA . A higher voltage gave a higher ion current, but the mass spectrum changed completely. The K^+ peak disappeared, and the mass spectrum was nearly identical to the spectrum obtained in corona discharge mode, with $\text{H}^+(\text{H}_2\text{O})_n$ clusters dominating the spectrum. It was concluded that at higher voltage, a corona discharge was running concurrently with the electrospray. It was generally found that ion signals produced by corona discharge ionization were more stable than the ion signals generated by electrospray ionization. The signal intensities of the corona discharge were also found to be higher than the signal of electrospray.

In practice, electrospray without corona discharge was achieved by carefully adjusting the voltage applied to the spray needle so that the electrospray current was in the range of 0.15 to 0.25 μA . Normally, the electrospray ion signal had good intensity, up to thousand counts per second. However, the signal could be lost suddenly. Sometimes

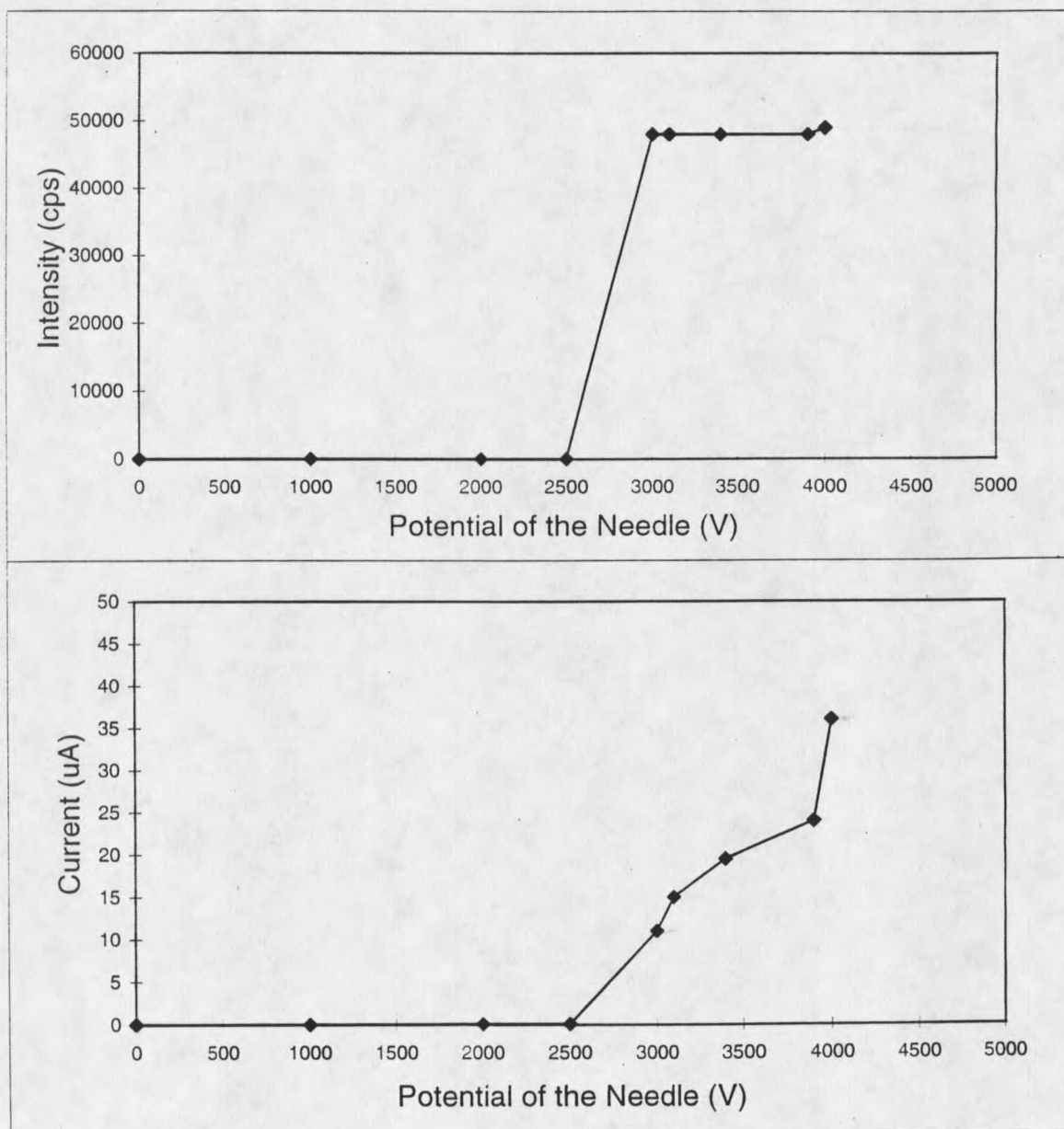


Figure 14. Signal intensity at $m/z=73$ and ES current as a function of the potential on the needle in corona discharge ionization.

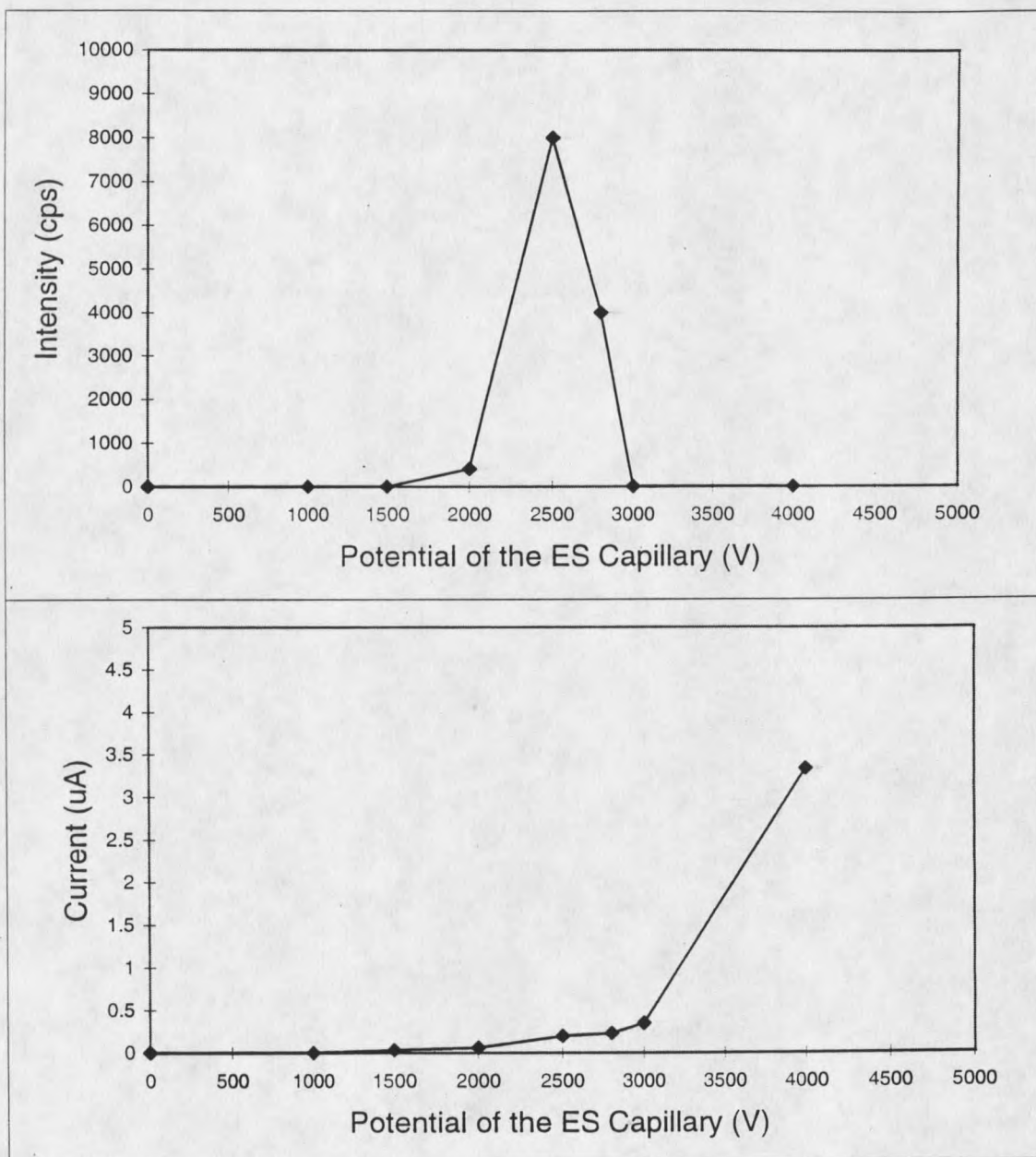


Figure 15. Signal intensity at $m/z=39$ and ES current as a function of the potential on ES needle in ES ionization.

this occurred when the syringe was reloaded with new spray solution with all conditions remaining the same. Instead, intense ion signals due to corona ionization appeared. At the same time, the electrospray current jumped to a much higher value. After such an "event", the mass spectrum showed that the signal of K^+ had totally disappeared and was replaced by $H^+(H_2O)_n$ clusters. This happened for no apparent reason. One is had happened, the corona discharge was initiated before the electrospray as the needle voltage was increased and it was very difficult to return to electrospray mode.

Because the voltage required to initiate a corona discharge was very close to that required for electrospray with the gold coated silica electrospray capillary tip, a means to add SF_6 gas was incorporated into the second electrospray device. It was observed that the pressure of the ion source decreased when SF_6 gas was added presumably due to a high concentration of SF_6 . The electrospray signals were found to be more stable when SF_6 was added. Unfortunately, the difficulty of obtaining electrospray without a corona discharge persisted.

The high-pressure ion source was designed to study ion-neutral associations. With water present in the ion source, the mass spectra obtained should show abundant $M^+(H_2O)_n$ clusters, like the $H^+(H_2O)_n$ clusters observed in corona discharge mode. The water would originate from the ambient air when ions were generated at one atmosphere. In most of the electrospray spectra, $M^+(H_2O)_n$ clusters were indeed present in the mass spectra. Occasionally, bare analyte ions were observed with no water cluster ions when running in electrospray mode. The reason for this is not known. When switching to

corona discharge mode, the mass spectra still were dominated by $H^+(H_2O)_n$ clusters as usual.

Because corona discharge ionization gave more intense ion signals that were also more stable than electrospray signal, corona discharge ionization was used for the following study of operating parameters. The quadrupole mass filter was tuned to $m/z=73$ to detect $H^+(H_2O)_4$. Only one parameter was varied for each part of the study.

Ion Transport Capillary

As shown in Figure 16, the influence on the ion signal intensities of the potential applied to the ion transport capillary was very small.

