

**STUDIES OF THE EFFECTS OF THE AMPLITUDE AND PHASE OF THE
RF POTENTIAL ON THE TRAPPING PROCESS IN LASER
DESORPTION QUADRUPOLE ION TRAP MASS SPECTROMETRY**

By

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ABSTRACT

The thesis is concerned with elucidating the mechanism by which ions are contained by the quadrupole field in laser desorption ion trap mass spectrometry (LD-ITMS). In the past, the process by which ions are trapped has been poorly understood. The several models that have been proposed to explain the dependence of trapping efficiency on the amplitude (q_z) and phase of the RF potential are inconsistent with each other. Previous experimental studies of the trapping process have been hindered by poor reproducibility in the ion production from standard laser desorption samples. A new sample type, electrodeposited polythiophene films, has been developed to resolve this problem. These films have been shown to be capable of providing consistent ion production over many thousands of laser shots. Reliable data have been acquired for the first time showing the dependence of mass spectral signal intensity on phase and q_z . The signal intensity for laser desorbed molecular ions was found to be inversely related to q_z . Contrary to previous assertions, this trend is not due to the inability of desorbed ions to penetrate a static "potential barrier" that has a magnitude proportional to q_z . Rather, experimental evidence indicates that collision activated dissociation at high RF potentials is a dominant process that reduces the signal intensity from molecular ions, while increasing those of their lower mass fragments. New experimental data also demonstrate the dependence of LD-ITMS sensitivity on phase. The range of phases over which ions may be trapped, as well as the value of the optimum phase for trapping, depends on q_z and the number of ions produced per laser shot. It is believed that these dependencies are related to the effects of Debye shielding, which are reduced if fewer ions are produced, or if q_z is raised. Presently, it is impossible to determine a priori the optimum value of the phase angle for trapping ions, because the effects of Debye shielding will vary unpredictably over the course of an experiment. Computer simulations utilizing SIMION 6 were also undertaken, to gain further understanding of the experimental data.

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LIST OF ABBREVIATIONS

α	optical absorption coefficient (cm^{-1})
AC	alternating current
ADC	analog-to-digital converter
a_u	Mathieu equation parameter
C	Coulomb
CI	chemical ionization
d	distance traveled by an ion since the last calculation (mm, SIMION 6 variable)
Da	Dalton (equivalent to atomic mass unit)
DAC	digital-to-analog converter
DC	direct current
e	elementary charge ($1.6021 \times 10^{-19} \text{ C}$)
EI	electron ionization
fp	mean free path between collisions (mm, SIMION 6 variable)
FT-ICR	Fourier transform ion cyclotron resonance mass spectrometry
I_0	laser irradiance (W/cm^2)
ITMS	ion trap mass spectrometry
LD	laser desorption
LD-ITMS	laser desorption ion trap mass spectrometry
m/z	the ratio between the mass (m) of an ion and the number (z) of electronic charges on it
MALDI	matrix-assisted laser desorption ionization
r	radial displacement coordinate (mm)
r_0	radius of the quadrupole ion trap ring electrode (mm)
RF	radio frequency

TBA	tetrabutylammonium cation
TEA	tetraethylammonium cation
TOF	time-of-flight mass spectrometry
u	represents either radial (r) or axial (z) dimension of ion trap
z	axial displacement coordinate (mm); also, the number of charges on an ion
z_0	shortest distance from the center of a quadrupole ion trap to one end-cap electrode
z_u	Mathieu equation parameter
β_u	parameter used to define trajectory of ion motion within the quadrupole ion trap

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CHAPTER 1

INTRODUCTION

1.1 Overview

Ion trap mass spectrometers have become important tools for analytical chemists, due largely to their high sensitivity, small size, relatively low cost, and excellent tandem mass spectrometry capabilities. Laser desorption (LD) and matrix-assisted laser desorption ionization (MALDI) are powerful methods capable of directly vaporizing and ionizing condensed phases species for subsequent mass analysis with little or no fragmentation.^{1, 2} While there has been considerable research regarding laser desorption ion trap mass spectrometry (LD-ITMS),³⁻²² the method has yet to find widespread usage among the analytical community. One of the challenges to be overcome, so that the potential advantages of LD-ITMS can be realized, is the efficient trapping of energetic laser desorbed ions.

Ions have the greatest likelihood of being confined if they are created with small displacements from the trap center with low translational energies.²³ For LD ionization, as for all ion sources situated by necessity outside of the trapping volume, the conditions for efficient trapping are not easily met. There exists a substantial body of theoretical work regarding the confinement of externally injected ions.²⁴⁻³⁷ Numerous laser desorption experimental studies have also been reported that regard the fundamental trapping process.^{8, 9, 13, 14, 18, 38} It is noteworthy, though, that there are inconsistencies present in the ion trapping literature between predicted theoretical behavior, reported experimental data, and the mechanisms proposed to explain experimental results. These discrepancies lead to a confusing situation whereby novices and experts in the field alike may be misguided in their rational analysis of experiments. Thus,

further research aiming to understand the process by which injected ions are trapped is of both fundamental and immediate interest.

This thesis concerns the process by which laser desorbed ions are confined by the quadrupole field in an ion trap mass spectrometer. In the remainder of Chapter 1, the theory and operating principles behind ion trap mass spectrometry, as well as laser desorption sampling and ionization, will be introduced. The following chapter, entitled “Instrumentation,” consists of a detailed description of the home-built laser desorption ion trap instrument that was developed during the course of the research chronicled here. Chapter 3 is a report on the development and characterization of electrodeposited polythiophene films as a new type of standard sample for fundamental laser desorption mass spectrometry studies. Chapters 4 and 5 comprise the bulk of the new and important findings of this thesis, including a critical review of the existing literature regarding the trapping of injected ions. The results of a host of computer-based simulation studies that were performed to gain further insight into the mechanism of ion confinement will be presented and discussed in Chapter 6. Finally, in the last chapter, the conclusions of this thesis are stated.

1.2 Quadrupole Ion Trap Theory and Operational Principles

For a comprehensive, detailed account of quadrupole ion trap theory, the reader is referred to March and Hughes.³⁹ More succinct versions have appeared elsewhere.⁴⁰⁻⁴⁴ Here, a synopsis of relevant theory will be provided as an introduction to the principles and methods of ion trap mass spectrometry.

1.2.1 Quadrupole Ion Trap Theory

It is important to appreciate from the onset that quadrupole ion traps are dynamic devices, and that the trajectories of ions within them depend upon time-varying forces. These forces are

due to quadrupole electric fields that can be established using a ring electrode and two end-cap electrodes, as portrayed in Figure 1.1. The ring electrode and the end-caps have hyperbolic cross-sections and are configured according to

$$r_0^2 = 2z_0^2 \quad (1.1)$$

where r_0 is the radius of the ring electrode and z_0 is the closest distance from the trap center to an end-cap. Quadrupole fields are strongly focussing and the forces upon ions within them are proportional to the displacement of the ions from the center of the field. The general case for quadrupole devices is that the forces must be considered simultaneously in several directions. For three-dimensional quadrupole ion traps, the resulting motion of charged particles can be separated according to the Cartesian coordinates x , y , and z . Since the electric field is symmetrical, it is convenient to consider only radial [$r = (x^2 + y^2)^{1/2}$] and axial (z) displacement. To operate as an ion trap, the electric field must periodically switch directions so that ions will not be accelerated continuously towards any one electrode. Hence, application of a radio frequency (RF) potential to the ion trap electrode structure may cause an ion to undergo oscillations within the quadrupole field that are stable and bounded by the dimensions of the device, provided the mass-to-charge ratio (m/z) falls within a certain range. Successful containment depends not only on m/z , but also on the initial RF phase and the displacement and velocity that an ion has upon introduction into the quadrupole field. Ions not satisfying the conditions necessary to achieve stable oscillatory motion will have trajectories that increase with time and will be lost from the trap.

The potential, ϕ , experienced by a single ion unaffected by space-charge at a point (x , y , z) within an ideal quadrupole field can be described by the relationship

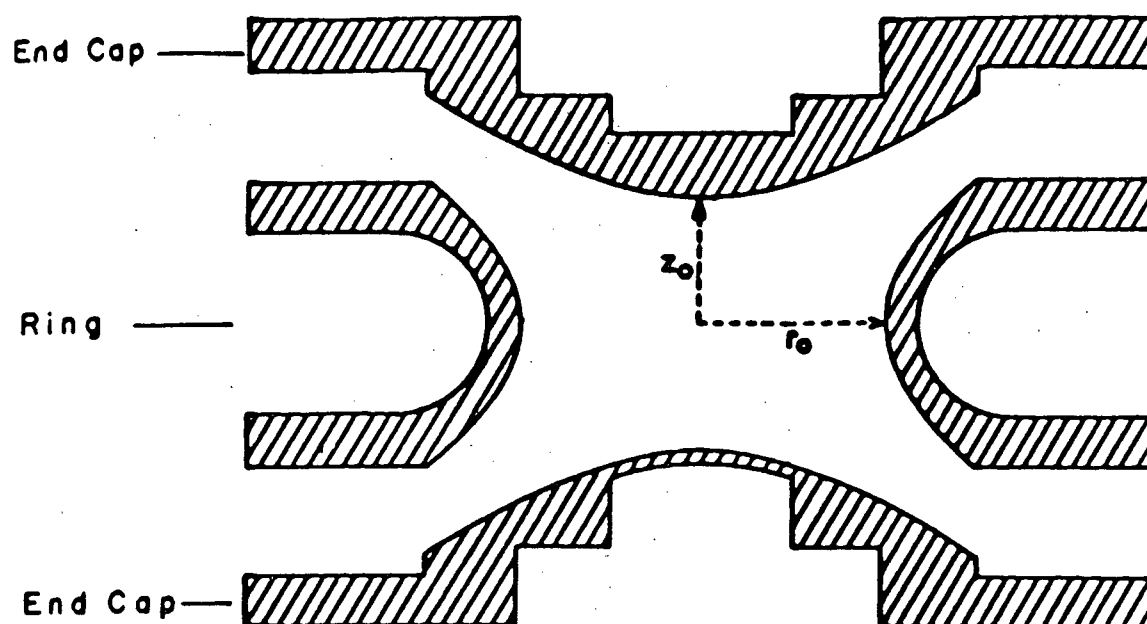


Figure 1.1 Schematic diagram showing a cross-section of the three-dimensional quadrupole ion trap (reprinted from "Quadrupole Storage Mass Spectrometry," March and Hughes, by permission of John Wiley & Sons, Inc.)

$$\phi(x, y, z) = \frac{\phi_0}{r_0^2} (\lambda x^2 + \sigma y^2 + \gamma z^2) \quad (1.2)$$

where ϕ_0 is the potential applied to the electrodes; λ , σ , and γ are weighting constants for the x , y , and z dimensions, respectively; finally, r_0 is the radius of the device, which is also constant. The applied potential at some time, t , may consist of a direct current (DC) and an RF component

$$\phi_0 = U - V \cos \Omega t \quad (1.3)$$

U is the amplitude of the DC potential, and V is the amplitude of the RF potential, measured zero to peak (V_{0-p}); Ω denotes the angular frequency of the RF field in radians per second and is equal to $2\pi f$ where f is the frequency in Hz (typically, $f \approx 1$ MHz). A requirement for quadrupole fields is that the values selected for λ , σ , and γ in (1.2) must meet the constraint³⁹

$$\lambda + \sigma + \gamma = 0 \quad (1.4)$$

For quadrupole ion traps, the weighting constants are most often determined as follows, although other assignments are possible⁴⁵

$$\lambda = \sigma = -\frac{\gamma}{2} = 1 \quad (1.5)$$

Substituting the values from (1.5) into (1.2), a final expression for the potential experienced by an ion in the three-dimensional field of a quadrupole ion trap is obtained

$$\phi(x, y, z) = \frac{\phi_0}{r_0^2} (x^2 + y^2 - 2z^2) \quad (1.6)$$

or, for cylindrical coordinates

$$\phi(r, z) = \frac{\phi_0}{r_0^2} (r^2 - 2z^2) \quad (1.7)$$

The relation expressed in (1.7) holds for the case when ϕ_0 is applied to the ring electrode and $-\phi_0$ is applied to the end-caps. In this situation the potential experienced by an ion at the center of the quadrupole field ($r = z = 0$) is zero. Under normal ion trap mass spectrometer operating conditions, however, the end-caps are grounded and the RF potential, V_{0-p} , is applied to the ring electrode only. U , specifically defined for ion traps to be the DC potential on the end-caps with respect to the ring electrode, is most often zero. This situation where the end-caps are earthed is a special case in which the potential at the trap center is equal to $\phi_0/2$, and equation (1.7) must be modified to become

$$\phi(r, z) = \frac{\phi_0}{2r_0^2}(r^2 - 2z^2) + \frac{\phi_0}{2} \quad (1.8)$$

Figure 1.2 shows the equipotential field lines in the r - z plane which result when the RF potential is applied only to the ring electrode.

The equations of motion for positively charged particles in a three-dimensional quadrupole field specified by (1.8) are given by

$$\frac{d^2 r}{dt^2} + \frac{e}{mr_0^2}(U - V \cos \Omega t)r = 0 \quad (1.9)$$

$$\frac{d^2 z}{dt^2} - \frac{2e}{mr_0^2}(U - V \cos \Omega t)z = 0 \quad (1.10)$$

where m represents the mass and e the charge of the ion. In order for an ion with a characteristic m/z , initial position (r, z) , and initial velocity $(\dot{r}, \dot{z})$ to remain trapped, the values of U , V , Ω , and r_0 , must combine such that its trajectory does not increase beyond the dimensions of the device as t increases. The solutions to such a multi-variable problem are not obvious, so it is fortunate that in the literature there is a very similar equation, the Mathieu equation (1.11), for

which the solutions are well-known.

$$\frac{d^2 u}{d\xi^2} + (a_u - 2q_u \cos 2\xi)u = 0 \quad (1.11)$$

u specifies the displacement in the dimension being considered. The solutions to the Mathieu equation are determined in terms of the parameters a_u and q_u . For each pair of a_u and q_u values, there will be a solution for u as a function of ξ which may be either stable or unstable. Stable solutions are those for which u is periodic and finite as ξ increases, whereas for unstable solutions u increases without limit as ξ increases.

