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:
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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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STATEMENT OF PERMISSION TO USE

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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.

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 90^0 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 equilibra 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:

$$Na^+(NH_3)_{n-1} + NH_3 \rightleftharpoons Na^+(NH_3)_n$$

$$K^+(H_2O) + CH_3OH \rightleftharpoons K^+(CH_3OH) + H_2O$$
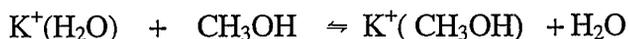
2. Proton transfer: gas phase acidities and basicities

$$NH_4^+ + CH_3NH_2 \rightleftharpoons NH_3 + CH_3NH_3^+$$

$$CH_3COO^- + CH_2ClCOOH \rightleftharpoons CH_3COOH + CH_2ClCOO^-$$
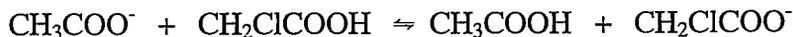
3. Electron transfer: electron affinities and ionization energies

$$C_6H_5NO_2^- + SF_6 \rightleftharpoons C_6H_5NO_2 + SF_6^-$$

$$Naphthalene^+ + Anthracene \rightleftharpoons Naphthalene + Anthracene^+$$
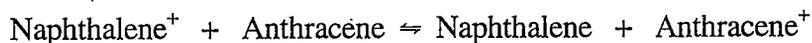
4. Hydride and chloride transfer: hydride and chloride ion affinities, stabilities of

carbocations.

$$tert\text{-}C_4H_9^+ + C_6H_5CH_2X \rightleftharpoons tert\text{-}C_4H_9X + C_6H_5CH_2^+$$
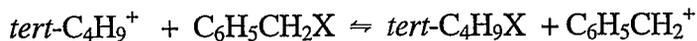
The determination of the equilibrium constant of a given ion-molecule reaction is

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^o can be obtained but also ΔH^o and ΔS^o by means of van't Hoff plots.

van't Hoff Plot

From equations 1 and 2,

$$\Delta G^o = \Delta H^o - T \Delta S^o \qquad (1)$$

$$\ln K = -\Delta G^o / RT \qquad (2)$$

equation 3 can be derived,

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

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

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 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 a 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 $E/p < 15$ V/(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,

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

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

$$\lambda = k / p$$ (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,

$$V_d = \mu E \tag{6}$$

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_o, by equation 7 [20],

$$\mu = (T/273.16) \times (760/p) \times \mu_o \tag{7}$$

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

$$t = d / V_d \tag{8}$$

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,

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

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],

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

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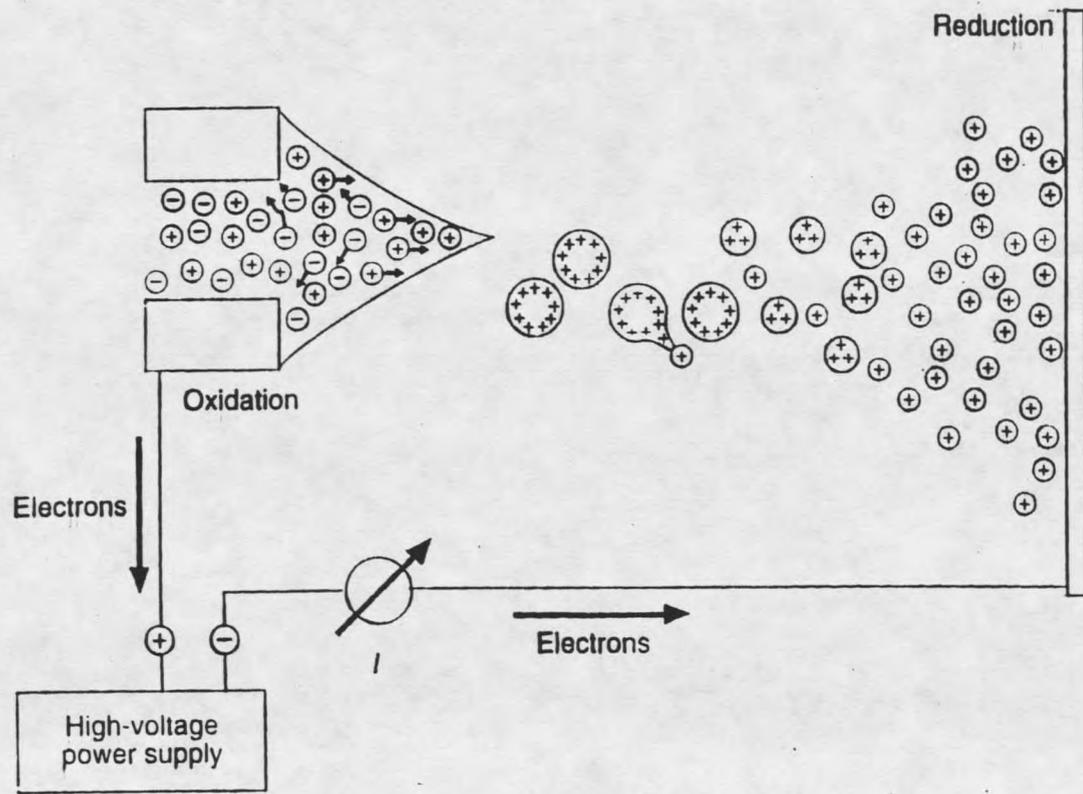
Figure 1. Schematic representation of processes in electrospray. Figure reproduced from reference [10].