Ion Source

There are two chambers inside the electrospray ion source: pre-reaction chamber and reaction chamber. The body of the ion source, and the exit orifice, was kept at a potential of +10 volts. Two electrodes were used inside the ion source to ensure that ions drifted towards the exit orifice: the deflector in pre-reaction chamber and the interface plate between the two chambers. The ion signal intensity at $m/z=73$, as a function of the potentials on the deflector and on the interface plate, are plotted in Figure 17 and 18, respectively.

In practice, the voltage on the deflector plate was adjusted so that maximum ion signal intensity was achieved. However, in the reaction chamber, where ion-molecule reactions occur, the internal energy of ions could be increased by increasing the applied

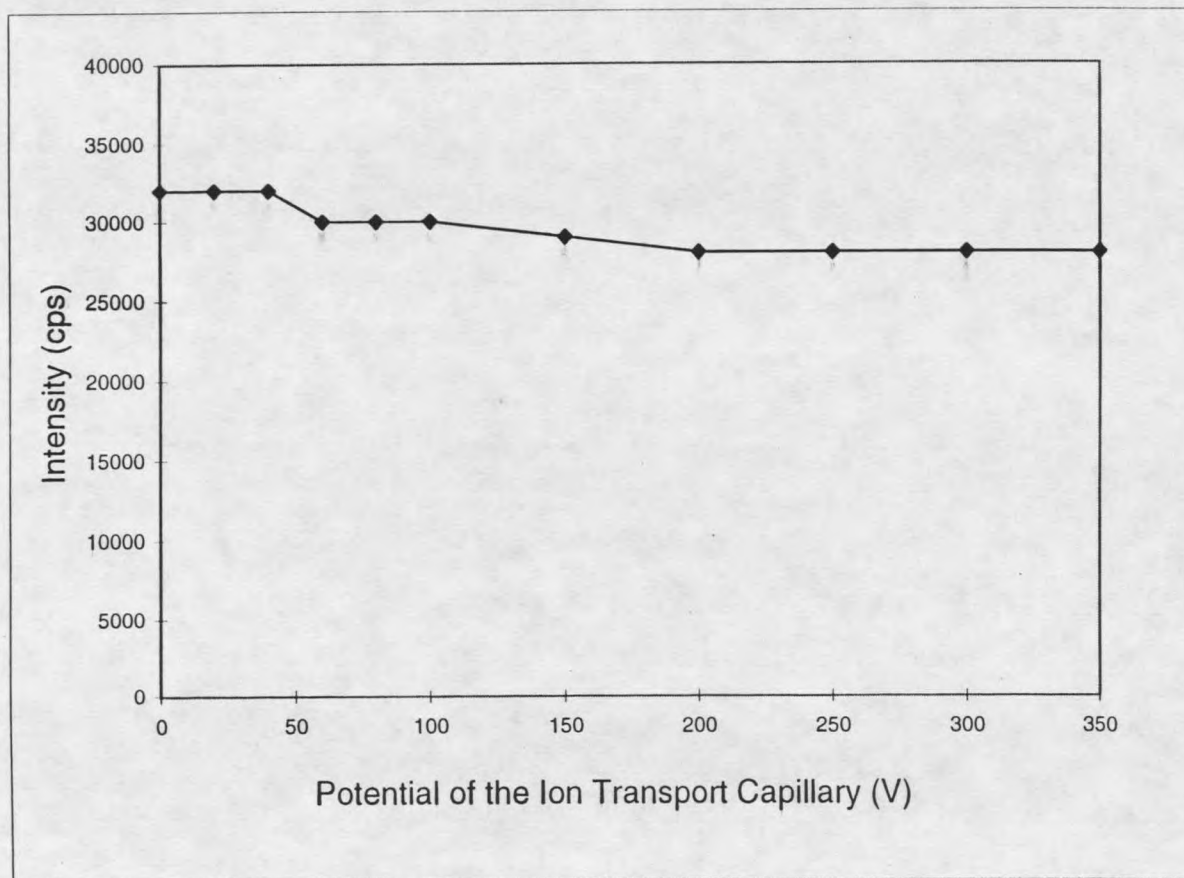


Figure 16. Signal intensity at $m/z=73$ as a function of the potential on the ion transport capillary.

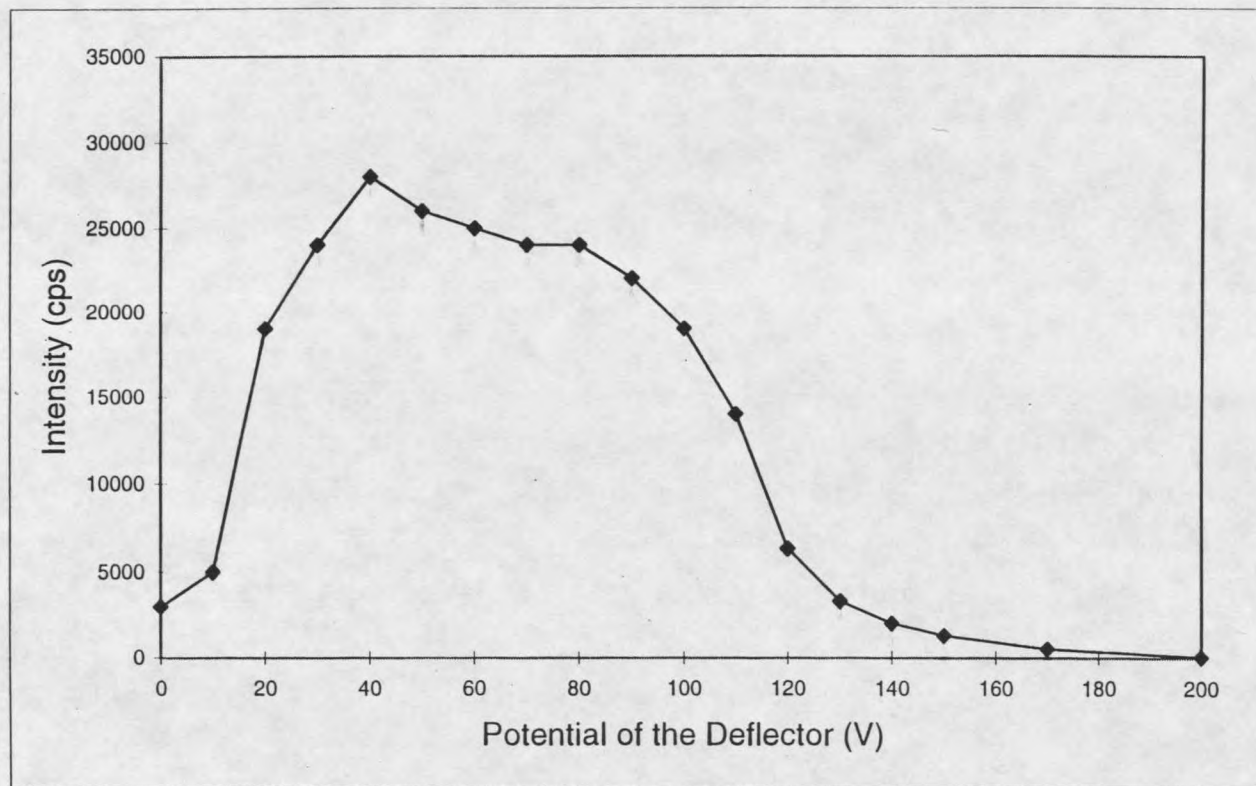


Figure 17. Signal intensity at $m/z=73$ as a function of the potential on the deflector.

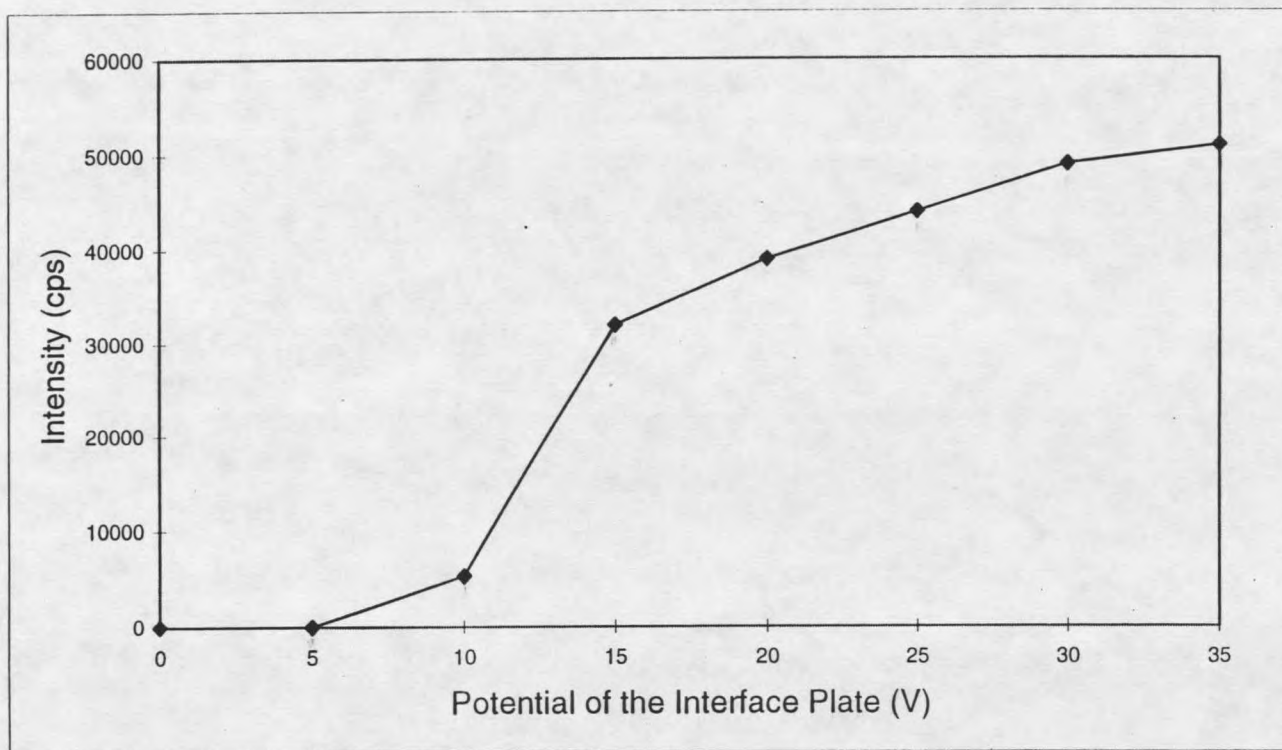


Figure 18. Signal intensity at $m/z=73$ as a function of the potential on the interface plate in corona discharge ionization.

electric field. This additional internal energy must be negligible in order to measure ion-molecule equilibrium constant. Therefore, the voltage applied to the interface plate should be low, but high enough that good signal intensity could still be obtained. In practice, +20 volts was applied to the interface plate against the +10 volts of the exit orifice. Since the distance between the interface plate and the exit orifice was 5 mm, the E/p value equaled $2.7 \text{ V}(\text{cmTorr})^{-1}$ when the source pressure was 7.5 torr. According to a study by Keesee and Castleman [19], ions drifting in an electric field are essentially in thermal equilibrium with the surroundings when the value of E/p is smaller than $15 \text{ V}(\text{cmTorr})^{-1}$.