Figure 1.3 is a simple example of a so-called "stability diagram," a graphical representation of the stable solutions to the Mathieu equation plotted in terms of a_u and q_u . These diagrams are symmetrical about the a_u axis, so only one half of the diagram needs to be shown. In order to utilize stability diagrams to predict the stability of ion trajectories within a quadrupole field, it is necessary to transform equations (1.9) and (1.10) into the form of the Mathieu equation. These transformations may be achieved by making the following substitutions

$$\xi = \frac{\Omega t}{2} \quad (1.12)$$

$$a_z = -2a_r = \frac{-8eU}{mr_0^2 \Omega^2} \quad (1.13)$$

$$q_z = -2q_r = \frac{-4eV}{mr_0^2 \Omega^2} \quad (1.14)$$

z and r have replaced the subscript u because these are the relevant dimensions for this case. In order for ions to be trapped, the ions must have trajectories that are stable simultaneously in both the axial and the radial dimensions. It is possible to obtain a single stability diagram for both dimensions if the one-dimensional stability diagrams for r and z are superimposed on each other,

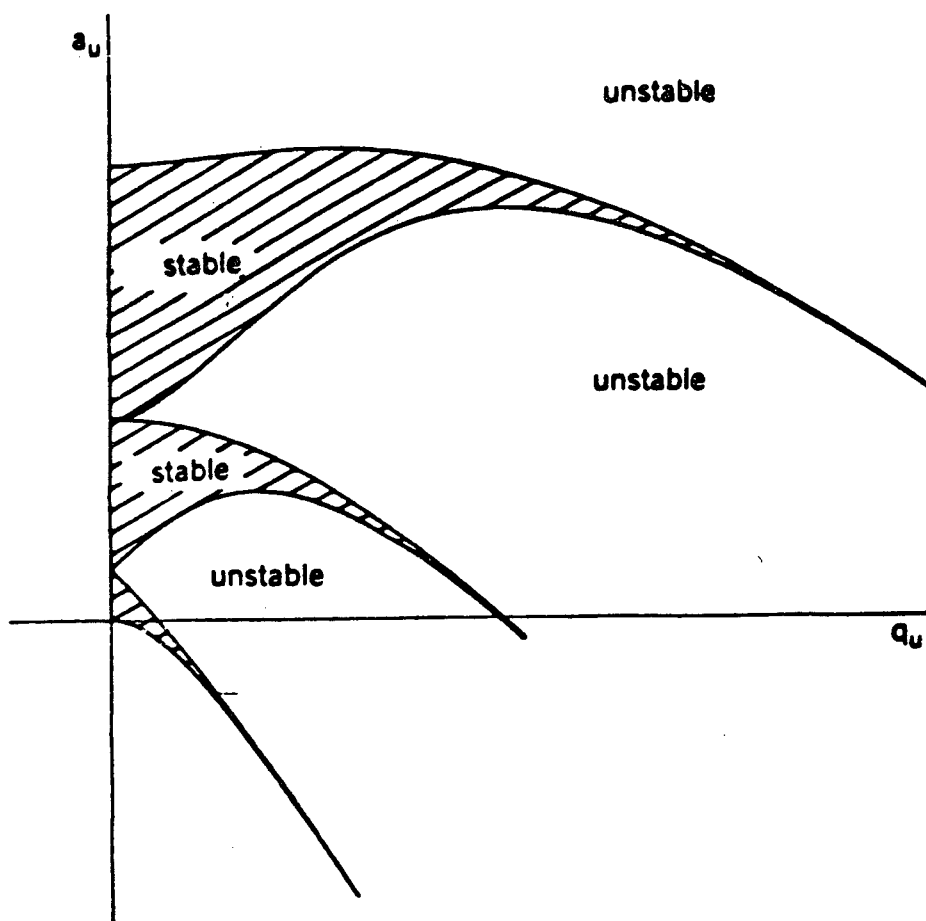


Figure 1.3 Graphical representation of stable solutions of the Mathieu equation plotted in terms of a_u and q_u (reprinted from "Quadrupole Storage Mass Spectrometry," March and Hughes, by permission of John Wiley & Sons, Inc.)

as displayed in Figure 1.4. An ion may thus have a stable trajectory within the quadrupole field only if it has values of a_u and q_u that lie within the intersecting regions of the resulting combined stability diagram.

Figure 1.5 is an expanded view of the area of primary interest in the stability diagram for the ion trap. This region is the most important because it encompasses the lowest values of the Mathieu parameters which enable trapping to occur. For practical reasons, it is desirable to trap ions at values of a_u and q_u that are lower than those of the other stability regions. As expressed in equations (1.13) and (1.14), a_u and q_u are directly proportional to the applied potentials for a given m/z ion when r_0 and Ω are constant. There are limitations to the amplitude of the RF potential that may be applied between the electrodes of a quadrupole ion trap without causing discharge in the vacuum chamber or instability in the high voltage power supply. Hence, because higher mass species may be trapped at lower potentials, it is advantageous to operate quadrupole ion traps in the stability region closest to the origin.

The iso- β_u lines depicted in Figure 1.5 are also consequential. These lines map out regions of the stability diagram which have constant values of β_u as a_u and q_u vary. β_r and β_z are parameters specified by a_u and q_u which are significant because they can be used to determine the frequencies of a trapped ion's oscillatory motion in the radial and axial dimensions, respectively. When $q_u \leq 0.4$, the fundamental, or "secular," frequency, ω_0 , of a trapped ion oscillating within dimension u of a quadrupole field can be calculated from

$$\omega_{0,u} = \beta_u \cdot \frac{\Omega}{2} = \left(a_u + \frac{q_u^2}{2} \right)^{1/2} \cdot \frac{\Omega}{2} \quad (1.15)$$

This is a critical relation to comprehend for future reference, because it shows that the effect that the quadrupole field has on an ion's motion depends only on the Mathieu parameters, and not on

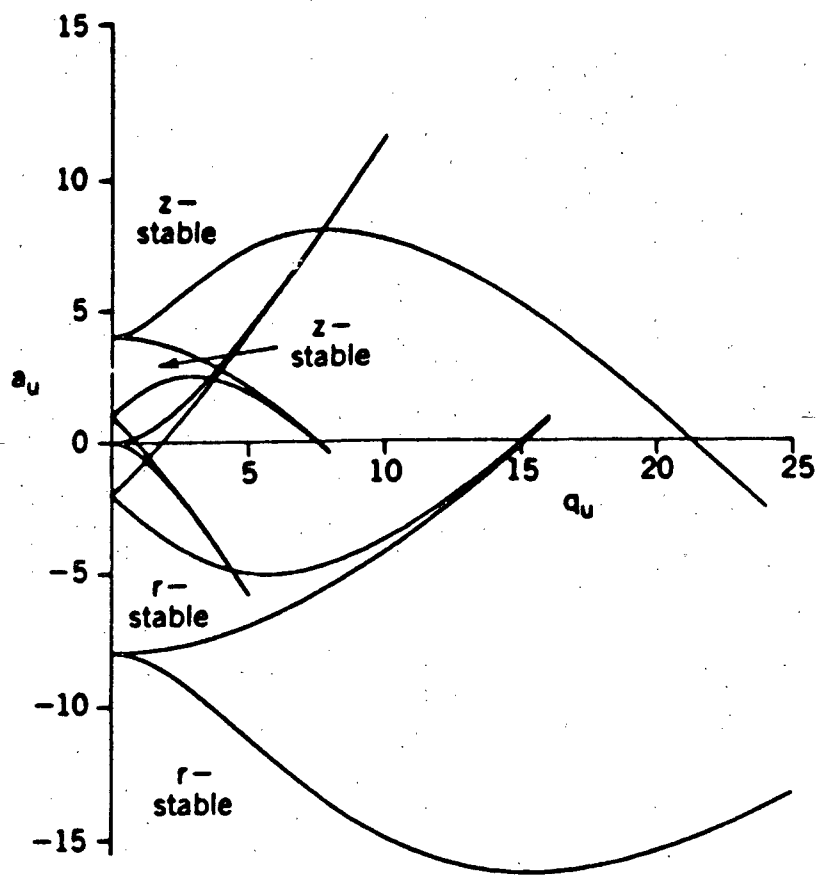


Figure 1.4 Mathieu stability diagram for the three-dimensional quadrupole ion trap (reprinted from "Quadrupole Storage Mass Spectrometry," March and Hughes, by permission of John Wiley & Sons, Inc.)

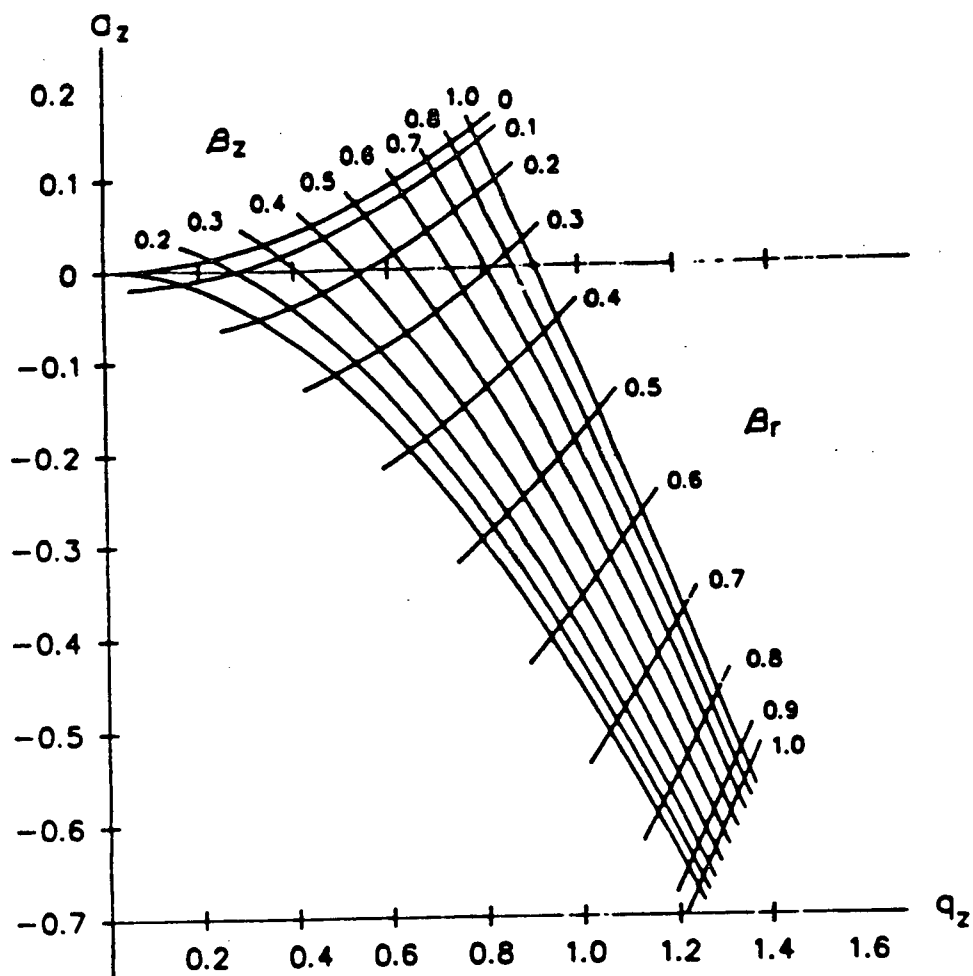


Figure 1.5 Stability region near the origin for the quadrupole ion trap showing the iso- β lines (reprinted from "Quadrupole Storage Mass Spectrometry," March and Hughes, by permission of John Wiley & Sons, Inc.)

m/z per se.

Ions undergoing stable oscillations within a quadrupole field can be described as being trapped within a so-called pseudopotential well of depth

$$\overline{D_z} = 2\overline{D_r} = -\frac{eV^2}{4mz_0^2\Omega^2} \quad (1.16)$$

Again, this calculation is valid only for $q_u \leq 0.4$. The pseudopotential well model assumes that ions undergo simple oscillatory motion within the trap at frequencies described by (1.15). The stipulations placed on (1.15) and (1.16) that q_u must be less than or equal to 0.4 are due to the consideration that ion motion becomes more complex at higher values of q_u . As q_u is raised beyond the defined range, the approximation that ions undergo simple oscillatory motion within the trap becomes increasingly inaccurate.

The pseudopotential well model is often misinterpreted to have a real physical presence within the quadrupole field. For instance, it has been stated that the pseudopotential well becomes steep and narrow at relatively high q_z values (0.5-0.9).³⁴ The physical significance that may properly be attributed to the pseudopotential well is that the depth as approximated by (1.16) corresponds to the maximum kinetic energy that an ion may possess when passing through the trap center and remain trapped. The model is most effective in describing the harmonic oscillator nature of ion motion within a quadrupole field. It follows that the depth of the pseudopotential well must not be taken to provide a quantitative indicator of the maximum energy that an ion injected into the quadrupole field from an external source may initially possess and still be confined. As will be discussed further in Chapter 4, the pseudopotential well model does not provide a means for describing how ions are contained in the trap when injected by processes such as laser desorption.

1.2.2 Operation of the Quadrupole Ion Trap as a Mass Spectrometer

Before 1983, quadrupole ion traps had been used as mass spectrometers for approximately 15 years, but only by a handful of dedicated researchers.⁴⁶⁻⁵⁴ The development of the “mass-selective instability” mode of operation by George Stafford and the subsequent introduction of the Ion Trap Detector™ (ITD) to the commercial market by Finnigan MAT in 1983 were milestones in the evolution of the quadrupole ion trap. The ITD and its successor, the Ion Trap Mass Spectrometer™ (ITMS), quickly gained great popularity among analysts who used them as sensitive and versatile detectors for gas chromatography. Widespread interest in the quadrupole ion trap arose simultaneously within the analytical chemistry research community. The resulting flurry of activity among researchers seeking to further expand the capabilities and range of applications for quadrupole ion traps continues to this day.

The majority of quadrupole ion trap instruments utilize the mass-selective instability operating mode to acquire mass spectra. This method relies upon the fact that if ions of a particular m/z trapped within a quadrupole field have their a_z and q_z values raised such that they cross the $\beta_z = 1$ line of the stability diagram, the ions will become unstable in the axial direction. The trajectories of the ions will increase in the axial dimension only, because the ions will retain radial stability (see Figure 1.4). If a detector is placed behind an appropriately perforated end-cap electrode, then a signal will be produced whenever ions are ejected. In practice, no DC potential is utilized for the trapping field, so a_z is zero. For the remainder of the discussion in this thesis, it will be assumed that this is the case. Thus, the region of the stability diagram of most interest is now the line along the q_z axis between $q_z = 0$ and $q_z = 0.908$. These points mark the intersections of the q_z axis with the $\beta_z = 0$ and $\beta_z = 1$ lines, respectively.