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

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

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

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/m^2; 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 $Na^+(NaCl)_n$. 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
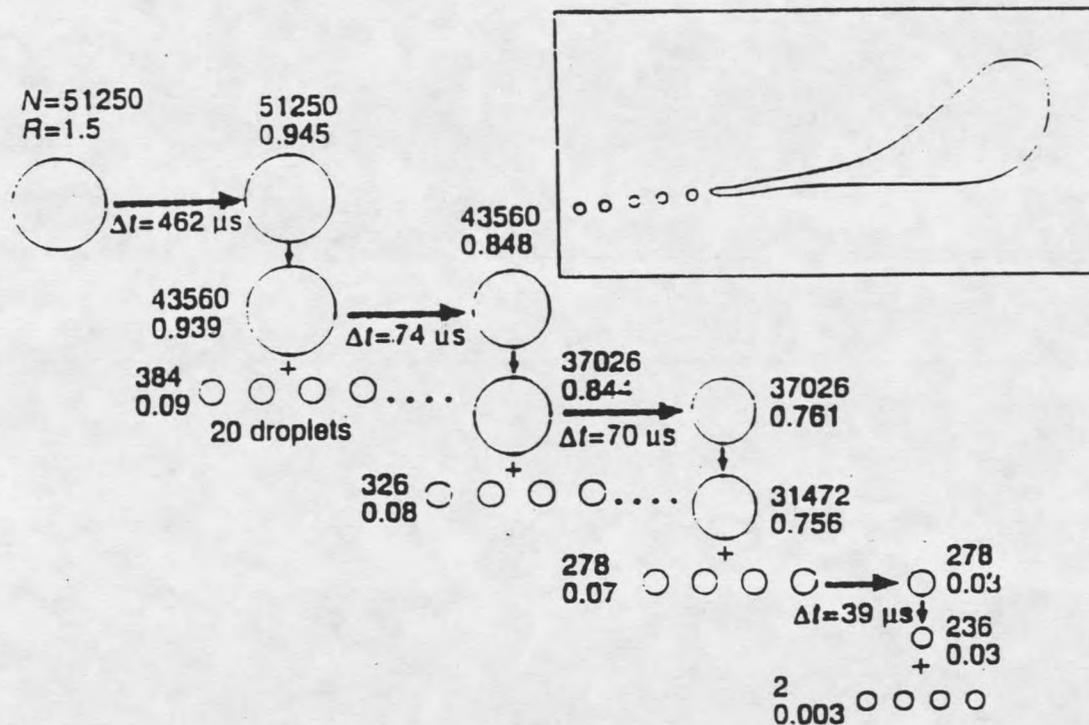
Figure 2. Schematic diagram of time history of parent and offspring droplets. Figure
reproduced from reference [10].

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 ~100 μm 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 glass 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.
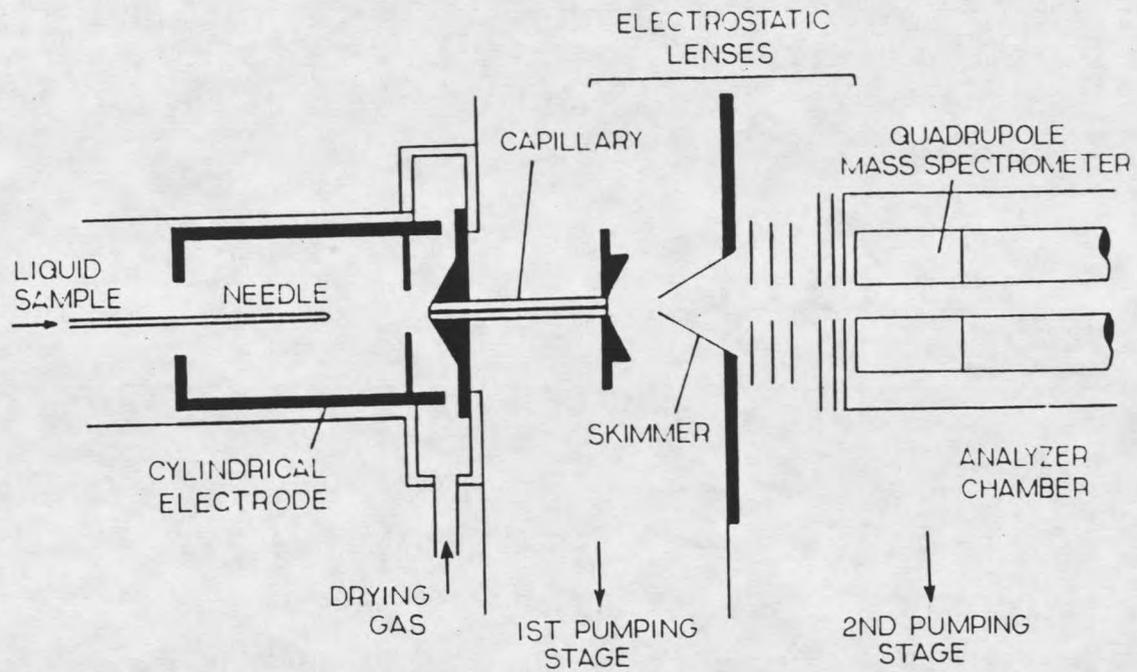
Figure 3. Schematic diagram of an ESMS apparatus. Figure reproduced from reference [9, 38] .

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

$$N_{Re} = D \nu \rho / \mu \qquad (12)$$

where D is inner diameter of tube, ν 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