The gas composition in the pre-reaction chamber and in the reaction chamber is usually different. The major gas flow into the pre-reaction chamber was through the ion transport capillary, and the gas composition is expected to be close to that in the ambient air electrospray chamber. The major gas flow into the reaction chamber was the reagent gas from the gas handling plant. The composition of the gas in the reaction chamber should, therefore, be very different from that in the pre-reaction chamber. Any neutrals diffusing through the 4 mm orifice connecting the two chambers would affect the composition of the reaction chamber gas. It was found that the pressure of the ion source increased by about 0.5 torr as the reagent gas started to flow. The chance of neutrals diffusing into the reaction chamber from the pre-reaction chamber should be minimized under such conditions.

Ion Optics

A detailed drawing of the ion optics was shown in Figure 11 in the Instrumentation section. With the mass spectrometer detecting ions from the high pressure ion source, most of the electrodes were grounded. Potentials on lens # 2 and #3 were adjusted for maximum signal intensity. Table 2 lists the potential applied to each lenses.

Table 2: Potential distribution of ion optics lenses.

Lenses	Potential (DC volt)
Cone	0 V
Extractor	0 V
Lens #1	0 V
Lens #2	0 V
Lens # 3	-14 V

It would be helpful to simulate the ion trajectories under the potentials applied to each electrode using the SIMION program [43]. Unfortunately, the exact dimension of the ion optics had not been provided by the manufacturer (Extranuclear Laboratories, Inc.). Rewiring the lenses so that varying potentials could be applied to each lens might provide better focusing and an increased ion transmission for ions entering the quadrupole.

Quadrupole Mass Filter

The maximum mass range of the quadrupole mass filter with the available High-Q Head was from about $m/z=25$ to near $m/z=250$. For most spectra recorded, we used a

mass range from $m/z=25$ to $m/z=220$ and the slowest scan speed possible. This required about 2 minutes for a scan of the whole mass range.

The quadrupole mass filter can be manually tuned. A LED display shows the voltage being sent from the HP oscilloscope to the quadrupole power supply. Figure 19 shows the relationship between the m/z values of transmitted ion and the displayed readings. The values was obtained by manually tuned the mass filter to each peak of the $H^+(H_2O)_n$ clusters obtained by mass spectrometer. The plot shows excellent linearity with the correlation coefficient $R = 1$. The displayed reading can be converted to real m/z value by the attached equation in Figure 19.

In the quadrupole mass filter scanning mode, the mass scan is triggered by a TTL pulse from the HP oscilloscope. In this mode, the mass spectra are collected by a multichannel scaler computer program (MCS). The x scale of the spectrum is time after sweep trigger and this is converted to m/z by the calibration function of the MCS program. The spectrum used for mass calibration will be described in the later. The sweep was triggered manually because the scanning voltage for the quadrupole mass filter, 0 to 120 volts, could not easily be used as a trigger signal to start the MCS program. Therefore, only a single slow scan was performed over the whole mass range. For the future, it would be advantageous to synchronize the scans of the quadrupole and the MCS program.

Quadrupole mass filters are known to have a mass dependent discrimination, which depends on the "high mass" and " ΔM " settings. Since ion-molecule equilibrium studies require the accurate determination of intensity ratios of ions with different mass, it is

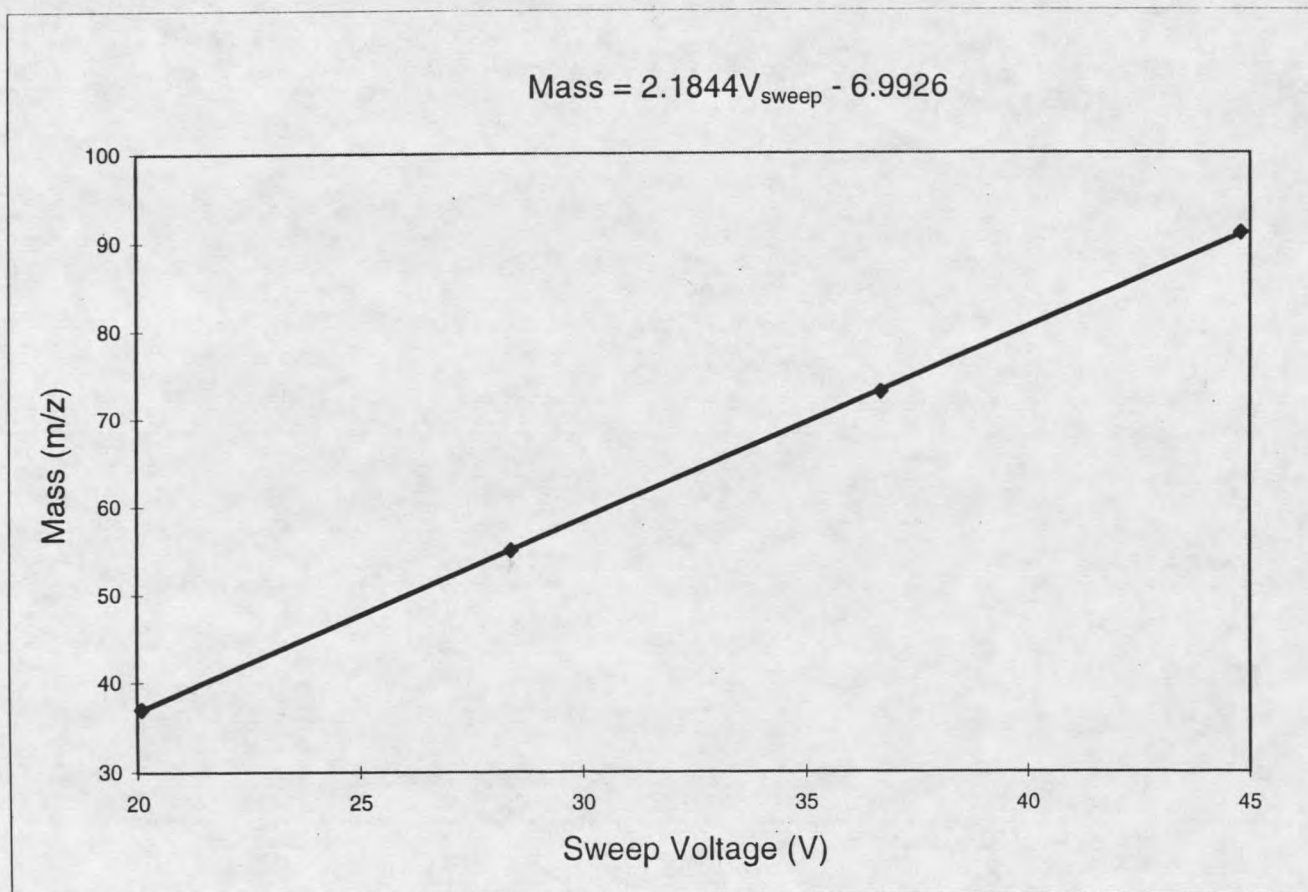


Figure 19. Relationship between m/z and sweep control voltage

necessary to correct for the mass dependent discrimination so that the corrected ratios are equal to the ratios of fluxes of ions exiting the ion source. No discrimination calibration has been performed for this quadrupole mass filter after it was put into operation in Bozeman. In most of this work, only ions with m/z values lower than 120 were measured. In many cases, two ion signals with a mass difference of 18 were compared. In such cases, the discrimination effects should not be serious.

Flow Rate of the Reaction Gas

It is critical to know accurately the partial pressure of the components of the gas phase in the reaction chamber in order to measure ion-molecule equilibrium constants. It is expected that the ratio of the partial pressures of gas phase components in the reaction chamber should be the same as that in the mixing bulb. The gas entering the pre-reaction chamber through the ion transport capillary is essentially room air. For example, water vapor will enter into the pre-reaction chamber. The reagent gas added to the reaction chamber serves a purge function and should prevent neutral molecule like water from entering into the reaction chamber from the pre-reaction chamber. The pressure of the ion source was about 7.2 torr when air entered the source through the ion transport capillary but no reagent gas was supplied. After starting the reagent gas flow, the ion source pressure would increase to a value that depended on the flow rate of the reagent gas. The gas mixture in the 5 liter bulb flowed through valve 1, valve 7, a flow meter with a valve, and a needle valve to the reaction chamber. Valve 1, 7 and the valve on the

flow meter were fully opened. The reagent gas flow rate was measured by the flow meter and controlled by the needle valve.

In this study, the pressure inside the 5 liter bulb was about 640 torr. The gas mixture contained a certain amount of water. The needle valve was carefully adjusted in order to control the flow rate as measured by the flow meter. All other parameters affecting the ion signal intensities were initially adjusted for maximum ion signal and then kept constant. The gas pressure in the flow meter should be close to 640 torr because the needle valve was positioned between the flow meter and the ion source. A flow rate of 5 ml/min at 640 torr equals about 414 ml/min, or 7 ml/s at an ion source pressure of 7.7 torr. This reagent gas flow rate was observed to increase the pressure of the ion source by 0.5 torr. Considering that the volume of the reaction chamber is less than 4 cm³, it was estimated that this flow was adequate enough to prevent neutral molecules in the pre-reaction chamber to diffuse into the reaction chamber. The most intense ion signals were obtained when the flow rate was in the range of 2 to 5 ml/min. A flow rate higher than 7 ml/min resulted in the complete loss of ion signal. This critical flow rate was much smaller than the 85 ml/min at STP reported by Kebarle's group [17] with a similar ion source design.

ION-MOLECULE ASSOCIATION EQUILIBRIA DETERMINATIONS

The equilibria studied can be described by the general reaction



where L is the ligand or ion solvating agent. The equilibrium constant can be obtained from

$$K_{n-1,n} = \frac{[M^{z+}L_n]}{[M^{z+}L_{n-1}][L]} \approx \frac{I_n}{I_{n-1} \times P_L} \quad (16)$$

where I_n and I_{n-1} are the ion abundance determined with the mass spectrometer under equilibrium conditions, and P_L is the known pressure of vapor L in the reaction chamber.