For a particular ion trap characterized by r_0 and Ω , there will be a lower limit to the m/z

range which will be stable within a quadrupole field created by applying an RF potential of amplitude V . Ions introduced into the trap having m/z less than the “low mass cut-off” will have $q_z > 0.908$, and will rapidly be ejected. The remaining ions will have $0 \leq q_z \leq 0.908$, depending on their respective masses. A mass spectrum of the trapped ions can be obtained by ramping the amplitude of the RF potential. If the potential is raised sufficiently, ions will be successively brought to the axial instability point of $q_z = 0.908$, in order of increasing m/z , at which time they will be ejected. A plot of detector signal intensity versus time will thus yield the desired mass spectrum. This direct scanning method is limited, however, because the ions of interest may be of too high mass to have their q_z values raised to 0.908. For commercial instruments operated in the mass-selective instability mode, the mass range is set by the available RF amplitude and is approximately m/z 650. In order to analyze higher mass species contained within the trap, some alternative means must be employed.^{13, 55, 56}

There is no well-defined upper limit to the mass of ion which may be trapped for a particular RF potential amplitude; however, equation (1.16) specifies that the pseudopotential well depth lowers as m/z increases. This means that for a given V , as m/z is raised, the kinetic energy that an ion may have and remain trapped decreases. At some point, the trapping field will not be able to effectively contain high molecular weight ions if they have any initial velocity whatsoever. Nevertheless, it is possible to create and trap species with m/z much greater than 650. One method that has been devised to extend the mass range of ion traps, described as either “axial modulation”⁵⁵ or “resonant ejection,”¹³ involves applying a supplementary alternating current (AC) potential of up to a few volts to the end-caps. The frequency of the additional potential is chosen such that it matches the secular frequency of ions in the axial dimension at some q_z value lower than 0.908. If the supplementary potential is applied during a normal mass-selective instability ramp, ions will come into resonance with the additional field between the

end-caps, gain translational energy in the axial dimension, and be ejected at a lower q_z value than usual. For example, an ion of $m/z = 3 * 650 = 1,950$ will only have a q_z value of $0.908 / 3 = 0.303$ at the highest RF amplitude available to a commercial instrument with an upper mass limit of 650. According to (1.15), if the main RF potential applied to the ring electrode has $f = 1.00$ MHz, then it will be possible to eject ions with m/z 1,950 at q_z 0.300 if the supplementary ac voltage has $f = 106$ kHz. Detection efficiency does suffer for higher mass species, however, so some means of accelerating the ions into the detector subsequent to ejection from the trap is ordinarily implemented. This method can be used to extend the mass range of a quadrupole ion trap to m/z 70,000.⁵⁶

Another important consideration for ion trap mass spectrometry is the pressure and composition of the background gas. It has been found that the presence of a bath gas of helium at a relatively high pressure (1 mtorr) improves the performance of the ion trap.⁴² Collisions between ions and the lighter helium atoms transfer energy from the ions to the much more abundant bath gas. The result is that within a few ms collisional cooling causes the trajectories of the ions to contract such that the ions are mostly contained within a small volume around the trap center. This bunching of ions provides an increase in sensitivity, possibly because ions have a minimum of radial displacement when they are ejected. This allows for a greater fraction of the axially unstable ions to pass through the small aperture in the center of the detector end-cap. Collisional cooling of the ion cloud also improves resolution. Ideally, ions should remain near the trap center during the RF voltage ramp until the onset of theoretical trajectory instability causes their axial displacements to rapidly increase. Without the damping effects of a background gas, however, the trajectories of many trapped ions will have significant displacements in the axial dimension. A loss of resolution will result if a fraction of these ions are transmitted through the end-caps prior to the time at which they attain theoretical

instability.³⁹

Quadrupole ion traps have become popular because they are simple to use, relatively inexpensive, and have the greatest sensitivity of all mass spectrometers.⁴⁰ Perhaps the greatest performance advantage of ion traps over other types of mass spectrometers, though, is their ability to perform efficient tandem mass spectrometry. Tandem mass spectrometry, or "MS/MS," is a method used to obtain structural information about a desired species by first isolating the ion of interest, then causing it to fragment, followed by mass analysis of the resulting daughter ions. Identification of the daughter ions can provide the desired structural information of the original parent ion. Ion traps are ideal for this application because they allow for tandem-in-time mass spectrometry.⁵⁷ This feature is unique to ion trapping devices, because isolation, excitation, and the subsequent analysis of fragment ions all take place within the same volume of space. There are a number of methods available to the analyst to isolate a desired species with the quadrupole ion trap.^{58, 59} Energy deposition into isolated ions is frequently achieved by applying a dipolar AC potential across the end-caps in much the same manner as in resonant ejection/axial modulation. The degree of excitation can be controlled by varying the amplitude and duration of the supplementary ac potential. Ions gain translational energy from the supplementary field, which is converted into internal energy during collisions with the background gas. It is important that the amplitude of the potential is not so high that the excited ions are ejected from the trap prematurely. Significantly, energy deposition is more efficient if the isolated ions are excited at a higher q_z . There is a limit to how high the RF amplitude can be, though, because for the lower mass fragment ions to be successfully trapped they too must satisfy the condition $q_z < 0.908$. Therefore, a compromise must be made between the ease of inducing fragmentation and the low mass cut-off. Regardless, the tandem mass spectrometry capabilities of quadrupole ion traps are excellent, as the process of converting parent ions to

daughter ions is extremely efficient,^{57, 58, 60-62} approaching 100% in many cases.

The benefits of the quadrupole ion trap as a mass analyzer are well-defined. One challenge facing researchers is to further extend the capabilities of ion trap mass spectrometers by successfully interfacing them with non-traditional ion sources, such as laser desorption.

1.3 Sampling and Ionization for Ion Trap Mass Spectrometry

Electron ionization (EI) of gaseous neutrals is the most commonly utilized ionization method for ion trap mass spectrometry. The eluent from the capillary column of a gas chromatograph (GC) can be introduced directly into the volume between the trap electrodes where sample molecules are ionized by an electron gun situated within one of the end-caps. Sensitivity is high for this method because the slow-moving sample molecules are ionized directly within the confines of the trap electrodes and thus have the greatest likelihood of being contained by the quadrupole field.²³ There are classes of compounds, however, which are not amenable to introduction into the ion trap as gas phase neutrals: high molecular weight (MW), non-volatile, polar, and/or thermally labile compounds may undergo decomposition during the vaporization step which precedes EI. Electron ionization is thus precluded for the analysis of these species, and some alternative means of sampling and ionization must be employed. Hence, efforts to extend the range of applications of the ion trap have resulted in it being coupled to a wide range of ionization methods, including laser desorption (LD),³⁻²¹ electrospray ionization (ESI),⁶³⁻⁶⁵ secondary ion mass spectrometry (SIMS),⁵⁵ and glow discharge (GD).⁶⁵⁻⁶⁸ Laser desorption is a technique that is capable of directly vaporizing and ionizing condensed phase species with little or no fragmentation, and it is the ionization method considered in this thesis.

1.3.1 Laser Desorption Sampling and Ionization

There has long been interest in utilizing lasers to provide direct sampling and ionization

for mass spectrometry.⁶⁹⁻⁷⁶ Lasers provide a facile means of directly vaporizing, and to varying degrees ionizing, condensed phase samples. One benefit of using lasers for direct sampling is that a minimum of sample preparation is required before analysis. This obviates the need for special sample preparation procedures which add time and expense to the analysis, and that also may dilute and/or contaminate the sample. As detailed in a recent review text,¹ an impressive range of sample types are accessible to mass spectrometry via laser sampling and ionization. For instance, lasers have been used for elemental analysis of metal ores, geological samples, semiconductors, and insulators. As well, lasers have found extensive use in the analysis of many classes of biological molecules, including peptides, proteins, nucleotides, and carbohydrates, to name a few. Structural characterization of organic molecules, such as polycyclic aromatic hydrocarbons, amino acids, polymers, ionic compounds, and salts, may also be achieved by laser mass spectrometry. Obviously, the above range of applications is too broad to be attended to by any one laser based method. There have in fact been nearly as many combinations of lasers and operating conditions experimented with as there are sample types to be analyzed.

Note: due to the myriad possible combinations of samples and laser operating conditions, and the lack of a general theory to adequately describe the effects of all the relevant parameters, it is impossible to provide detailed, accurate descriptions of all the mechanisms involved in laser-solid interactions. Accordingly, the mechanistic descriptions provided below have been simplified and are meant only to introduce the relevant processes for laser sampling and ionization.

The type of information required from the analysis in question, as well as the resources available, will determine the best choice of laser and operating conditions. It is crucial to appreciate that even for the same sample there are several different processes which may occur due to the interaction of laser radiation with the sample surface. Although this list is somewhat

simplified, the following processes are considered to be relevant possibilities¹:

- a. Surface heating with thermal desorption
- b. Surface melting with surface evaporation
- c. Volume evaporation
- d. Formation of an optically thick plume
- e. Plasma absorption
- f. Optical breakdown (in transparent insulators)

The extent to which these processes occurs depends primarily upon the laser irradiance, I_0 , and the optical absorption coefficient of the substance, α , at the wavelength of the laser. Irradiance can be thought of as the power density at the sample surface, and is calculated from the laser pulse energy divided by the duration of the pulse and the area of the sample irradiated. The thermal conductivity, latent heats of fusion and vaporization, and the ionization potential of the sample will also be important to varying degrees. The separation of the above processes according to I_0 and α is shown in Figure 1.6. Thresholds irradiance values for volatilization, plasma ignition, and optical breakdown are marked by dashed vertical lines. These threshold values are well-defined, but vary for different samples. Volatilization, at least, is required for direct sampling of solids for mass spectrometry. As well, a requisite for sensitivity is the efficient production of ions from neutral species. Ionization efficiency increases with irradiance, and nearly 100% conversion of neutral atoms into ions is possible just above the threshold for plasma formation.⁷⁰ In general, though, fragmentation of molecular species becomes a dominant process well before ionization efficiency in the laser plume becomes high. Therefore, a trade-off between efficiency of ionization and loss of structural information due to rupturing of covalent

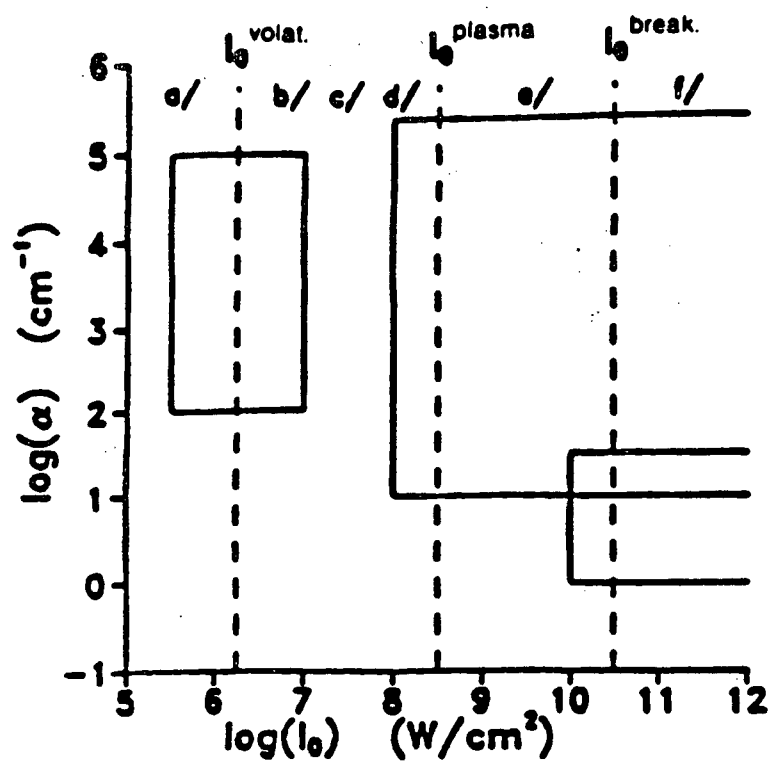


Figure 1.6 The processes occurring due to the interaction of laser light with solid surfaces are roughly divided according to irradiance and optical absorption coefficient (reprinted from "Laser Ionization Mass Analysis," Vertes, Gijbels, and Adams, by permission of John Wiley & Sons, Inc.)

bonds must be made for analysis of molecular ions. No such compromise must be made when utilizing lasers for elemental analysis. Since different processes are involved when laser sampling is used for molecular and elemental analysis, it is appropriate to consider these separately. The less energetic processes used for molecular analysis may be termed "laser desorption," whereas "laser ablation" is used to describe the high irradiance processes employed in elemental analysis.

Laser ablation sampling requires high irradiance, and some of the processes resulting from the accompanying intense localized heating are melting, vaporization, plasma formation, and absorption of incoming radiation by the plasma. These processes are too energetic to be of any use for mass spectrometry other than for the production of atomic ions. With suitably high irradiances ($\sim 2 \times 10^9 \text{ W/cm}^2$) representative sampling of the solid surface is feasible.⁷⁰ This means that the composition of the laser generated plume above the sample accurately reflects the sample composition, an important consideration for analysis. Also, as stated above, the ionization efficiency of the ablation process approaches 100% under these conditions. Unfortunately, high power densities bring about not only efficient sampling and ionization for mass spectrometric analysis, but deleterious effects as well. For instance, multiple charging results as the irradiance increases above the plasma formation threshold. The extent to which this occurs depends upon the ionization potentials of the element being considered. Thus, peak intensities for singly charged ions in the mass spectra obtained will not accurately reflect the ratio of neutral elements in the sample. Most detrimental for mass spectrometry, however, is that a broad distribution of kinetic energies, centered at very high values, is imparted to ablated species. Energies in excess of 1000 eV may easily be reached by atomic ions created by laser ablation. For mass analyzers that require ions to be confined before analysis, such as quadrupole ion traps and ion cyclotron resonance (ICR) instruments, ion containment efficiency, and thus

sensitivity, suffers as the energy of ions upon injection increases. Some means of moderating the initial energies is necessary to trap ions in these devices. Efficiency of containment is believed to always be low, so ion traps of any variety are poorly suited as mass analyzers for laser ablation. Time-of-flight (TOF) mass analyzers, on the other hand, do not require that ions be trapped before analysis and are better suited for ablation applications. Resolution problems for TOF instruments are exacerbated, however, by the initial spread in energy of ablated ions.

The kinetic energies of ions created by laser desorption are much lower (< 10 eV), so this method is better suited to ion trapping devices. Laser desorption, like laser ablation, may consist of several processes, depending on the laser irradiance and the sample characteristics. In its simplest form, laser energy is absorbed by either the substrate or the sample itself (often combined with a large excess of an absorbing matrix—see below) followed by rapid heating of the sample. Thermally labile molecules may be desorbed without degradation if the rate of heating of the sample or substrate is sufficiently high. Although counterintuitive, the intact release of heat-sensitive molecules is a fundamental effect which occurs for ultrafast heating, because at very high temperatures the rate constant for vaporization may exceed that of decomposition reactions.¹ Fast heating is required so that labile molecules are quickly vaporized and spend very little time at lower temperatures, where thermal degradation is inevitable. Since rapid heating is essential for laser desorption of intact molecules, pulsed lasers with short pulse widths (< 100 ns) and energies between the μ J and mJ range are best.