The temperature of the ion source was measured by thermocouples attached to the bottom of the ion source, near the exit orifice. There was no heating of the ion source. The temperature of the source usually remained at about 28 °C, or 301 K, and this was used as the temperature, if not otherwise indicated, in equilibrium constant calculations.

Corona Discharge Ionization

A typical mass spectrum obtained in corona discharge ionization mode in ambient air (i.e. no electrospray solution was supplied to the needle), is shown in Figure 20. The mass spectrum consists of the ion series $H^+(H_2O)_n$ ($n=2$ to 5) with the highest intensity signal at $m/z=73$. The intensity of this signal was usually higher than 10,000 counts per second. The $H^+(H_2O)_n$ clusters are known to form in ambient air with $n \sim 3-10$ [44] because of the high water partial pressure in air. The spectra obtained by corona discharge ionization like Figure 20 were very stable and corona discharge ionization was used daily to check the condition of the instrument.

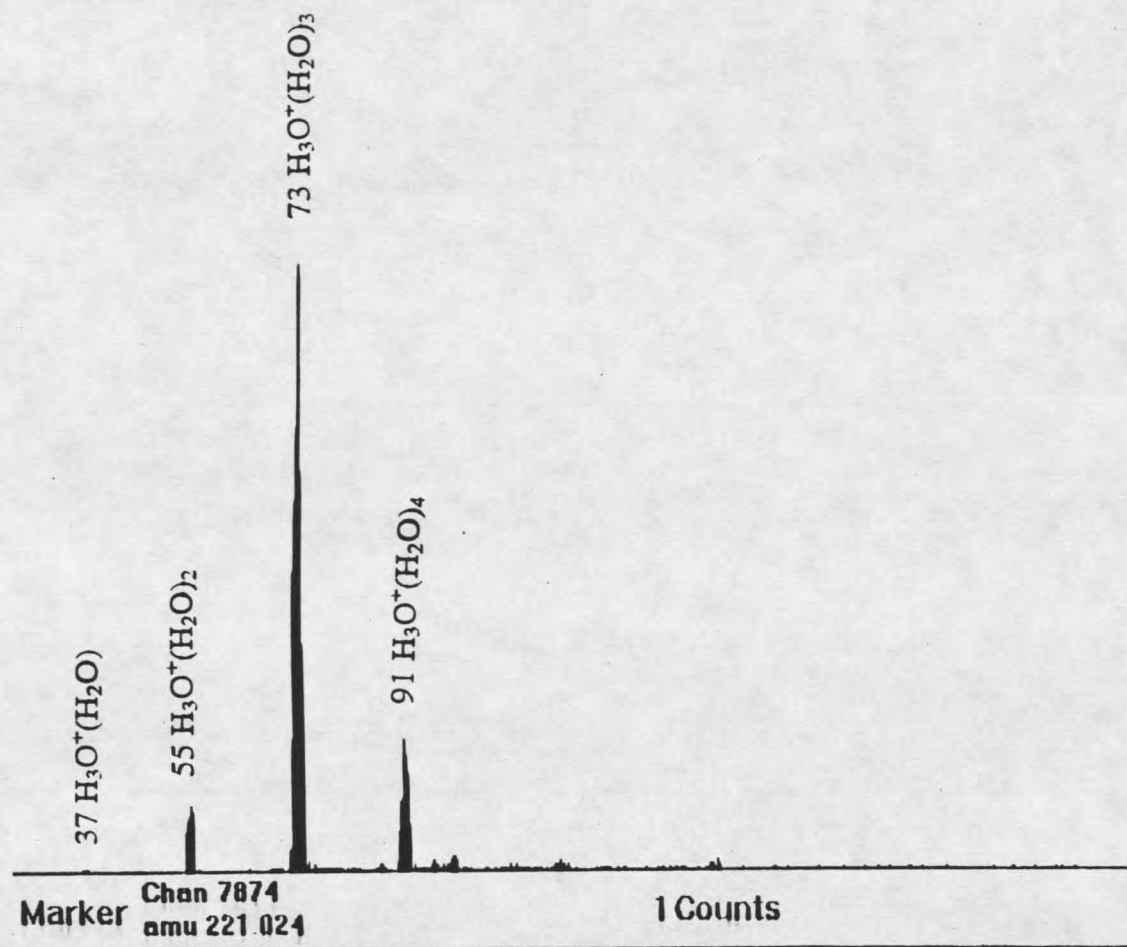


Figure 20. Mass spectrum obtained by corona discharge ionization in ambient air.

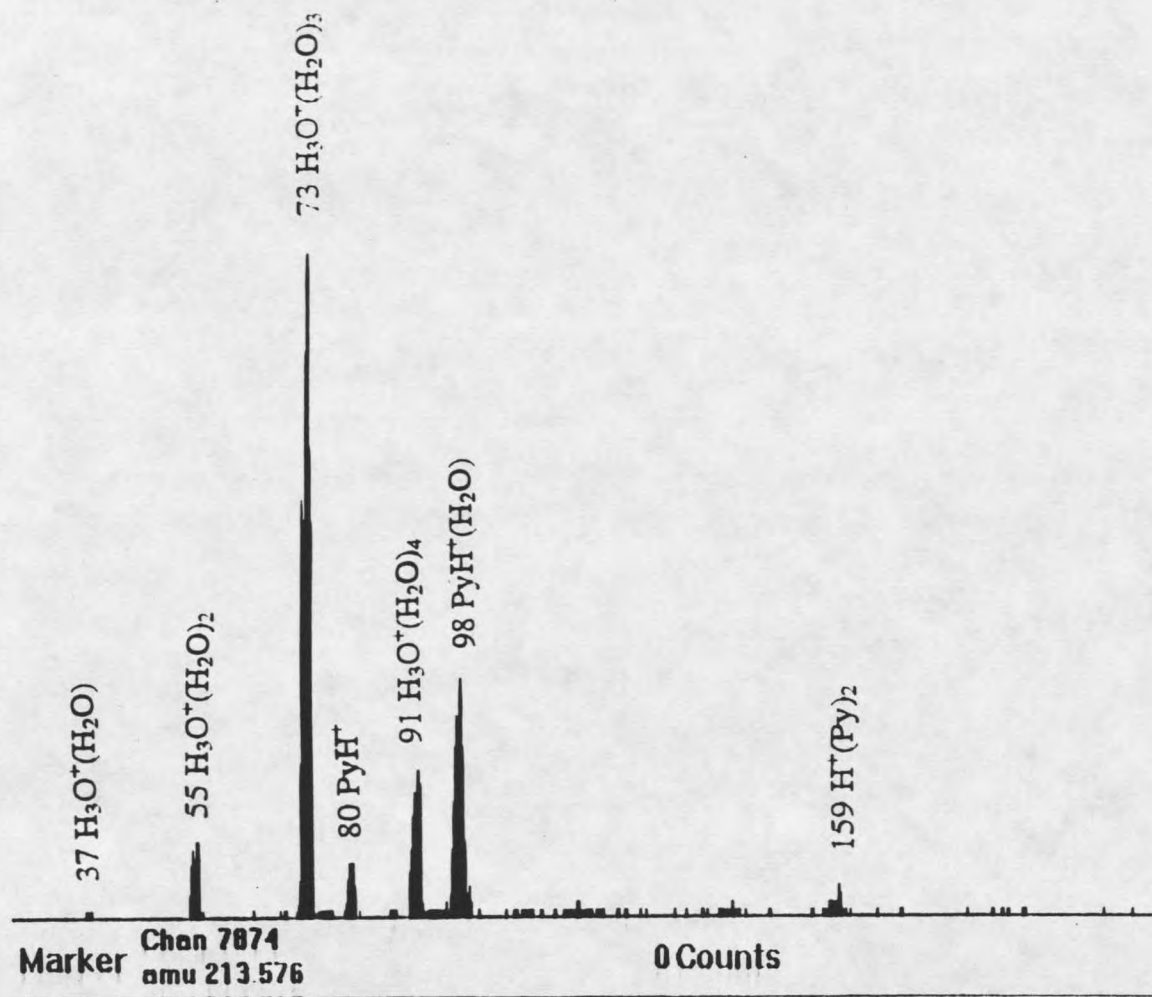


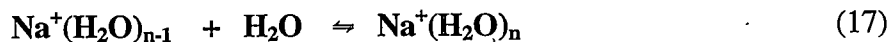
Figure 21. Mass spectrum obtained by corona discharge ionization in ambient air with added pyridine vapor.

If equilibrium was established in the ion source when it contained only room air (i.e. no added reagent gas), the intensity ratio of $\text{H}^+(\text{H}_2\text{O})_5 / \text{H}^+(\text{H}_2\text{O})_4$ could be used to calculate the water content in the room air by using published free energy data [5, 45, 46]. It was concluded that there are about 0.10 torr water in the ion source, which equals to 8.5 torr or 1.3% water in the room air.

During corona discharge conditions, pyridine vapor was being introduced into the air around the needle. It was observed that the spectrum with $\text{H}^+(\text{H}_2\text{O})_n$ clusters quickly changed and become dominated by protonated pyridine water clusters. Protonated pyridine dimer was also present. The intensities of protonated pyridine water clusters gradually decreased as the pyridine vapor diffused away or was removed through the ion transport capillary. A spectrum consisting of both protonated pyridine water clusters and $\text{H}^+(\text{H}_2\text{O})_n$ clusters with the expected intensities is shown in Figure 21. Two peaks, usually $\text{H}^+(\text{H}_2\text{O})_2$ and the protonated pyridine dimer, with m/z equal to 37 and 159, respectively, were used to calibrate the mass scale of the quadrupole.

$\text{Na}^+(\text{H}_2\text{O})_n$ Clusters

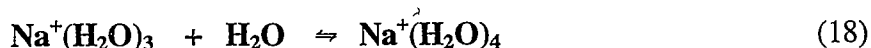
Experiments were made to conform the equilibrium constant published in the literature for the clustering reaction



The sodium ions were generated by electrospray and the electrospray solution contained 10^{-5} M sodium acetate. The reagent gas was prepared in the 5 liter bulb by adding a measured volume of water to 643 torr high purity nitrogen gas. The mixture

was allowed to equilibrate and supplied to the reaction chamber at a rate of 5 ml/min at about 640 torr. The ion source pressure increased from 9.3 torr to 10 torr after adding the reagent gas flow. As before, the temperature of the ion source was near room temperature, at 28 °C. Spectra of $\text{Na}^+(\text{H}_2\text{O})_n$ clusters were obtained at several different water partial pressures.