Direct laser desorption as described above is limited to species with molecular masses below approximately 9,000 Daltons.⁷⁷ For samples which resonantly absorb the incoming laser energy, this is believed to be because the excitation of the analyte molecules needed for the controllable, nonexplosive energy transfer also puts energy into photodissociation channels.⁷⁷ In non-resonant laser desorption experiments, the necessary irradiances for high mass molecules are

near the threshold for plasma formation, which destroys molecules as well. In 1988, though, a breakthrough was made towards higher masses when Karas and Hillenkamp introduced a new laser based desorption technique for the production of parent ions from very large non-volatile molecules.⁷⁸ This new technique, matrix-assisted laser desorption ionization (MALDI), is based upon mixing a small amount of analyte with a large excess of a solid or liquid matrix which absorbs strongly at the laser wavelength. The method was originally devised as a means of improving the efficiency of coupling laser energy into poorly absorbing samples. Quite unexpectedly, the MALDI method was found to yield intact molecular ions for extremely large molecules ($MW > 100,000$ Da). Research interest in MALDI has experienced terrific growth since its astonishing initial report. Presently, the mechanisms for MALDI are not well-understood, and successful matrices for new sample types are often discovered through laborious trial-and-error procedures. Nevertheless, MALDI has revolutionized the use of laser sampling for mass spectrometry, and has spurred the development of many commercial instruments which are being utilized to provide accurate molecular weight information of large molecules in countless laboratories throughout the world.

Nearly all the research with MALDI has involved TOF mass analyzers. The TOF technique is well-suited for the analysis of large molecules because of its inherently high mass range. TOF analyzers, though, are limited by their modest resolution, and they do not have the MS/MS capabilities of other mass analyzers. Fourier transform-ion cyclotron resonance (FT-ICR) instruments, on the other hand, have the greatest resolution of all mass analyzers, and allow for efficient MS/MS within the trapped ion cell. Hence, MALDI combined with FT-ICR is a technique with powerful capabilities. MALDI-FT-ICR instruments are commercially available, but these too have their limitations. Firstly, FT-ICR instruments may be prohibitively expensive for many laboratories, and secondly their m/z range of 20,000 is lower than is ideal for MALDI.

Quadrupole ion traps are capable of very high resolution,⁷⁹⁻⁸² as well as high mass range,^{55, 56} and are only a fraction of the cost of FT-ICR instruments. With the demonstrated utility of LD for direct sampling and ionization of a wide range of sample types, and the recent advent of MALDI for large molecules, there is great potential to extend the range of applications of the quadrupole ion trap. In order for the mating of these techniques to be successful, there are challenges that must be overcome. One of these challenges is to devise methods of efficiently containing laser desorbed ions with the quadrupole field of the ion trap.

CHAPTER 2

INSTRUMENTATION

The laser desorption quadrupole ion trap mass spectrometer used here is a third generation in-house built instrument. Earlier versions of the instrument have been described elsewhere.⁴⁻⁶ The main components of the new instrument are detailed below, and accounts of the specific procedures for each experiment are to be found in the pertinent chapters. Figure 2.1 is a schematic of the complete experimental system.

2.1 Ion Trap Electrodes and Vacuum Manifold

Machining for the in-house built ion trap mass spectrometer was accomplished by members of the Mechanical Services Shop (Chemistry Department, U.B.C.) The apparatus consists of a stainless-steel vacuum manifold and ion trap electrode assembly. The manifold was specially designed to allow for laser desorption sampling from a probe inserted radially through the ring electrode. Additional quartz windows were included in the manifold to facilitate prospective experiments involving optical interrogation of trapped ionic species. The arrangement of the end-caps and ring electrode is characterized by an ideal, non-stretched geometry,* a ring electrode radius of 10.00 mm, and extended hyperbolic surfaces to provide a more homogeneous quadrupole field. The sample and laser apertures machined through the ring electrode have inner diameters of 2.5 mm. The sample probe and the ring electrode through which it was inserted were always at the same potential, because there was a stainless-steel

* Some commercial ion traps are "stretched," i.e., the end-caps have a greater separation than specified by $r_0^2 = 2z_0^2$. Stretching the end-cap separation ~10% has been empirically determined to enhance performance of the instrument in some cases.

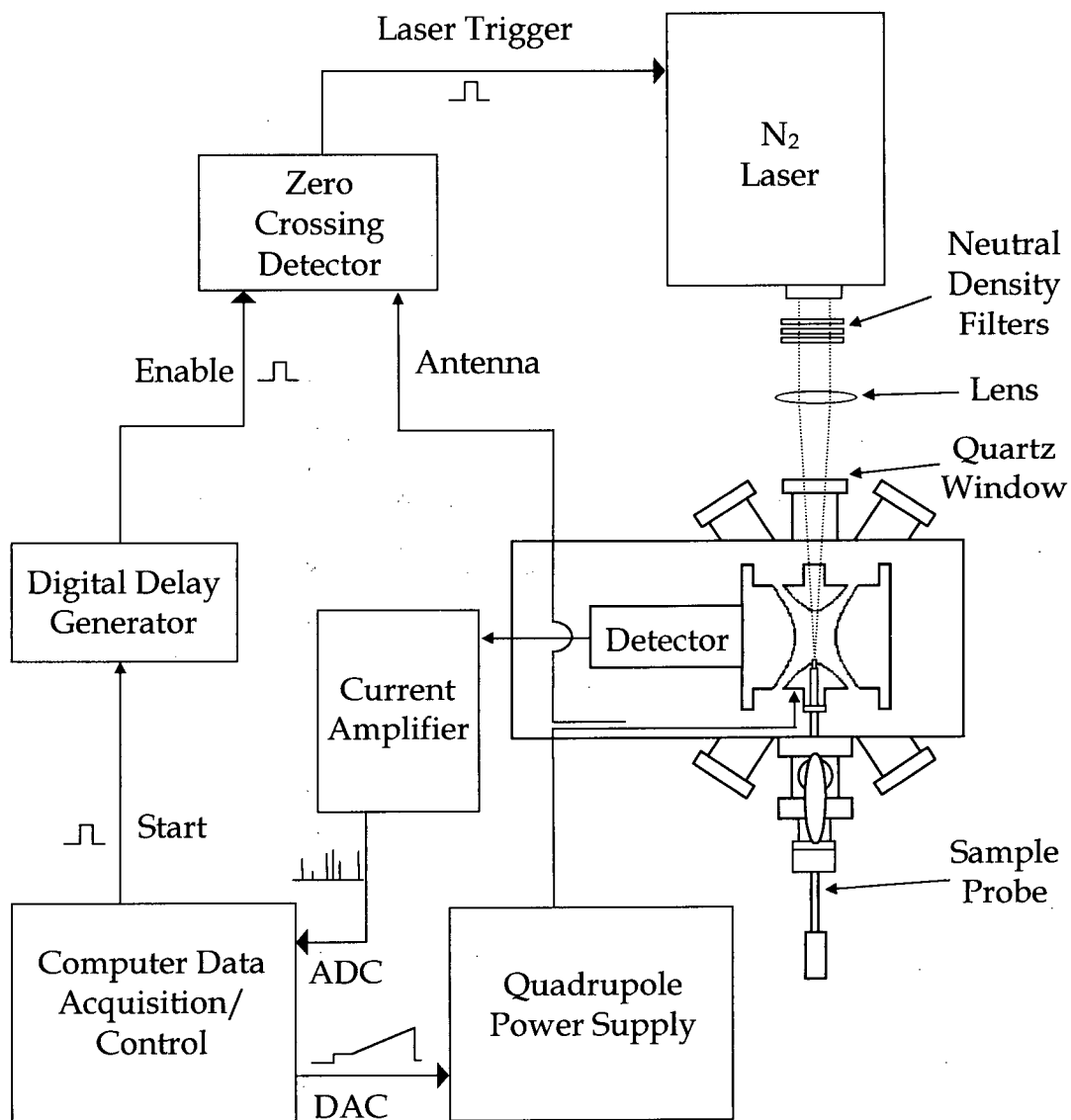


Figure 2.1 Schematic diagram of the laser desorption ion trap mass spectrometer.

washer at the base of the probe tip maintaining electrical contact between the two. The electron multiplier detector was mounted so that it was recessed into one end-cap, positioned as close to the trap center as possible. An electron gun filament assembly was located in the other end-cap to allow for calibration using electron ionization of perfluorotributylamine (FC-43). Unless otherwise noted, both end-caps were held at ground potential.

2.2 Electronics, Timing, and Operation

User-written programs running on a 133 MHz Pentium computer controlled the experiments. Instrument control and data processing software was written in Microsoft QuickBasic, version 4.5. The computer was equipped with an RC Electronics (Santa Barbara, CA) model ISC-16 analog-to-digital converter (ADC), a QuaTech (Akron, OH) PBX-721 data acquisition parallel expansion board, and a QuaTech DM12-10 digital-to-analog converter (DAC).

The RF quadrupole supply used was an Extranuclear Laboratories Inc. (Pittsburgh, PA) model number 011-1, modified for operation from 0.6-3.0 MHz. Capacitance matching was achieved using a High-Q Head model number 012-16, also from Extranuclear Laboratories. The maximum output of the RF supply was ~3000 V (measured zero-to-peak), and the frequency was tuned to 0.967 MHz. The amplitude of the RF potential was governed by the output of the DAC, which was sent to the "external command" connection of the quadrupole controller. The risetime of the DAC output is nearly instantaneous; the RF amplitude, however, does not also rise immediately from zero to its specified value. The risetime (10-90%) of the RF amplitude was measured with an antenna and an oscilloscope, and was determined to be ~800 μ s for a potential of 400 V.

A Stanford Research Systems (Palo Alto, CA) model SRS DG535 digital delay generator

was used to control the bulk delay between when the initial DAC command initiated the rise in the RF amplitude and when the laser fired. Short delays (< 1 ms) could be used so that the laser fired during the risetime of the RF, allowing for "dynamic trapping."^{8, 9} Dynamic trapping is discussed in detail in Chapter 4. Alternatively, longer delays (e.g. 5 ms) ensured that the amplitude of the RF potential had stabilized and was unchanging during the trapping process.

The trigger from the digital delay generator was sent to a zero-crossing detector built by the Electrical Services Shop (Chemistry Dept., U.B.C.) This device monitored the RF via an antenna, and, once enabled, detected the next positive going zero-crossing of the RF voltage. A trigger was sent to the laser after the zero-crossing was detected at a small adjustable delay relative to the period of the RF. This allowed for the laser firing time to be synchronized with the phase angle of the RF potential. A 400 MHz Tektronix (Wilsonville, OR) model TDS 380 digital oscilloscope was employed to correlate the delay setting of the zero-crossing detector with the phase angle at which the laser fired. This was accomplished by comparing the signal from the antenna placed near the ring electrode to the signal from a fast photodiode sampling a portion of the laser pulse. All connections were terminated into $50\ \Omega$ to ensure fast risetimes. The antenna signal was also corrected for the $+90^\circ$ phase shift resulting from the capacitive pick-up. Uncertainty in the phase measurements is due primarily to jitter in the laser firing time, which was measured to be no more than ± 30 ns, corresponding to a maximum phase uncertainty of $\pm 10^\circ$.

After the laser fired and the desorbed ions were initially trapped, the RF potential was held constant for a period to allow for the ions to be cooled by collisions with the helium buffer gas. Subsequent to the cooling period, the RF potential was ramped to generate a mass spectrum of the trapped ions by the mass-selective instability operating mode. The ejected ions were detected using an ETP (Sydney, Australia) model AF138 electron multiplier held at a high

negative potential (-1.7 kV or -1.8 kV, depending on the experiment). The signal from the detector was then amplified with a gain of 10^7 V/A by a Kiethley (Cleveland, OH) model 428 current amplifier. The rise time (equivalent to two times the RC time constant) of the current amplifier was always set to 10 μ s to provide low-pass filtering of the analog signal. Reduction of RF noise in the signal was thereby achieved without significant distortion of peaks in the mass spectra. The amplified and filtered signal was sampled by the ADC with a period of 4 μ s over the duration of the RF ramp. Figure 2.2 depicts the complete timing sequence for a single data acquisition run.

2.3 Laser and Optics

A PRA Laser Inc. (London, Ont.) UV-12 nitrogen laser was used for all the experiments. The pulsed energy output at 337 nm was ~ 1.5 mJ over 10 ns. A series of Oriel (Stratford, CT) neutral density filters was used to attenuate the laser energy, which was focused onto the tip of the probe holding the sample by a 30.00 cm focal length silica plano-convex lens from Newport (Irvine, CA). The lens was mounted on an x-y-z translation stage and was moved back and forth along the laser beam axis to find suitable focal conditions for the experiments. With the filter combinations used to collect the data presented in this thesis, the lens was positioned such that the laser was focused to a point slightly behind the probe tip (which was aligned flush with the inner surface of the ring electrode). By translating the lens back, a tighter focus of the beam could be realized leading to more ion production and increased fragmentation of the desorbed species.

The irregular beam profile of the nitrogen laser rendered precise determination of the area of the focal spot difficult. Microscopic inspection of the surface of a polythiophene film (see Chapter 3) after many thousands of laser shots showed wear on the surface in a roughly elliptical

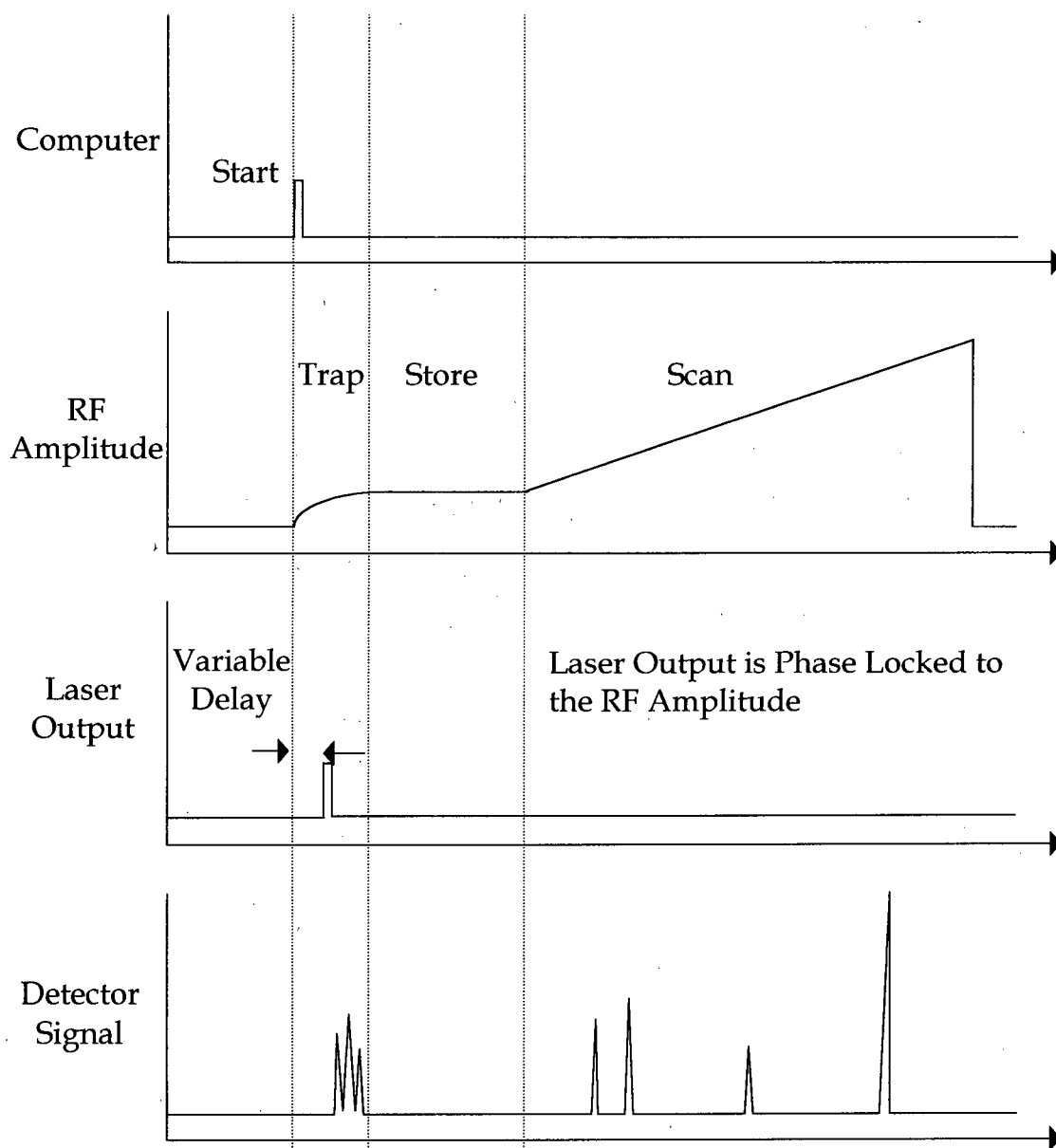


Figure 2.2 Timing diagram for single data acquisition sequence (not to scale). The slow risetime of the RF potential is exaggerated for illustrative purposes. The period for a complete cycle is ~200 ms.

shape. The ellipse had dimensions of approximately $400\text{ }\mu\text{m} \times 200\text{ }\mu\text{m}$, from which the irradiance could be estimated for a given pulse energy. Unless otherwise stated, once a set of conditions was found that provided a strong signal level, yet did not lead to significant performance degradation through space-charge effects, the lens position was fixed for the remainder of the experiment in question.

2.4 Pressure and Composition of Gas Inside the Vacuum Manifold

The manifold was evacuated by a Pfeiffer-Balzers (Mississauga, Ont.) turbomolecular pumping system, consisting of a model TPU 170 turbomolecular pump, a TCP 300 pump control system, and a DUO 010 B rotary vane pump. Pressure in the manifold was monitored with a Balzers model PKG 020 pirani-cold cathode gauge meter, equipped with a model IKR 020 cold cathode gauge head. An uncorrected base pressure of 8×10^{-7} mbar was the lowest that could be achieved for this system.

Before introducing the direct insertion probe into the manifold, it was first necessary to evacuate the sample introduction vacuum interlock. A Varian (Lexington, MA) model SD-90 rotary vane pump was used to rough out the small volume of air in the interlock before it was opened to the high vacuum region of the manifold. No special care needed to be taken to prevent oil vapor from back streaming into the sample introduction port, as had been the case in previous versions of the instrument.

Helium was introduced into the vacuum chamber during experiments to improve the performance of the ion trap. Pre-purified grade helium was used. A needle valve rendered coarse control only over the pressure within the manifold, but this was sufficient for the relatively high pressure operation of the ion trap (helium pressure ≈ 1 mtorr). For all the LD-ITMS experiments described in this thesis, measurements of pressure within the manifold were

made directly with the Balzers meter and cold cathode gauge head; however, cold cathode gauges are sensitive to gas composition and do not provide absolute pressure measurements. Accordingly, a capacitive manometer (Type 120 MKS Baratron® Vacuum Gauge) which provides absolute pressure measurements was used to calibrate the cold cathode gauge meter. The pressure readings reported in subsequent chapters have been corrected based upon the calibration data presented in Figure 2.3. A final note: the pressure within the ion trap was assumed to be equal to the measured ambient pressure within the manifold, as the volume between the trap electrodes was not sealed.

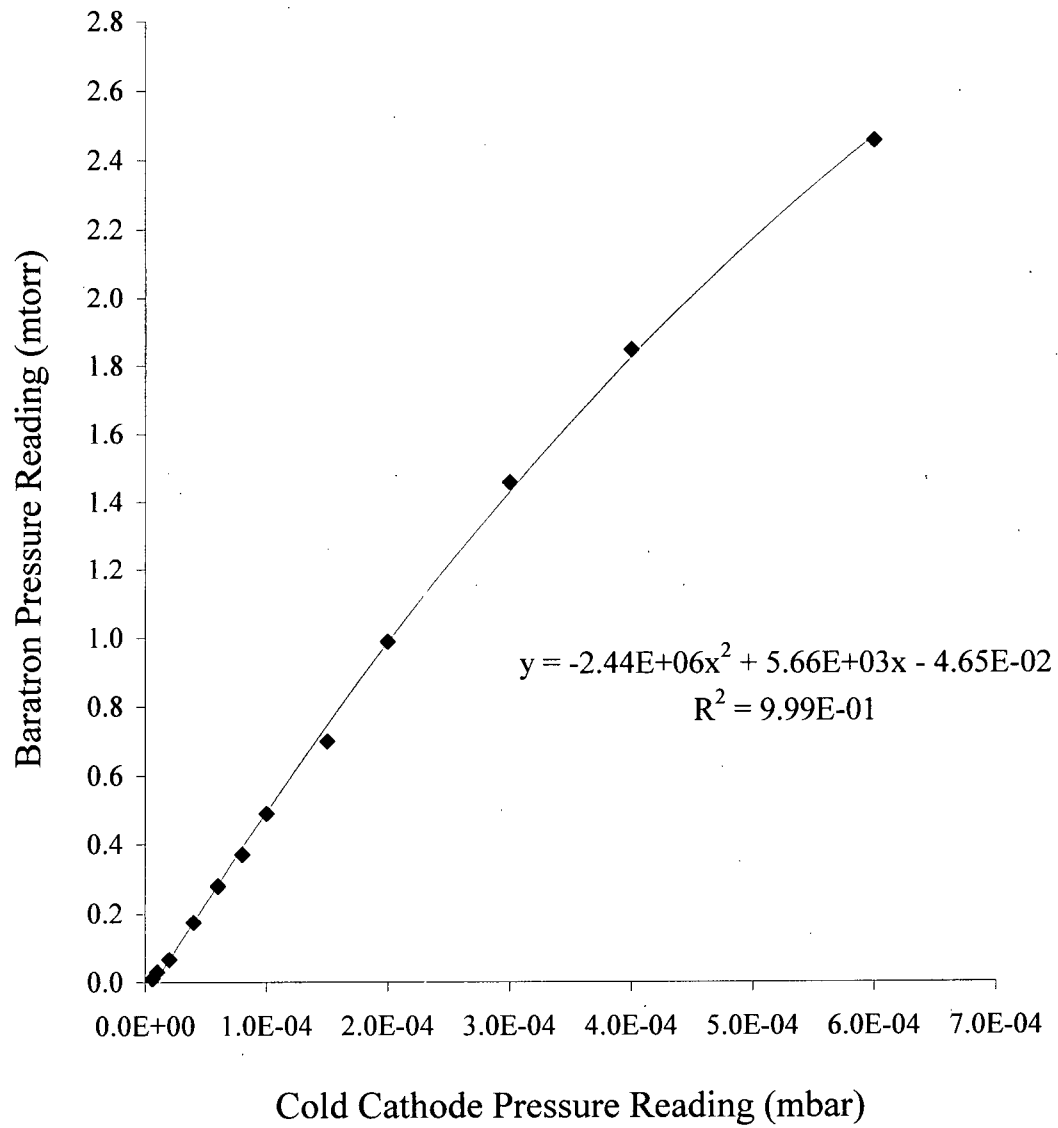


Figure 2.3 Calibration data for Balzers cold cathode meter and gauge (see explanation in text).

CHAPTER 3

SAMPLE PREPARATION FOR FUNDAMENTAL STUDIES OF LASER DESORPTION ION TRAP MASS SPECTROMETRY

3.1 Introduction

Previous experimental studies of the trapping of ions created by pulsed laser desorption have been hindered by the poor reproducibility in ion production between laser shots and between samples. Ideally, only the parameter being isolated for study should vary over the course of an experiment. It is presently not possible to eliminate the excessive shot-to-shot variation in ion production, so, to compensate for this uncertainty, the mass spectra from many laser shots must be averaged for each value of the parameter being varied. Thousands of shots may then be required to complete a parametric study of ion trapping using laser desorption. Since it is desirable to exclude all extraneous variables, it is best that the mean number of ions produced for each laser shot remain constant over the number of shots used in the experiment. If the mean ion production cannot be made to be even throughout, then at least it should have a reproducible decay trend, so that deviations can be corrected for.

The intensity and duration of ion production from laser desorption is strongly dependent on the local structure of the sample where the laser impinges on it. If the samples have irregular surfaces, then, when a fresh sample surface is exposed to the laser, there can be no way of predicting what the local structure at the laser focus will be. Consequently, when a new sample is used, or when a fresh surface is exposed by rotating the probe, there will necessarily be uncertainty in the signal level and decay trend when the sample has an irregular structure. The uncertainty in ion production attendant with laser desorption from imperfect samples makes it

difficult to determine the extent to which changes in signal from an ion trap can be attributed to changes in trapping efficiency when trapping parameters are varied.

In the past, samples for pulsed laser desorption ion trapping experiments have been either quaternary alkylammonium salt residues, or biological samples combined with a matrix (MALDI), dried on a probe tip. Neither of these sample preparation methods provide uniform surfaces. The objective of the work described in this chapter was to develop a sampling methodology that would reduce the uncertainty in ion production inherent in laser desorption ion trapping experiments. The absolute goal was to develop a sample film of uniform surface composition and structure that, when introduced on a probe into an ion trap, would yield long lasting, consistent signals of predictable intensity for a given set of laser and ion trap operating parameters.

Electrodeposition is a technique that has been used extensively for numerous applications requiring the fabrication of homogeneous films. For an electrodeposited film to be useful as a standard sample for laser desorption studies, it must provide abundant ions in the mass range of interest for the mass analyzer. Furthermore, it should be thick enough to provide a consistent signal level over many thousands of laser shots. Polythiophene was chosen as a sample to be tested, because it is an air stable conductive polymer which can be electrochemically grown to arbitrary thickness using a simple two electrode cell.⁸³ The polymer is grafted as an insoluble film to the anode as a result of the oxidation of the thiophene monomer. For a set thiophene concentration, film thickness can be controlled by varying the electrodeposition time and/or the cell potential.

For the experiments described here, macroscopically uniform polythiophene films were grown on the platinum tip of a laser desorption probe. This was accomplished by applying a potential between the probe and a counter electrode while the tip of the probe was submersed in

an acetonitrile solution containing thiophene and an electrolyte. The electrolyte was always a tetraalkylammonium salt having perchlorate as the counter-anion. Depending on the experiment, the alkyl group selected for the cation was either butyl or ethyl. A strong signal was readily observed due to the tetraalkylammonium cations embedded in the film. For thick films, it was found that a steady signal could be had from the electrolyte for over twenty thousand laser shots on the same position of the probe tip. A similar lack of signal decay was observed for multiple positions on the same film. The consistency and longevity of the ion signal resulting from laser desorption of a uniform polythiophene film are much greater than those typically obtained from simple solution residue samples.

3.2 Experimental

3.2.1 Polythiophene Film Preparation

After it was first realized that the residual electrolyte in polythiophene films could be used as an ion source for laser desorption mass spectrometry studies, efforts to optimize the formation of uniform films resulted in a host of electrodeposition parameters being experimented with. Some of the parameters that were investigated included concentration of thiophene, concentration of the electrolyte, electrodeposition time, and applied cell potential. For any set of solution concentrations, the thickness and degree of uniformity of the polythiophene films produced were found to depend on the applied potential and the time used for electrodeposition. Significantly, it was found that the cell potentials normally utilized for polythiophene film applications (≤ 2.5 V)⁸³ were not suitable for production of electrolyte enriched films for laser desorption studies.

It is believed that rapid polythiophene deposition causes solvent to be entrained in the film, ultimately providing the source of electrolyte cations to be utilized. The low cell potentials

typically used to create polythiophene films were found to have insufficient rates of polymer deposition. After deposition at 2.5 V for one hour, the tip of the probe was not coated thickly or uniformly, and there was very little signal due to electrolyte cations observed in the laser desorption mass spectrum of this sample. Higher voltages (≥ 2.7 V) were required to achieve rapid polymer deposition. Under these conditions excess polythiophene could be seen precipitating from the probe tip into the solution. At the higher potentials, rapid electrodeposition of polythiophene resulted in uniform coverage of the tip with a thick, opaque, brown/black film. For moderately high potentials in the range of 2.8-3.2 V, short deposition times (≤ 3 minutes) produced films that appeared perfectly uniform to the naked eye; examination with a video-microscope corroborated this observation. When introduced into the ion trap, however, it was found that the signal level from the electrolyte ions in these films decayed substantially even after only a few thousand laser shots. Longer deposition times at these potentials yielded ion signals for much longer periods, but the thick, crusty films produced lacked uniformity and often cracked or peeled off of the probe.

Higher voltages, up to 4.0 V, resulted in nearly instantaneous film formation. For short deposition times, highly uniform films could be obtained. For the range of potentials between 3.3 V and 4.0 V, an inverse relationship was noted between voltage and maximum deposition time that would provide a uniform film. For instance, at 4.0 V, deposition times longer than one minute resulted in a crusty ridge forming around the probe tip. In general, excessive deposition times were characterized by overly thick films that cracked or peeled when dried. The crusty films, though not as homogeneous as thinner films, did however provide consistent signals for a large number of laser shots.