According to Equation 16, a plot of I_n / I_{n-1} versus P_L should result in a straight line with slope equal to $K_{n-1,n}$. Shown in Figure 22 is the plot of the ion intensity ratio for the equilibrium



versus the water partial pressure in the reaction gas at a constant total ion source pressure of 10 torr. However, the plot does not show a very good linearity, especially at high water pressure. The $\text{Na}^+(\text{H}_2\text{O})_n$ ion intensities are plotted versus the water partial pressure and the results is shown in Figure 23. The total ion intensity was not well preserved.

The equilibrium constant values were calculated by Equation 16 and are shown in Figure 24 as a function of water partial pressure. The plot shows that the measured equilibrium constant decreased with increasing water partial pressure. There are two possible explanations. It is well known that cluster dissociation will occur in the jet expansion as the gas at 10 torr passes through the 80 μm orifice into the vacuum.



Because of this process, Kebarle has recommended [6] that cluster equilibria only be measured when the abundance of the large cluster is significantly smaller than the

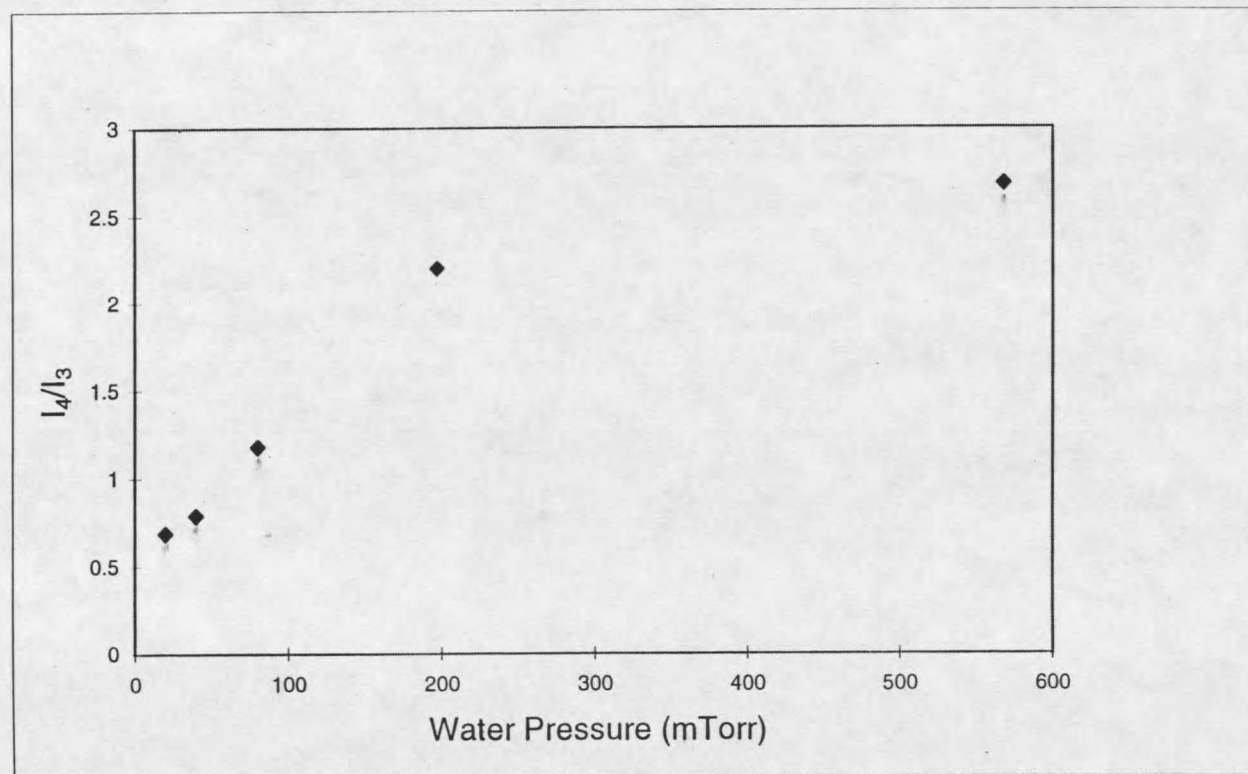


Figure 22. Abundance ratio of $\text{Na}^+(\text{H}_2\text{O})_4$ to $\text{Na}^+(\text{H}_2\text{O})_3$ versus water partial pressure in the reaction chamber.

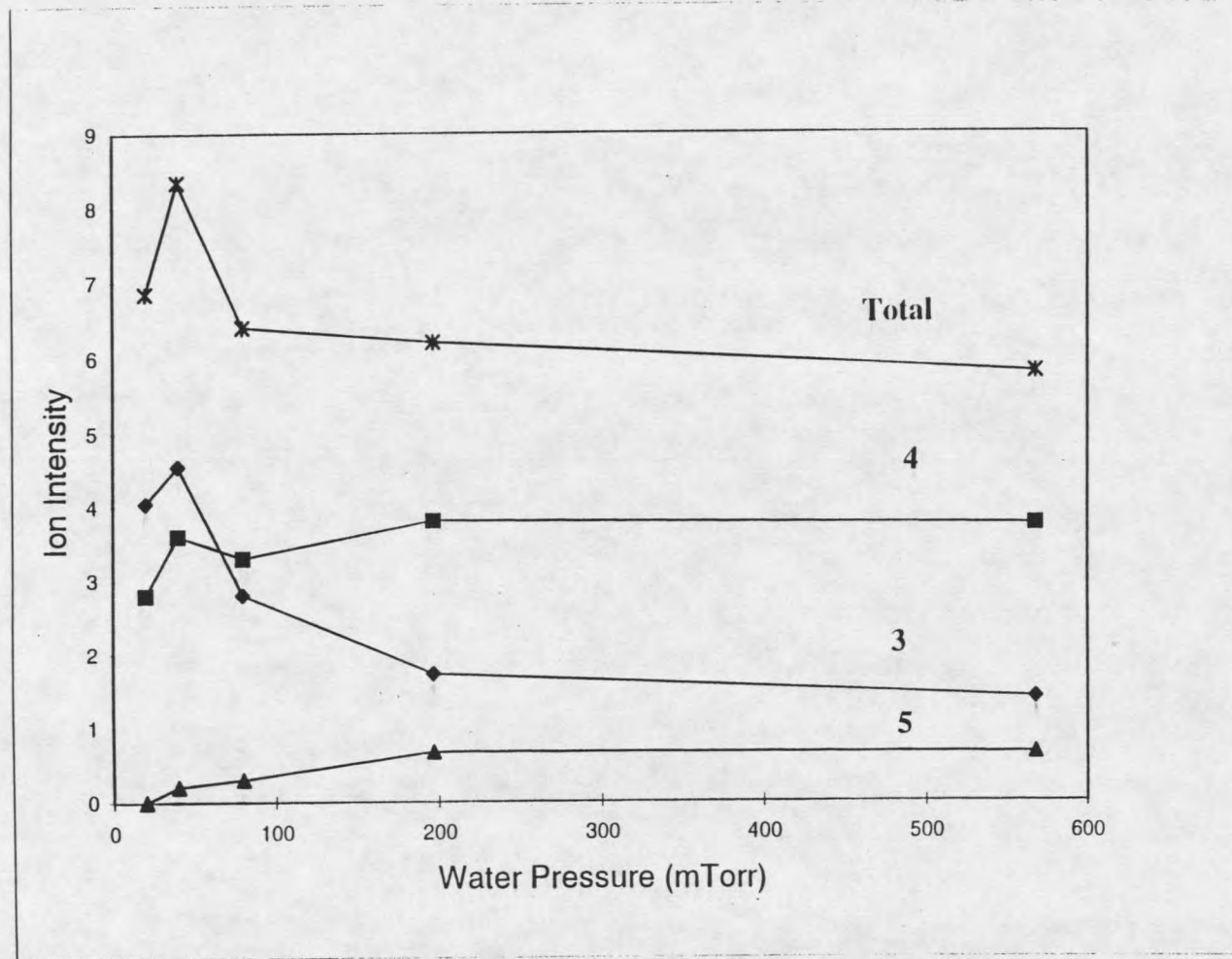


Figure 23. Dependence of the abundance of $\text{Na}^+(\text{H}_2\text{O})_n$ clusters on water partial pressure in the reaction chamber.

abundance of the smaller cluster. An alternative explanation for the trend in Figure 24 could involve the use of a flow meter and needle valve on the reagent supply line. Originally, these two units were located outside the heating plant and operated at room temperature. Water vapor in the very hot reagent gas (110 °C) may well condense in these two sites, especially when the water content was high. This should cause water partial pressure in the reaction chamber to be smaller than expected. The other problem seen in Figure 21 is that the I_4/I_3 abundance ratio does not extrapolate to zero at zero water partial pressure, as expected. This shows that a residual water pressure of about 50 mTorr existed in the reaction chamber. The reason for this may well have been leakage in the needle valve. However, we do not know why the measured equilibrium constant is wrong. It was found that the calculated equilibrium constant was lower than the literature value [47] by a factor of about 5.

The $\text{Na}^+(\text{H}_2\text{O})_n$ cluster equilibrium measurement described above was the first study made with the new electrospray ion source. The spray needle used for these measurements was the gold coated silica capillary. The signal intensities were fairly low, only a few thousand counts per second for the strongest signal. The signal of the electrosprayed ions was lost after the initial measurements and could not be obtained again. The most likely reason was interference by a corona discharge because the mass spectra obtained were dominated by $\text{H}^+(\text{H}_2\text{O})_n$ clusters. In efforts to restore electrospray conditions, several new silica capillaries were gold coated and installed. However, the results were the same: no electrospray ions were observed. Under the microscope, most of the capillaries used were shown to have tips with sharp irregular edges. Because of the