A deposition time of 3 minutes at 3.5 V was empirically determined to yield a suitable compromise between film uniformity and signal level. The films produced under these

conditions yielded strong, consistent signals over tens of thousands of laser shots, and were perfectly uniform to the eye. Before rinsing with acetonitrile, microscopic observation showed these films to be coated with a thin electrolyte residue. The underlying thiophene surface appeared highly uniform with some small bubbles. After rinsing, the surfaces of these films were observed upon drying to crack slightly and form minute craters as the trapped solvent escaped. To the naked eye, there was no difference between the films before and after rinsing. The absolute signal levels obtained between rinsed and unrinsed films were found to be very similar, indicating that the electrolyte surface residue present before rinsing did not contribute significantly to ion production. The unrinsed films had a higher degree of uniformity, and were found to give more reproducible signal behavior when multiple positions from the same film were probed with the laser.

The observations recorded above suggest that a relatively high voltage is necessary to trap the solvent which provides the source of electrolyte ions; however, if the combination of deposition time and potential is too great, then a reduction in uniformity will ensue because, apparently, evaporation of excessive solvent causes the film to crack and crater. A compromise must be made in selecting deposition parameters that allow for sufficient solvent to be trapped so that the polythiophene will be enriched with electrolyte ions, but that do not ruin the uniformity of the film.

The polythiophene films used in the sample characterization experiments reported on in this chapter were electrodeposited from acetonitrile solutions containing 0.25 M thiophene (Sigma, St. Louis, MO, USA) and 0.05 M tetrabutylammonium (TBA) perchlorate (Sigma). Prior to deposition, the solutions (10 ml) were first deoxygenated for five minutes by gently bubbling nitrogen through them. During this period, the probe tip was prepared by polishing with 5 μm grit polishing paper, followed by rinsing with methanol, then acetonitrile. Following

deoxygenation, the probe was inserted into the cell and electrical connection was established between the two electrodes and the DC power supply. A gentle stream of nitrogen was held over the solution for the duration of the electrodeposition period. All of the polythiophene data presented here came from an unrinsed film that was deposited at 3.5 V for 3 minutes.

Figure 3.1 is a schematic of the cell used to prepare the polythiophene films. The cell consists of a glass tube with Teflon™ stoppers at each end. The top stopper holds the probe firmly in place, and it also has a hole through which a needle is introduced to admit the nitrogen gas required to deoxygenate the solution. The bottom stopper has a concentric stainless-steel disk counter electrode press fit into it. This geometry was chosen so that a radially symmetric electric field would result when a potential was applied between the probe tip and the counter electrode.

3.2.2 Laser Desorption Ion Trap Mass Spectrometer

For the experiments discussed here, the home-built ion trap mass spectrometer described in Chapter 2 was used. The “dynamic trapping”^{8, 9} mode of operation was employed for these experiments. The bulk delay between when the RF potential amplitude started to rise and when the laser was triggered was 500 μ s. Since the risetime of the RF potential was 800 μ s, ions were created when the amplitude of the RF had yet to reach its full value, which was 400 V. The supposed principle behind dynamic trapping is that the relatively low potential at the time the ions are created allows them to more easily reach the trap center. The RF potential then continues to rise creating a deeper potential well, which has been claimed to enhance the trapping efficiency. Preliminary experiments, however, did not show any enhancement in sensitivity for this method relative to simply using a lower RF amplitude and a longer delay such that the amplitude reached its plateau value. The purported mechanism of dynamic trapping is a

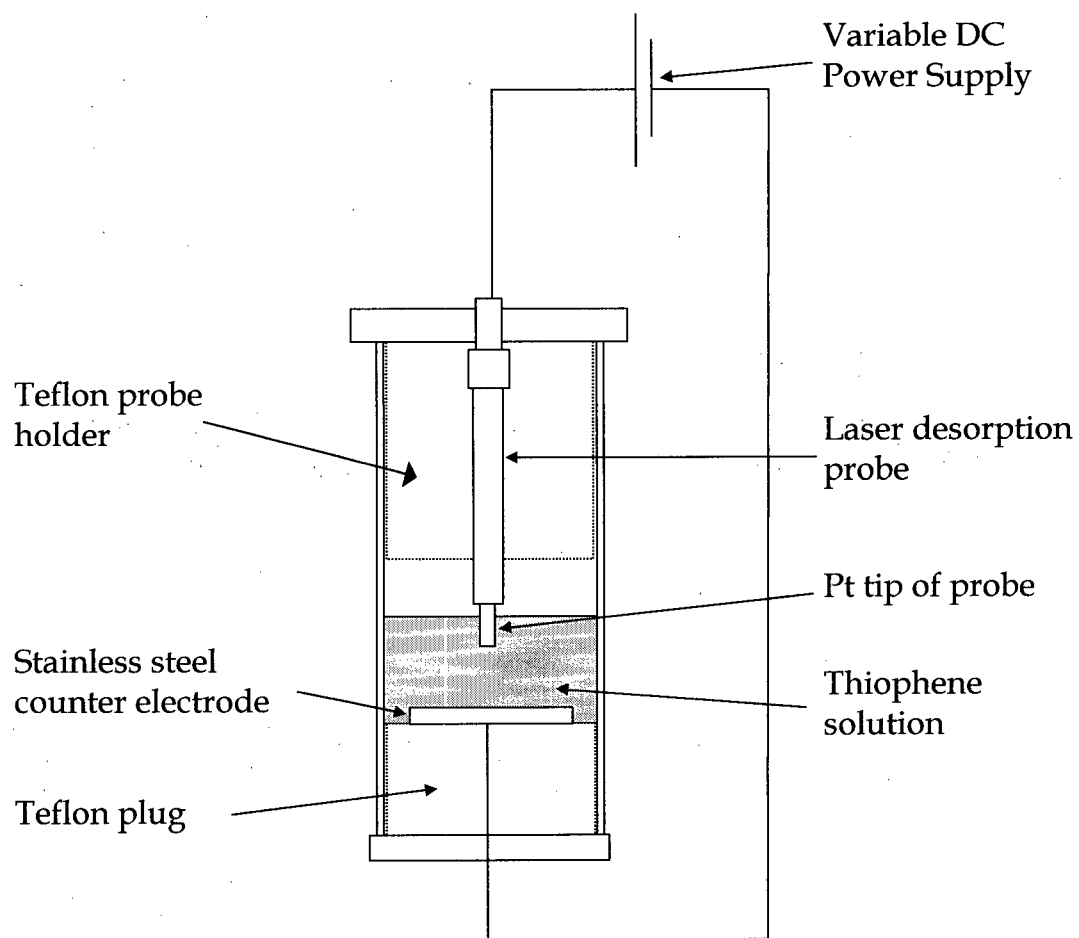


Figure 3.1 Schematic of the electrochemical cell used for deposition of polythiophene films onto the tip of the laser desorption probe. Only the extreme tip is coated because the rest of the probe is insulated.

contentious matter which is discussed further in the next chapter.

The zero-crossing detector enabled the laser firing to be synchronized with the phase of the RF potential, an essential step in optimizing trapping efficiency. The small delay between the positive zero-crossing and the laser trigger was adjusted until the signal from TBA ions was maximized. The experiments discussed in this chapter were performed prior to having accurately calibrated the delay setting of the zero-crossing detector with respect to the phase angle at which the laser fired. The absolute value of the phase angle at which the data presented below was acquired is thus unknown.

Subsequent to the laser firing, the RF amplitude continued to rise until it reached its plateau of 400 V. The potential was held at this level for 5 ms to allow for collisional cooling to occur, then it was ramped to 3000 V to eject the trapped ions and to generate a mass spectrum. Next, the amplitude was set to zero to clear the trap of any remaining ions, and the cycle was repeated as indicated in the discussion.

For laser desorption of polythiophene films, neutral density filters were used to attenuate the laser energy to $\sim 50 \mu\text{J}$, leading to an estimated irradiance of $8 * 10^6 \text{ W/cm}^2$. With the focal conditions used for all these experiments (see Section 2.3) only very weak ion signals could be obtained for the crystalline electrolyte residue sample. Ion signals comparable to those observed for the polythiophene films were realized for the residue sample by removing two of the three filters used to attenuate the laser energy. In this case, the energy incident on the residue sample was increased to $\sim 200 \mu\text{J}$ per pulse, and the calculated irradiance becomes $\sim 3 * 10^7 \text{ W/cm}^2$.

The lens was positioned so that the focal area of the beam was off the center of the probe tip. This enabled a fresh sample surface to be exposed to the desorption laser whenever the probe was rotated. Care was taken to prevent overlap of successive sample areas exposed to the

laser beam when the probe was turned. With the beam area used here, six positions on the sample tip could be interrogated with minimal overlap between them.

A bath gas of He at 3 mtorr (corrected, as discussed in Section 2.4) was utilized for all the experiments described in this chapter.

3.3 Results and Discussion

Polythiophene films were found to yield strong ion signals from the residual electrolyte trapped within them. Figure 3.2 is a positive ion mass spectrum obtained by laser desorption from a polythiophene film in the ion trap. The base peak at m/z 242 is the molecular ion for the TBA electrolyte. Other prominent peaks in the spectrum are due to fragment ions resulting from loss of alkyl groups, followed by rearrangement in some cases. Structural assignments for the peaks in the desorption spectra of TBA have been made previously.^{84, 85} The source of the major peaks was confirmed to be TBA by comparing the spectra obtained from the polythiophene films with a spectrum collected from a sample prepared by directly depositing a drop of electrolyte solution onto the polished probe tip. The same peaks were observed for both the polythiophene sample and for the pure electrolyte residue sample.

The spectrum in Figure 3.2 was obtained by averaging the spectra from one hundred consecutive laser shots. Specifically, this mass spectrum is from the final hundred shots of an experiment evaluating the signal decay that occurs during twenty thousand laser shots on the same position of a polythiophene film. The height of the peaks relative to the noise in the baseline of the spectrum presented indicate that the ion production from the film is substantial even after twenty thousand shots.

Figure 3.3 is a plot of the peak area versus shot number at the same location on the film for the molecular ion at m/z 242, and for the fragment ions at m/z 142 and 100. Each point on

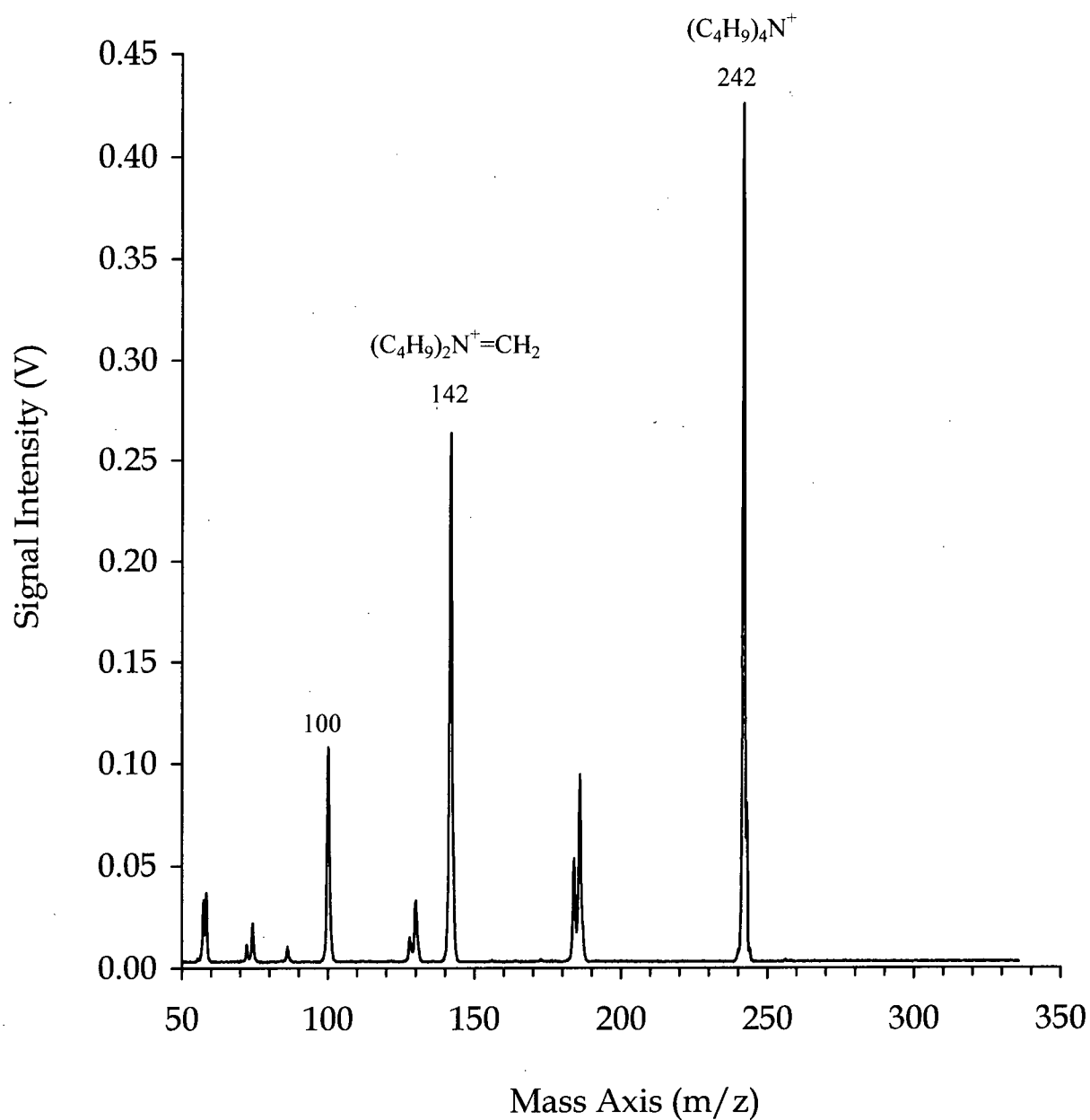


Figure 3.2 Mass spectrum of TBA obtained by laser desorption of a polythiophene film. The spectrum was obtained by averaging the spectra for one hundred laser shots on the same spot on the film. The film had previously been exposed to nearly twenty thousand shots at the same position.

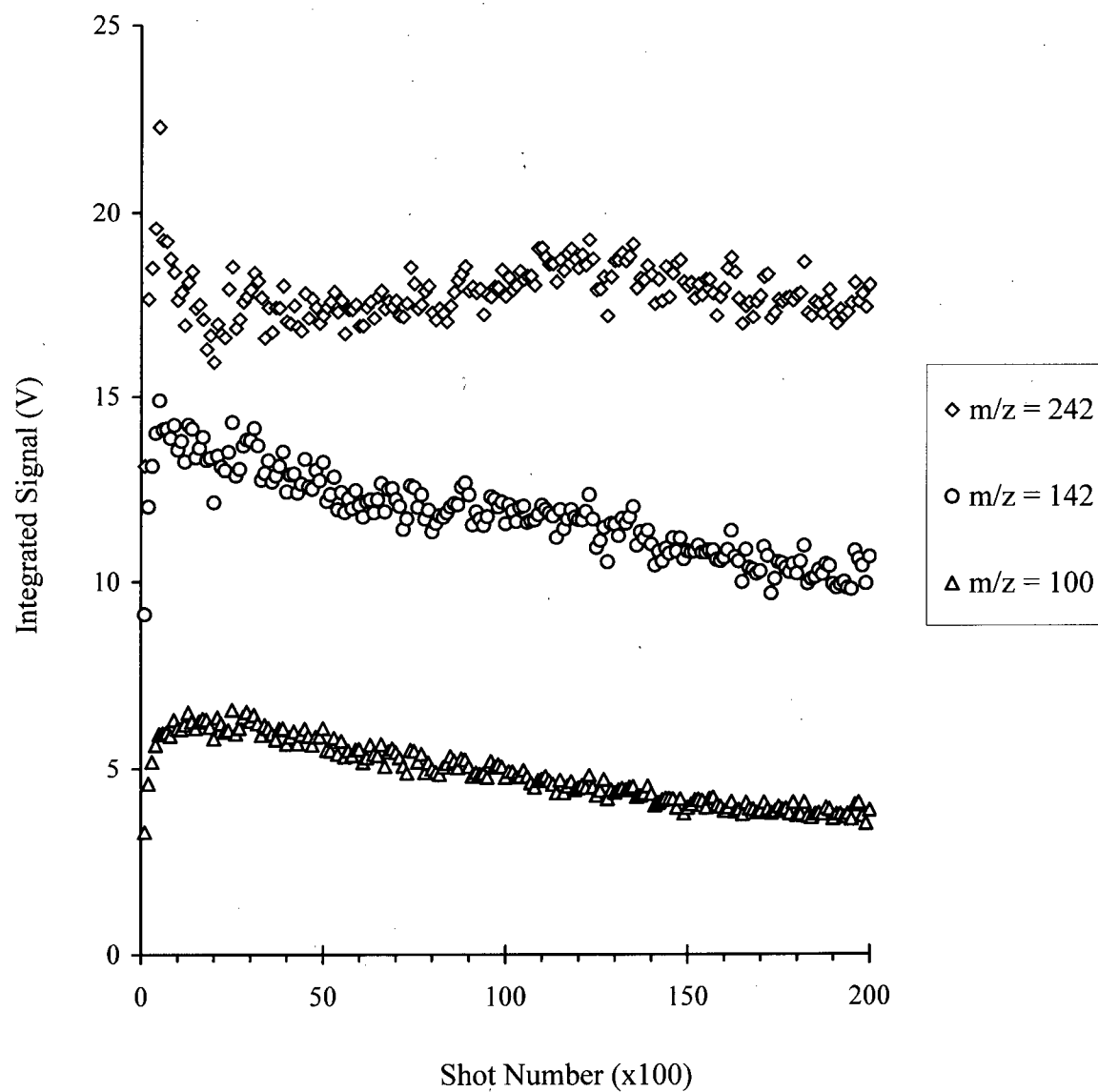


Figure 3.3 Decay trend in TBA ion production over twenty thousand laser shots on the same position of a polythiophene film. The mean molecular ion signal level remains essentially unchanged over the period of data collection.

the plot represents the average of one hundred laser shots. Over twenty thousand shots, the production of the molecular ion remains essentially constant, demonstrating the consistency and the duration of ion production that is possible from laser desorption at a single location on a polythiophene film.

Another desirable property that a sample film should have to render it suitable as a standard for laser desorption experiments is consistent behavior between positions on the sample. Assuming that only a finite number of ions can be produced from each position on a sample film, then, when performing experiments regarding the trapping efficiency of laser desorbed ions, it will be necessary on occasion to rotate the sample probe so that a fresh film surface can be exposed to the laser. Thus, it is best that there be confidence that the decay trend in ion production over a number of laser shots is the same for all positions on a sample. To test the extent to which polythiophene films can meet this requirement, the mass spectra from ten thousand laser shots on each of six discrete positions on a film were collected. Ten thousand spectra were obtained from one position, then the probe was rotated one sixth of a turn to expose a new sample surface. The decay trend for the TBA molecular ion for six positions on the film is displayed in Figure 3.4(a). Each point represents the average integrated peak height from one hundred individual mass spectra. Over ten thousand shots, it can be seen that for each of the six positions the mean signal level remained effectively constant, although the absolute signal level varied slightly between positions. The observed deviation in absolute signal level between positions can likely be attributed to microscopic irregularities noted in the film surfaces; however, the degree of uniformity in the surface structure obtained with the conditions described above clearly suffices to provide consistent behavior.

To compare the performance of a polythiophene film to a conventional laser desorption standard sample, the same experiment was repeated with a solution residue sample. The residue

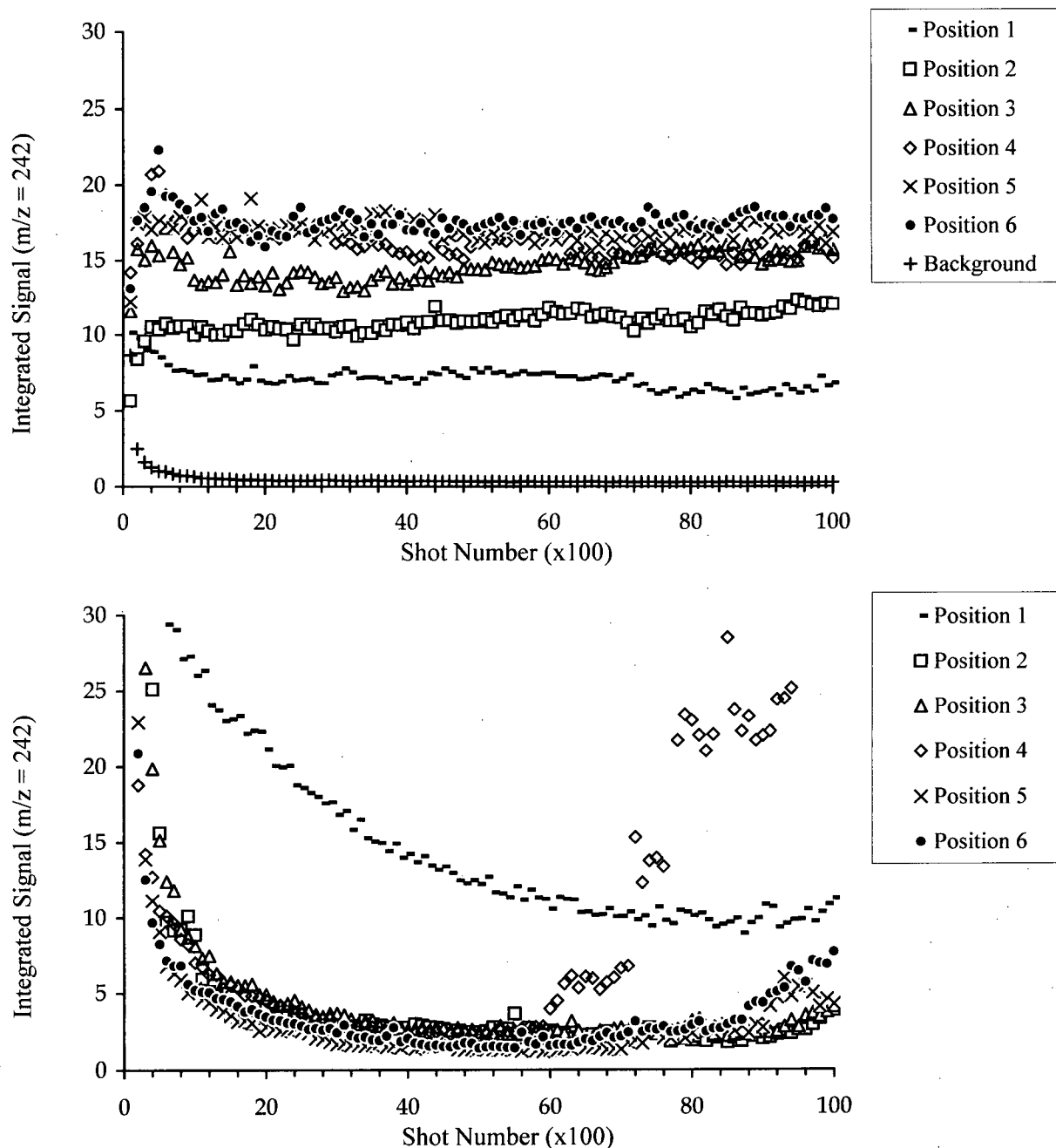


Figure 3.4 (a) Decay trend in production of TBA molecular ions by laser desorption over ten thousand shots at six discrete positions on a polythiophene film. There is no significant decay evident for any of the positions analyzed. (b) Decay trend for six positions on an inhomogeneous crystalline solution residue film. The results obtained for positions one and four are dramatically different from those of the other positions.

sample was prepared by depositing an excess of electrolyte solution onto the probe tip. Upon drying, a crystalline film remained, but the tip was not covered uniformly. Figure 3.4(b) illustrates the inconsistent ion production that resulted. Although the magnitude of the signal was initially substantial for all six positions probed, the signal levels decayed rapidly through only one thousand shots. The anomalous behavior recorded for positions one and four is characteristic of the performance normally experienced when solution residues are used as laser desorption samples. Such irregular sample surfaces are poorly suited for fundamental ion trapping studies utilizing laser desorption sampling, because the attendant uncertainty in ion production introduces an extraneous variable to the experiments.

3.4 Complication in Film Preparation Technique

Further experience with polythiophene film preparation has demonstrated that the technique described above is imperfect. The principal difficulty arises from inconsistent production of the films from a specified voltage and deposition time. The age of the solution appears to be a dominant factor in determining the consistency of the preparation. (The films described above were made from a fresh solution made the day of the experiments.) It has been repeatedly observed that older solutions require a greater voltage to produce suitable films than new solutions. One likely variable that depends upon age, if the solution is exposed to air, is water content. Efforts to eliminate water content as a variable (storing the thiophene and electrolyte solutions over molecular sieves and under a dry nitrogen atmosphere) did not eliminate the inconsistency in the preparation method. Presently, the origins of this problem are not well-understood. Despite this complication, it has nevertheless been the author's experience that polythiophene films are far better suited to be standards for fundamental ion trapping studies than all others that have been tried in this laboratory.

CHAPTER 4

A CRITICAL INVESTIGATION OF THE EFFECTS OF THE AMPLITUDE AND PHASE OF THE RF POTENTIAL IN LASER DESORPTION ION TRAP MASS SPECTROMETRY

4.1 Introduction

The sensitivity of ion trap mass spectrometry using laser desorption is dependent upon the trapping efficiency of the instrument. For laser desorption, it is known that the phase and amplitude of the RF potential applied to the ring electrode at the time of the laser firing are critical parameters governing trapping efficiency. It is remarkable that in a considerable body of literature, no consensus exists regarding the effects of these parameters on the efficacy of trapping externally generated ions. New laser desorption ion trap mass spectrometer data have been acquired that clarify some of the discrepancies present in the literature. It will be argued that the decrease in signal intensity that is commonly observed to accompany higher RF potentials is not due to the presence of a static "potential barrier" that injected ions are unable to penetrate. Rather, the evidence indicates that the apparent decrease in trapping efficiency is an artifact of fragmentation at high RF potentials as the ions undergo energetic collisions with the background gas. In this chapter, differences between models of trapping behavior that have been proposed in the literature and the present experimental results will be discussed.

To establish the extent that incongruities exist in the literature of trapping injected ions, it is necessary to present a summary of some findings that have been published recently. Firstly, there have been studies which indicate that it is desirable to have a relatively high q_z value to trap

injected ions. In a review text for ion trap instrumentation,⁸⁶ two such instances are cited. The first case describes an experiment where N_2^+ ions created in an external source were injected through one end-cap electrode into an ion trap at varying RF voltages.⁸⁷ The trapped ion signal intensity was found to be greatest for $q_z = 0.44$ ($a_z = 0$, as is implicit for all the discussions in this thesis). Nearly identical results were obtained independently for injection of Ar^+ (trapping efficiency best at $q_z = 0.43$).⁸⁸ The second experiment described in the review text, however, involved a completely different instrumental arrangement. For $^{56}Fe^+$ ions created by laser desorption from a stainless-steel probe inserted into the trap ring electrode, the sensitivity (proportional to the trapping efficiency) was found to be greatest at $q_z = 0.62$. Although the results of these investigations are not identical, they do suggest that injected ions may be best trapped at an intermediate value of q_z between the minimum and maximum permissible values of 0 and 0.908. This is qualitatively in agreement with a reviewer's conclusion that the efficiency for trapping injected ions appears to be maximized when the potential well is deepest (around $a_z = 0$ and $q_z = 0.5$).⁸⁷

In the laser desorption experiment cited above, however, it was noted that the expected trend was not followed when repeated for molecular ions of larger mass. For protonated spiperone at m/z 396, very few ions were detected when the RF amplitude was set greater than that corresponding to $q_z = 0.34$. No detailed explanation was provided for the discrepancies between the two sets of experimental results. It was suggested that the differences could be attributed to a decrease in trapping efficiency arising from a reduction in "trapping volume"* at

* "Trapping volume" is often used loosely to describe the space between the electrodes of the ion trap, and as such has no bearing on discussions of trapping efficiency. Strictly speaking, this term refers to the volume between the trap electrodes that a single ion of zero initial kinetic energy, unaffected by space charge, may originate within and retain a stable trajectory. Trapping volume decreases as q_z is raised.

higher RF amplitudes, but this is incorrect: trapping volume is the same for ions of the same q_z , regardless of mass,⁸⁹ and, therefore, ions of disparate mass should show identical trends of sensitivity as a function of q_z if trapping volume is the primary factor determining trapping efficiency.

The decrease in signal intensity for molecular ions reported for laser desorption at high RF amplitudes is in fact a commonly observed experimental trend. In order to rationalize these observations, another model of the trapping process based upon Dehmelt's pseudopotential well approximation has been proposed.^{8, 9} The crux of the proposed model is that there is a "potential barrier" that ions must penetrate in order to enter the trapping volume and thus have a chance of being contained. At lower applied potentials, the "barrier" is smaller so that ions can penetrate the trap, while as the potential increases, the barrier to admission increases, eventually causing the ions to be reflected at the entrance of the trap.⁹ Similar arguments have been used to describe the trapping process elsewhere in the literature.^{14, 18, 22, 34, 38}

To overcome the limitation to trapping efficiency imposed by the supposed "potential barrier," several researchers have devised new methods of operation for the ion trap which have been stated to provide substantial enhancement of sensitivity for laser desorption.^{8, 9, 14, 18} Citing the inability of the injected ions to penetrate the RF field at higher amplitudes, the developers of the new methods exploit the slow risetime of the RF potential from zero to the desired level. These methods are collectively referred to as "dynamic" because the amplitude of the RF potential is rapidly changing during the time of ion creation/injection. Ions are created or injected at a short delay after the RF controller initiates the rise of the potential, such that the potential "barrier" is low and ions are able to penetrate the trapping field. As the ions traverse the trapping volume, the "barrier" continues to rise, causing the ions to be reflected and trapped before being lost at the electrode opposite from which they originated.