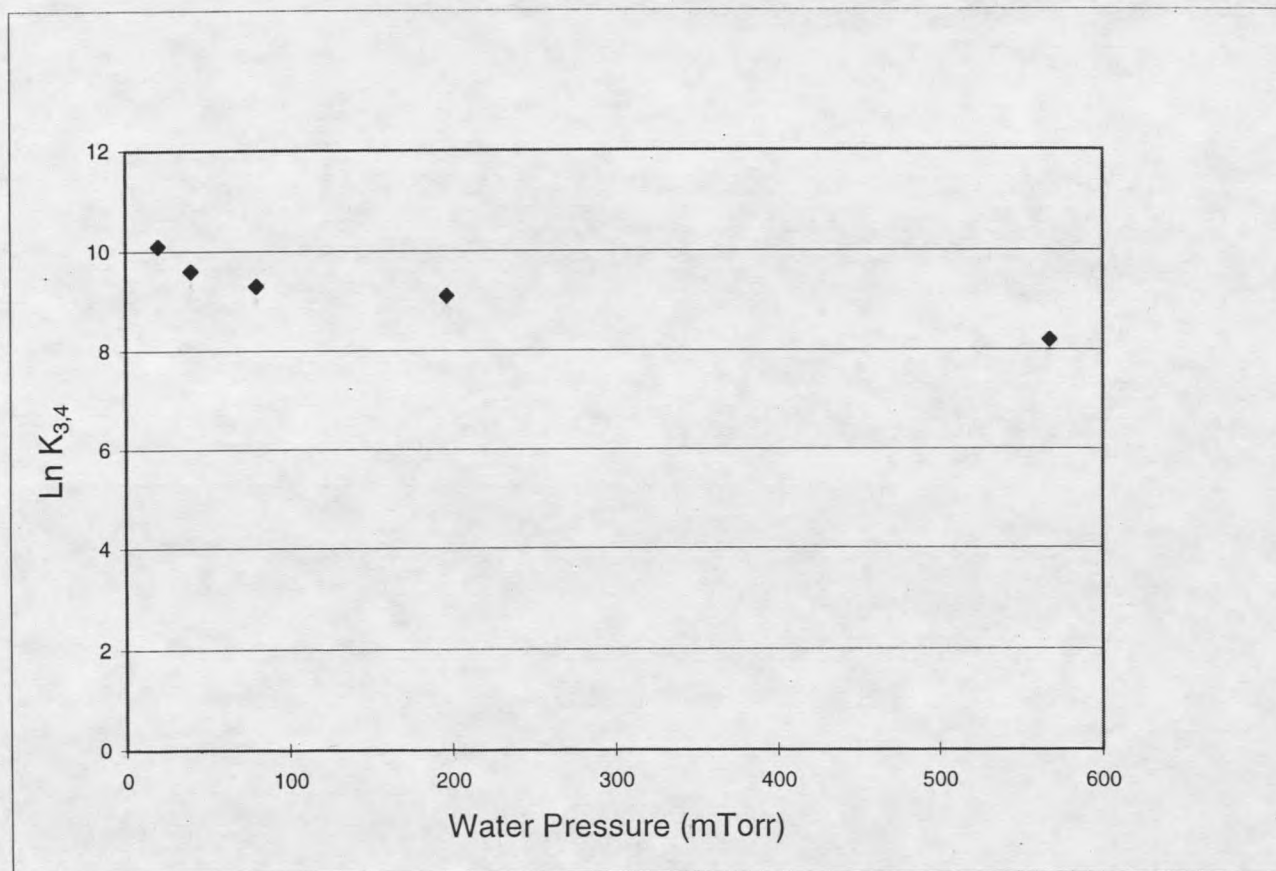


Figure 24. $\text{Ln}(K_{3,4})$ versus water partial pressure in the reaction chamber.

difficulty to remove these sharp edges with regular tools, the electrospray needle was replaced by the second design, as described in the Instrument section. The end of the stainless steel capillary was cut nearly perfect at delivery.

Protonated Pyridine Water Clusters

Mass spectra of pyridine were easily obtained in corona discharge ionization and used for mass calibration purpose. However, it proved to be much more difficult to obtain spectra of pyridine from electrospray ionization.

In order to generate protonated pyridine in the gas phase by electrospray, pyridine must exist in protonated form in the spray solution. Pyridine is a weak base ($pK_b=8.771$). In pure methanol solvent, only a small fraction of the pyridine will exist in protonated form. Acid has to be added to increase the amount of protonated pyridine in the spray solution. Since pH papers and pH electrodes are designated to be used in water solutions, the acidity of the methanol solution could not be easily measured. Instead, an equimolar amount of acid was used. The spray solution used contained 10^{-3} M pyridine and 10^{-3} M acetic acid.

The mass spectrum of pyridine obtained in corona discharge ionization (Figure 20) clearly shows peaks due to $C_5H_5NH^+$, $C_5H_5NH^+(H_2O)$ and $H^+(C_5H_5N)_2$ with $m/z=80$, 98 and 159, respectively. No $C_5H_5NH^+(H_2O)_2$ peak at $m/z=116$ was observed even though $C_5H_5NH^+(H_2O)$ dominated the spectrum. In electrospray ionization mode, the mass spectrum from the pyridine solution was not the same as that obtained in corona discharge ionization. Figure 25 shows the pyridine spectrum obtained by electrospray

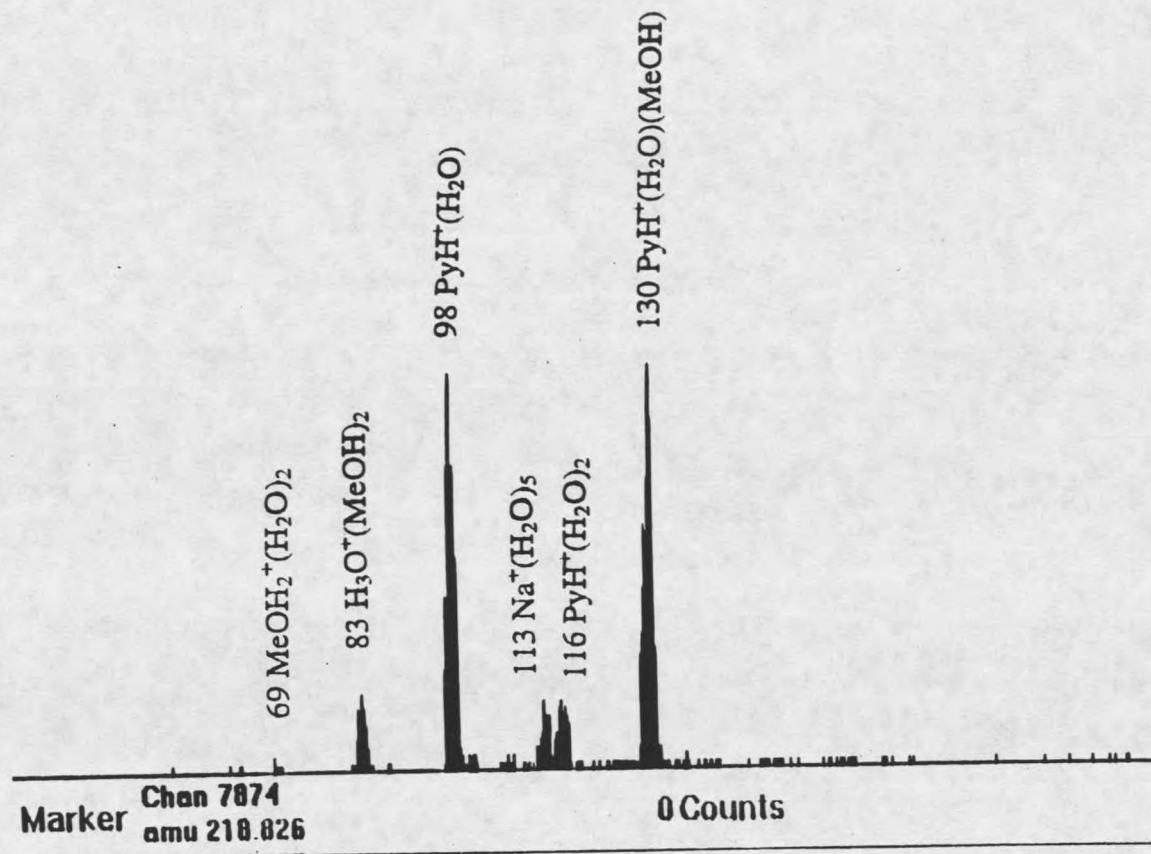


Figure 25. Mass spectrum of protonated pyridine obtained by electrospray ionization with no reagent gas added to the reaction chamber.

with no reagent gas added to the reaction chamber. No peak of protonated pyridine dimer at $m/z=159$ is observed in Figure 25. This is easily understood as a result of the low concentration of pyridine in the spray solution. Second, the $C_5H_5NH^+$ peak at $m/z=80$ did not show up in most of the experiments but there was a small peak at $m/z=116$ for $C_5H_5NH^+(H_2O)_2$. The strong peak at $m/z=98$ for $C_5H_5NH^+(H_2O)$ was a sign that the ions were generated by electrospray. Sometimes a strong peak at $m/z=130$ for $C_5H_5NH^+(H_2O)(MeOH)$ also appeared. The methanol came from the electrospray solvent. In addition to protonated pyridine, protonated methanol also formed during the electrospray as shown by the presence of peaks at $m/z=69$ for $(MeOH)H^+(H_2O)_2$ and at $m/z=83$ for $(MeOH)_2H^+(H_2O)$. These fairly intense peaks were always observed when pyridine solution was electrosprayed.

The mass spectrum in Figure 26 was obtained under the same conditions used for the spectrum in Figure 25 but pure nitrogen was added to the reaction chamber. The disappearance of $C_5H_5NH^+(H_2O)(MeOH)$ at $m/z=130$ and $C_5H_5NH^+(H_2O)_2$ at $m/z=116$ clearly shows the declustering of methanol and water in the reaction chamber due to the purge function of the reagent gas. The intensity of the $C_5H_5NH^+(H_2O)$ peak at $m/z=98$ increased. However, still no $C_5H_5NH^+$ peak was observed at $m/z=80$.

The objective of the work with pyridine was to measure the equilibrium constant $K_{0,1}$ for the clustering reaction



Unfortunately, the signal of $C_5H_5NH^+$ at $m/z=80$ was usually absent in the electrospray spectra. Occasionally, the $C_5H_5NH^+$ ion was observed. What caused this

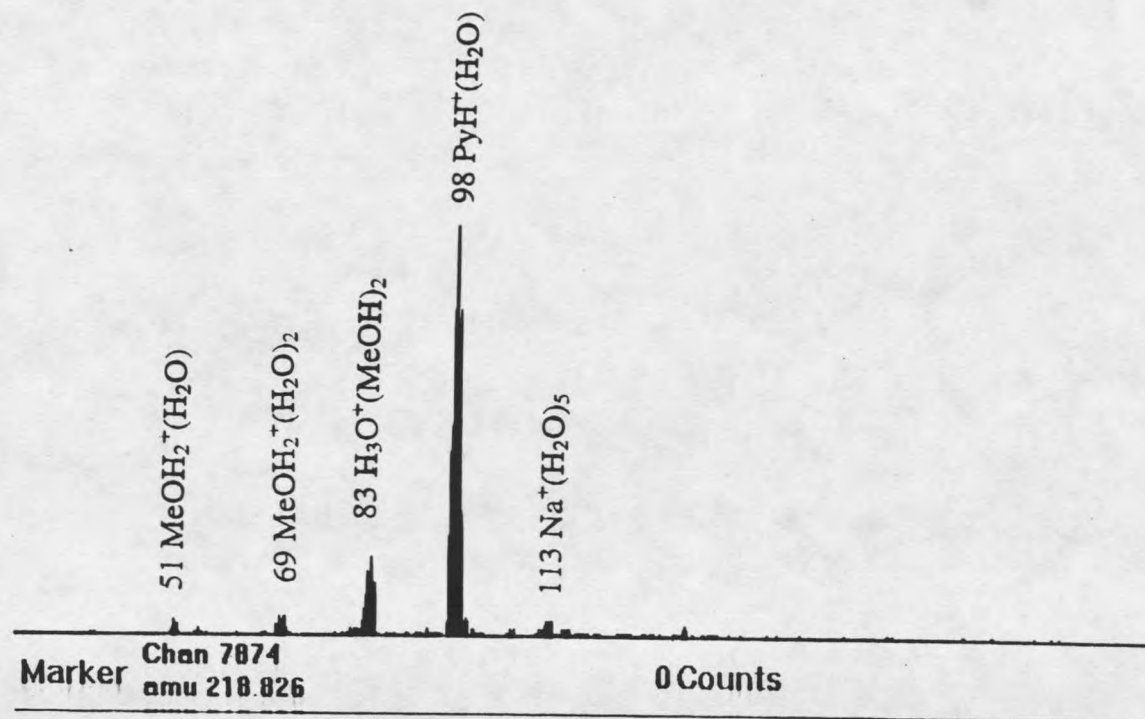


Figure 26. Mass spectrum of protonated pyridine obtained by electrospray ionization with pure nitrogen gas added to the reaction chamber.

variation is not clear. Water was then added to the reaction chamber in order to measure the protonated pyridine water equilibrium constant $K_{0,1}$. The water partial pressure in the reaction chamber was 12 mTorr, the total pressure was 7.6 torr and temperature of the ion source was 25 °C. Peaks due to $C_5H_5NH^+$ and $C_5H_5NH^+(H_2O)$ at $m/z=80$ and $m/z=98$ were observed but no peak due to $C_5H_5NH^+(H_2O)_2$ at $m/z=116$. The measured values of $-\Delta G^{\circ}_{0,1}$ were 7.3, 7.5, and 7.5 kcal/mol in three experiments over a period of about 12 minutes. Previously, equilibrium measurement of protonated pyridine by PHPMS [48] has provided values of $\Delta H^{\circ}_{0,1}$ and $\Delta S^{\circ}_{0,1}$. Using the equation $\Delta G^{\circ}_{0,1} = \Delta H^{\circ}_{0,1} - T \Delta S^{\circ}_{0,1}$, a value of 7.4 kcal/mol is obtained for $-\Delta G^{\circ}_{0,1}$ at 25 °C. It is seen that the agreement with the data obtained here is nearly perfect. This supports that equilibria are indeed obtained and observed in the new design of the electrospray high pressure ion source. Unfortunately, these equilibrium measurements were not performed at varying water pressure. Instead, experiments with new ion-molecule reaction systems were carried out.

$K^+(H_2O)_n$ Clusters

Experiments were performed to measure equilibrium constants for the clustering reaction



The electrospray solution contained 10^{-3} M potassium acetate in methanol with no acid added. Mass spectra obtained by electrospraying the K^+ solution and with no reagent gas added showed a sequence of $K^+(H_2O)_n$ ions. No K^+ peak was observed probably

because of the high water pressure in the ambient air. No problems with an interfacing corona discharge were encountered in these experiments.

Figure 27 shows the mass spectrum obtained when water vapor was added to the reaction chamber in order to measure the equilibrium constant. For this spectrum, the water partial pressure was 47 mTorr in the reaction chamber. The experimental $-\Delta G^{\circ}_{2,3}$ and $-\Delta G^{\circ}_{1,2}$ values were 5.4 kcal/mol and 7.5 kcal/mol respectively at 298 K. Previous work [49] has reported 6.3 kcal/mol and 8.9 kcal/mol respectively. Thus, our values of $K_{1,2}$ and $K_{2,3}$ were lower by factors of 4.6 and 10.6, respectively. For this reason, we concluded that the ion source still did not work properly.

The mass spectra of potassium ions obtained after the valve was removed were similar to the ones measured before. However, the signal was lost after these results were obtained. The spectrum reappeared later, was a surprise, and is shown in Figure 28. It has an intense peak due to bare K^+ and no or very low intensity peaks due to water associated clusters. The instrument was switched back to corona discharge ionization and the spectrum shown in Figure 29 looks similar to the corona discharge spectra previously obtained with a series of $H^+(H_2O)_n$ cluster peaks dominated by $H^+(H_2O)_4$. However, several new peaks have appeared in the low mass range. These peaks had not been observed in the spectra obtained previously. The peak at 31 m/z is still not identified.

The question arises as to why the electrospray mass spectrum suddenly changed dramatically? Considering that the potassium ions were produced in room air which contains water in the torr range, $K^+(H_2O)_n$ clusters should form with high cluster numbers. These ions might decluster when entering the ion source but total declustering

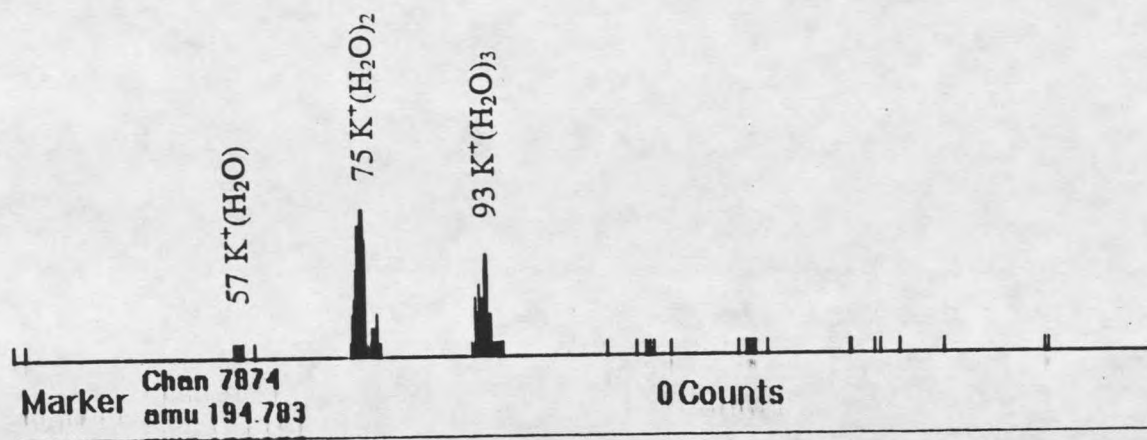


Figure 27. Mass spectrum of K^+ obtained by electrospray ionization with 47 mTorr water partial pressure in the reaction chamber.

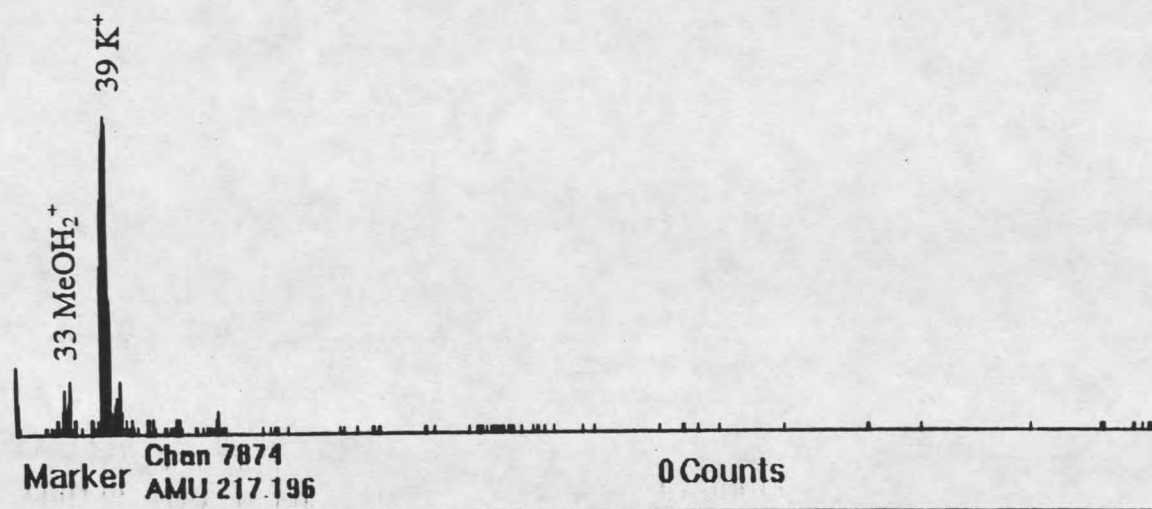


Figure 28. Mass spectrum of K^+ obtained by electrospray ionization with no reagent gas added to the reaction chamber, unknown problem caused the intense K^+ peak.

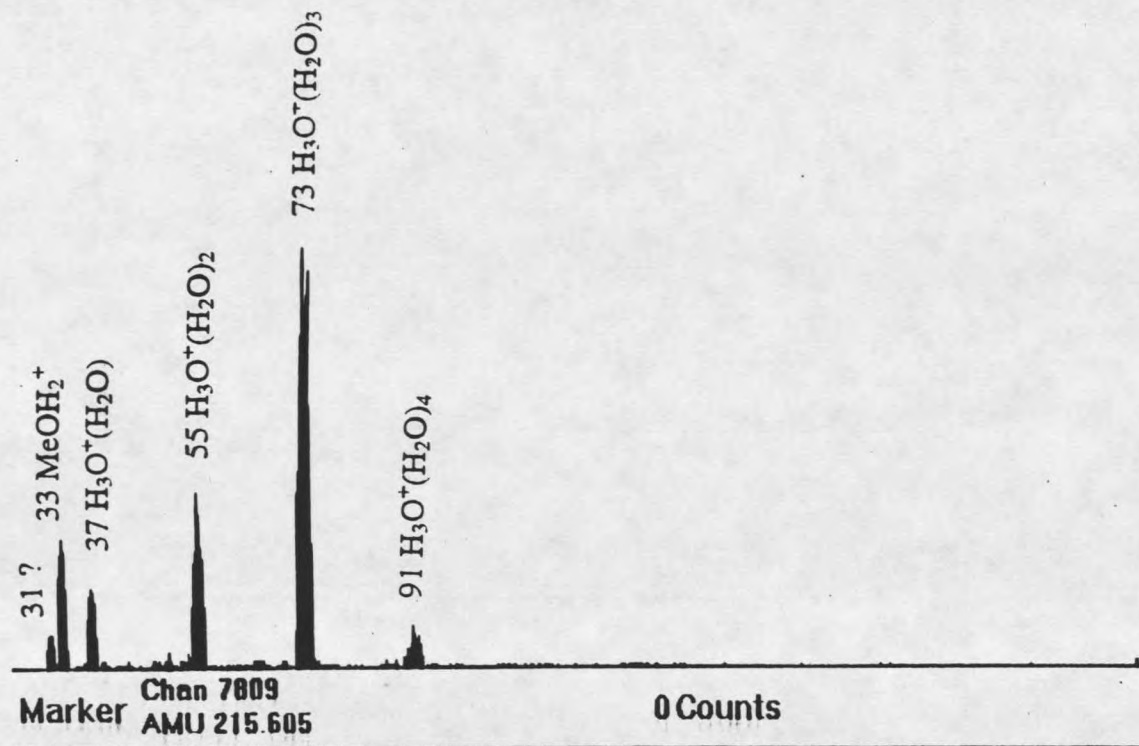


Figure 29. Mass spectrum obtained by corona discharge ionization in ambient air.

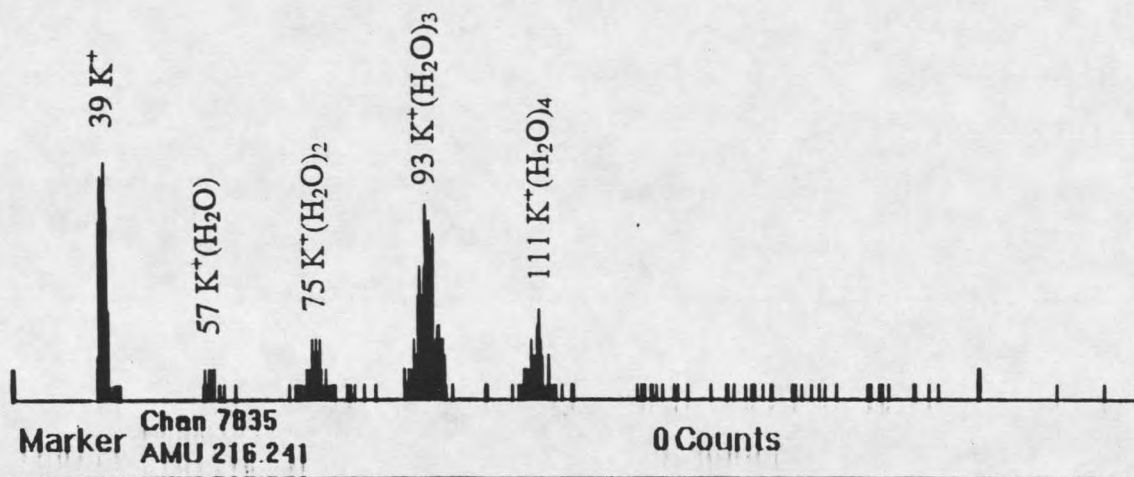


Figure 30. Mass spectrum of K^+ obtained by electrospray ionization with 686 mTorr water added to the reaction chamber, unknown problem caused the intense K^+ peak.

could not occur because both the pre-reaction chamber and the reaction chamber contained room air with a high water content. Besides, the $-\Delta G_{0,1}^{\circ}$ value was ~ 11 kcal/mol according to previous work [49, 50]. This large free energy change means that the equilibrium can be measured only at high temperatures, $> 180^{\circ}\text{C}$, and in our experiments room temperature was used. When additional water was added to the reaction chamber, formation of $\text{K}^+(\text{H}_2\text{O})_n$ clusters was observed, see Figure 30. However, the intensity of K^+ decreased little and K^+ was still the strongest signal in the spectrum. One can only speculate as to why the intensity of K^+ did not decrease when the water pressure was increased.

It is known that the first clustering step



is much slower than the subsequent clustering steps. Thus, if K^+ is formed close to the exit of the ion transport capillary, which might happen if a discharge was running in the pre-reaction chamber, the first clustering step would serve as a kinetic "bottleneck". The second possibility is that K^+ was formed outside of the sampling orifice. The question is then why increasing the water pressure in the reaction chamber would cause the appearance of the cluster ions.

$\text{K}^+(\text{C}_6\text{H}_6)_n$ Clusters

Benzene is generally considered a nonpolar molecule, because it does not have a permanent dipole moment. Cations, from simple ions like K^+ to more complex organic

ions, are attracted to the π face (cation- π interaction) of benzene and other aromatic structures as shown in Figure 31 [51].

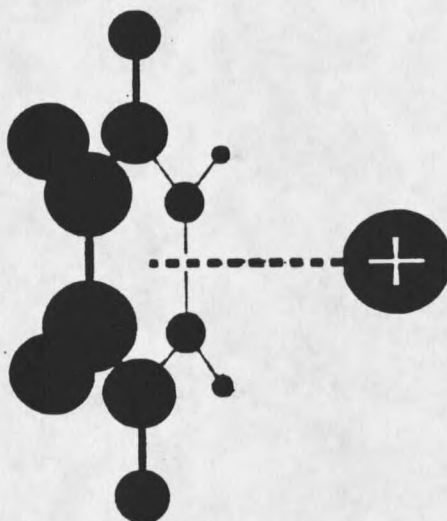


Figure 31. Schematic diagram of cation- π interaction [51] .

Noncovalent intermolecular forces play a major role in determining the structures of biological macromolecules and in mediating processes such as receptor-ligand interactions, enzyme-substrate binding, and antigen-antibody recognition [51]. The equilibrium data on cation- π interactions, like K^+ and benzene, will help to understand how these aromatic binding sites of a macromolecule compete with the highly favorable solvation of an ion provided by an aqueous medium to pull the ion out of water and into a hydrophobic, nominally nonpolar environment.

The final test system to be described here is K^+ clusters with benzene



with clusters up to four benzene molecules have been observed at room temperature [52]. For these experiments, benzene was mixed with nitrogen gas in the 5 liter bulb and the reagent gas mixture was supplied to the reaction chamber. A typical mass spectrum is shown in Figure 32, which was obtained with 2.5 mTorr benzene added to the reaction chamber. In these experiments, both K^+ and $\text{K}^+(\text{C}_6\text{H}_6)$ signals were observed at 2.5 and 7.5 mTorr benzene partial pressure in the reaction chamber. When the partial pressure of benzene increased to 12 mTorr, the peak of K^+ disappeared or had very low intensity. The cluster $\text{K}^+(\text{C}_6\text{H}_6)$ at $m/z=117$ was still present but no $\text{K}^+(\text{C}_6\text{H}_6)_2$ at $m/z=195$ was observed. Because of the upper mass limitation of the quadrupole mass filter, higher clusters could not be observed. The equilibrium constant $K_{0,1}$ was calculated for benzene partial pressures of 2.5 mTorr and 7.5 mTorr. The values of $-\Delta G^\circ_{0,1}$ were 7.6 kcal/mol and 7.4 kcal/mol, respectively. In contrast, the value obtained in previous work [52] was 11.9 kcal/mol. This difference is very large. The reason for the discrepancy must be the same as the reason for the intensity of K^+ was unreasonably high in figure 30. What caused this phenomenon is still not understood.

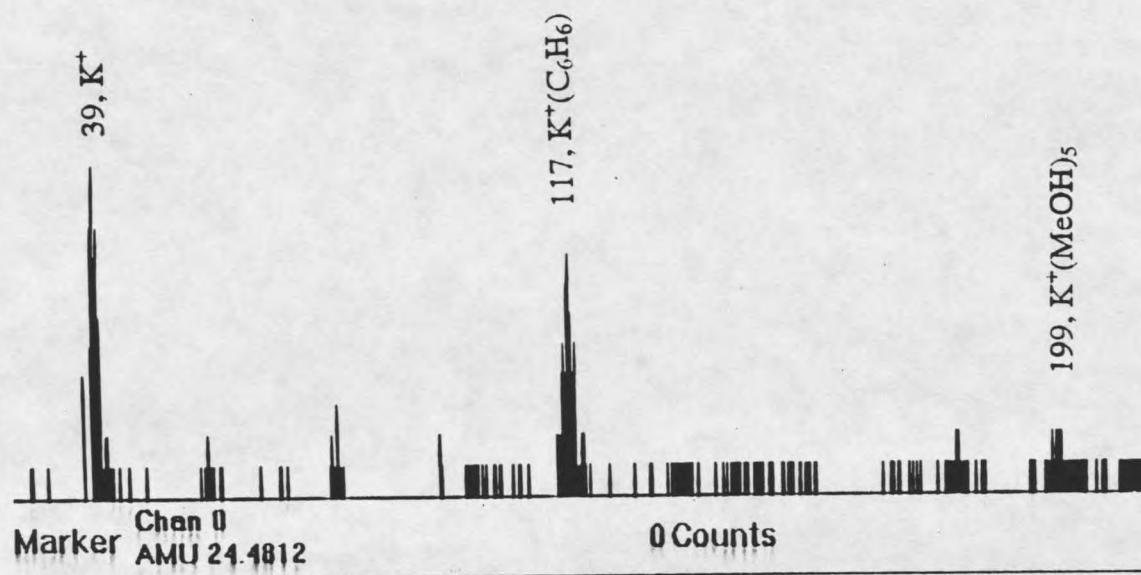


Figure 32. Mass spectrum of $K^+(C_6H_6)_n$ obtained by electrospray ionization with 2.5 mTorr benzene added to the reaction chamber.

SUMMARY

A PHPMS was successfully reinstalled. Damaged electronic units were either replaced or upgraded. A new MCS data acquisition system was installed. The mass spectrometer is in good operating condition.

Electrospray is a convenient technique to introduce ions produced in solutions by conventional wet chemistry into the gas-phase. Electrospray is a very "soft" ionization technique and will cause minimum fragmentation. An electrospray ion source with the ability to measure ion-molecule equilibria was designed and installed. Ions generated by electrospray and clustered with water molecules were successfully detected by the mass spectrometer. The operating parameters were studied and optimized. Equilibrium constants of selected ion-molecule reactions were measured. However, not all equilibrium constants match previously reported data.

It is still unclear why measured equilibrium constants were wrong. But the major difficulty was maintaining electrospray conditions. Most of the time, electrospray generated ions was not observed by the mass spectrometer. In contrast, the corona discharge was very stable. Frequently, it was only possible to run in corona discharge mode. To solve this problem, SF_6 gas was added, and it was found that this suppressed the corona discharge to some degree.

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