The two models described above presuming to provide the best method for trapping ions are clearly inconsistent. The first model discussed here suggests that a deep potential well is desirable to maximize trapping efficiency. The "barrier" model, though, implies that a deep potential well excludes ions from the trapping volume, because ions are unable to penetrate the strong electric field. The situation is not at an impasse, however, because the two models have been developed for experiments which are significantly different: data supporting the first model were obtained when stable species were being injected and trapped, whereas the barrier model arose from experiments trapping larger, fragile molecular species. Both models neglect the effects of fragmentation on the observed ion signal. For the experiments described first, N_2^+ , Ar^+ , and $^{56}Fe^+$ are species which will not dissociate upon collisions with background gases in the ion trap, so fragmentation was not a concern. Spiperone and the other species desorbed in the experiments that were instrumental in applying the "potential barrier" model to the trapping process are relatively fragile molecules which are susceptible to collisional decomposition within the trap. It is informative that elsewhere in the literature fragmentation of ions upon injection into the trap has been reported to be an important experimental consideration.⁹⁰⁻⁹⁵ Furthermore, the degree of fragmentation has been shown to be directly related to the amplitude of the RF potential applied during injection. This factor reconciles some of the differences between the two sets of observations. Collisional fragmentation has even been used as a means to obtain structural information of the analyte.⁹⁵ Evidence taken from the literature alone thus suggests that neglecting to include fragmentation as an important effect when describing the trapping process could lead to erroneous interpretation of the data.

Another critical parameter that is not explicitly considered in the above models is the relationship between the time of ion injection and the phase angle of the RF potential. Again, theoretical and experimental evidence exist that demonstrate the significance of this factor,^{9, 13,}

^{34, 35, 38} although there remains some uncertainty regarding its ramifications.¹⁸ The first model only describes the optimum q_z value for trapping, and makes no mechanistic assumptions. The “potential barrier” model, however, implies a static situation in which ions will always be repelled by an uphill potential barrier. This argument appears to have first been proposed for ion trapping with an FT-ICR instrument that utilized DC potentials to retard energetic laser desorbed ions.⁹⁶ It is incorrect to apply a model based upon static barriers to the quadrupole ion trap, though, because a dynamic RF field is employed. When created at the ring electrode, positive ions only face a barrier to entrance into the trap when the potential at the ring is negative. Similarly, positive ions injected through an end-cap electrode will be repelled from the trap center only when the potential applied to the ring is positive. It is ludicrous to suggest, for instance, that a positive ion formed at the ring electrode when the RF phase angle is 0° will be unable to penetrate the trapping volume.** The hypothetical ion in question will initially be accelerated away from its point of origin for an entire half cycle of the RF period, regardless of the amplitude of the potential.

Some of the inconsistency regarding the best conditions for trapping ions created outside of the trapping volume, specifically for laser desorption, stems from a dearth of reliable experimental data regarding the effects of q_z and phase on LD-ITMS signal intensity. As discussed at length in Chapter 3, there are substantial difficulties inherent to the acquisition of quantitative laser desorption data. For most sample types, ion production, and thus signal intensity, varies dramatically between laser shots. To obtain a meaningful measure of the signal intensity resulting from even one pair of q_z and phase values, it is thus necessary to repeat an experiment many times. Thousands of laser shots may then be required to complete a parametric

** Zero degrees is defined here to be the phase angle at the positive going zero-crossing of the RF potential.

study testing the effects of phase and q_z on trapping efficiency. There has never been a standard sample utilized for LD-ITMS that could reliably provide stable ion production over the requisite large number of laser shots. Hence, parametric studies of the trapping process for laser desorbed ions have been hindered. Electrodeposited polythiophene films, though, are a recently developed sample type capable of providing steady ion production for thousands of laser shots.^{83, 97}

In the remainder of Chapter 4, new LD-ITMS data will be presented, from which it will be argued that the decrease in molecular ion signal at higher q_z values for a given ion is not due to the presence of a large, static “barrier” that the ions are unable to penetrate. Rather, experimental evidence confirms that this decrease can be attributed primarily to fragmentation of the molecular ions as collisions with the background gas become increasingly energetic at higher applied potentials. The phase dependence of trapping efficiency is also demonstrated conclusively. The significance of these findings will be discussed with respect to the models proposed previously for the trapping process, and some questions will be posed regarding the relative efficacy of the various trapping methods.

4.2 Experimental

4.2.1 Laser Desorption Ion Trap Mass Spectrometer

The home-built instrument described previously was used for the laser desorption ion trap experiments presented in this chapter. Laser desorption mass spectra were collected as a function of the amplitude (q_z) and phase angle of the RF potential used to trap the ions. The RF potential amplitude for each trial was calculated from the desired q_z value for the m/z of interest. An experimental sequence began with the RF potential being set by computer. Following a 5 ms delay to allow for the RF amplitude to stabilize at the level for trapping, a trigger was sent to the zero-crossing detector. Subsequent to the detection of the next positive going zero-crossing, a

trigger was sent to the laser at a small variable delay. After the laser firing event, the trapping potential was held constant for 10 ms to allow for any trapped ions to collisionally cool. The potential was then reset for $q_z = 0.1$ for an additional 10 ms of cooling regardless of the q_z used for trapping. This was to maintain a constant period for each data acquisition cycle. The mass-selective instability mode of operation was employed next by ramping the potential from the value determined by $q_z = 0.1$ for the m/z of interest to the maximum amplitude of the supply ($\sim 3000 V_{o-p}$). The ejected ions were detected using the electron multiplier held at -1.7 kV. During the ramp, the signal from the detector was amplified and sampled as detailed in Chapter 2. The RF amplitude was then set to zero to clear the trap, and the data was saved by the computer.

For each trapping q_z value, data were acquired for 25 phase angles spanning one RF cycle. To compensate for random fluctuations in ion production between laser shots, 30 spectra were acquired for each phase angle at a rate of five spectra per second. The maximum q_z used for a particular experiment varied (up to a maximum of 0.9), while a minimum of $q_z = 0.1$ was used for all trials described here. The experiments were always carried out starting at the highest q_z and lowered with a step size of 0.1. This was to ensure that the observed increase in molecular ion signal at lower q_z values could not be attributed to signal decay due to sample erosion after thousands of laser shots.

The laser and optical components were described in Section 2.3. Here, the neutral density filters were used to attenuate the nitrogen laser energy output at 337 nm to $\sim 30 \mu J$ over 10 ns. The lens focused the laser pulse to an ellipse of approximately $400 \mu m \times 200 \mu m$, leading to an estimated irradiance of $\sim 5 * 10^6 W/cm^2$ at the surface of the probe tip.

An ambient bath gas of helium held at 1 mtorr was utilized. The pressure in the manifold

was directly measured with the Balzers cold cathode gauge and meter, then the reading was corrected as described in Section 2.4.

4.2.2 Sample Preparation

Thousands of laser shots are required to carry out parametric studies of trapping efficiency for a particular species as a function of RF amplitude and phase angle. It is thus necessary that the mean number of ions produced per shot remain constant over the duration of the experiment, so that trends in signal levels can be attributed to ion trap parameters, and not to sampling artifacts. Electrodeposited polythiophene films^{83, 97} provide suitable ion production stability and were used as samples for all the experiments. Residual supporting electrolyte embedded within the films was the source of positive ions for the LD-ITMS experiments. Tetraethylammonium (TEA) and tetrabutylammonium (TBA) perchlorate were both used as supporting electrolyte. TBA was used for the first experiments, then TEA was used so that the effect of ion mass on the trapping process could be observed.

The solutions used to electrodeposit the polythiophene films consisted of 0.25 M thiophene (Sigma, St. Louis, MO, USA) and 0.10 M supporting electrolyte in acetonitrile. The potential between the platinum probe tip and the counter electrode was ~3.5 V, and a suitably thick film could be deposited in 2-3 minutes.

4.3 Results and Discussion

Figure 4.1 shows a series of LD-ITMS spectra of TBA acquired as a function of phase and q_z of the molecular ion. The major peaks in the spectra correspond to the TBA molecular ion and decomposition products. The effect of the low mass cut-off is apparent in the spectra acquired at higher RF amplitudes. For instance, in Figure 4.1(c) the potential is too high for the fragment ions with $m/z < 80$ to have stable trajectories within the trap: their q_z values are above

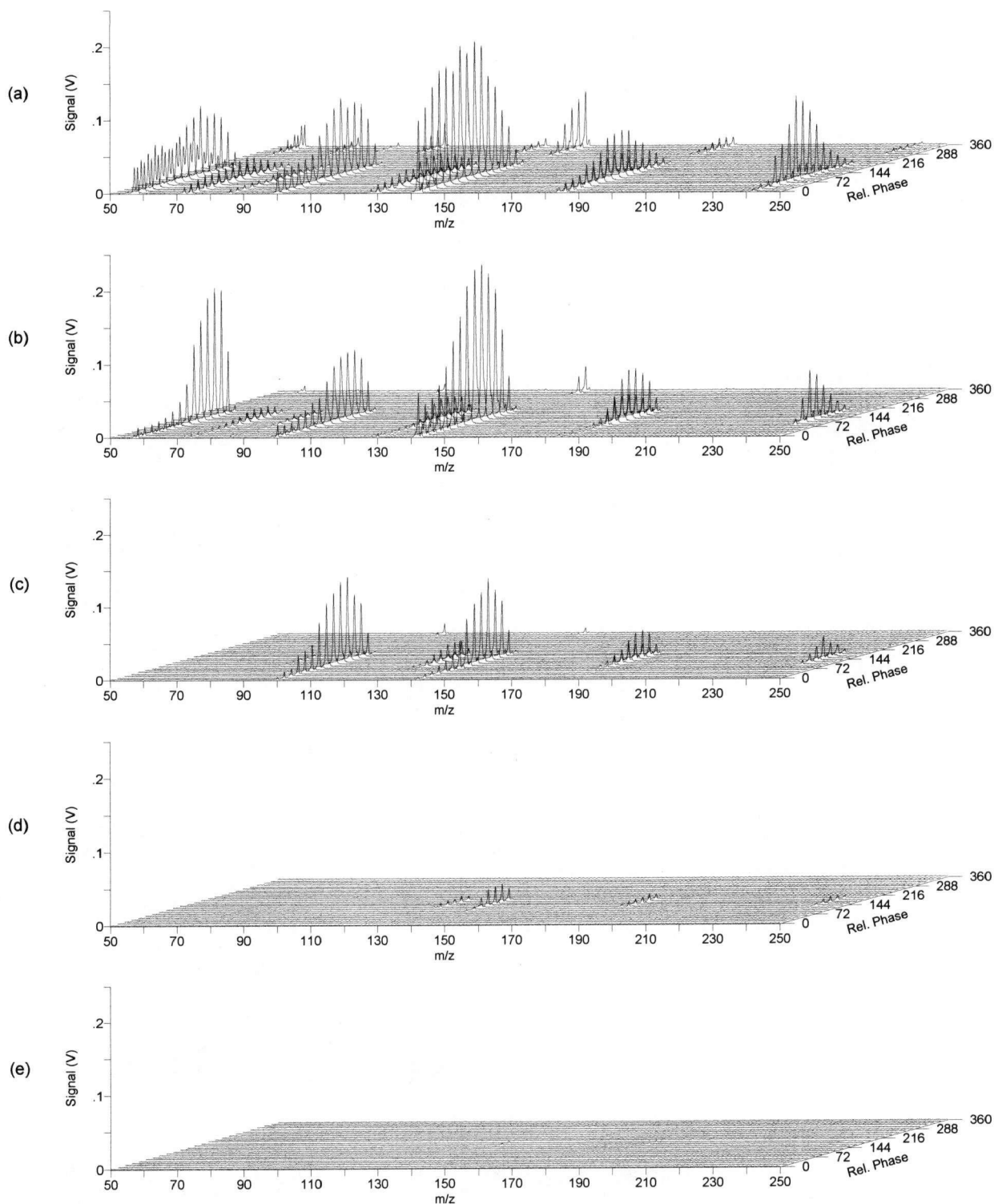


Figure 4.1 Laser desorption mass spectra of tetrabutylammonium (TBA) acquired as a function of the phase angle at the time of the laser pulse and q_z for the molecular ion (m/z 242). Plots (a)-(e) correspond to $q_z = 0.1$ -0.5, respectively, and the step size is 0.1. The calibration of the z -axis is relative. Unless indicated otherwise, all other plots with a phase axis are calibrated absolutely.

the exclusion limit of 0.908. In Figure 4.1(d), the low mass cut-off has risen to m/z 107, and the prominent signal at m/z 100 has also disappeared. Another conspicuous feature of Figure 4.1 is that with increasing RF amplitude the abundance of the TBA molecular ion diminishes relative to that of its fragments.

From the mass spectra displayed in Figure 4.1, it is apparent that the m/z 242 signal suffers a significant decrease in intensity as q_z rises. This type of behavior has been observed by others, and has been attributed to the inability of the desorbed ions to penetrate the hypothesized “potential barrier” that increases in magnitude as q_z increases for a given ion. The data, however, indicate that this trend is not consistent with the response for other ions in the spectra. For example, the signal intensity from the TBA fragment ion with m/z 142 can be seen to increase as q_z for the molecular ion changes from 0.1 to 0.2. Recall that q_z is inversely related to m/z for a constant amplitude of RF potential. Thus, when $q_z = 0.1$ for m/z 242, q_z for m/z 142 is $0.1 * 242/142 = 0.17$. Figure 4.2 exhibits the dependence of the integrated signal from the m/z 242 and the m/z 142 ions on the phase of the RF potential as a function of their respective q_z values. The intensities of these ions clearly follow different trends. To confirm this behavior, an experiment was undertaken in which the RF potentials were determined by the q_z values tuned for m/z 142. The results of this study are illustrated in Figure 4.3. For m/z 142, the peak in signal intensity is for a q_z value of 0.3. In contrast, Figure 4.2(a) shows that the peak signal for m/z 242 has been reduced to less than a third of its maximum value by $q_z = 0.3$.

For a given q_z value, the “pseudopotential well” used to describe trapping behavior has an increased depth as m/z increases.³⁹ Similarly, the “potential barrier” referred to previously will be greater for higher m/z ions with the same q_z . A possible explanation for the preponderance of m/z 142 signal relative to that of m/z 242 at higher q_z follows from the “barrier” model: there is a lower barrier for m/z 142 ions to penetrate relative to that experienced by the m/z 242 species at

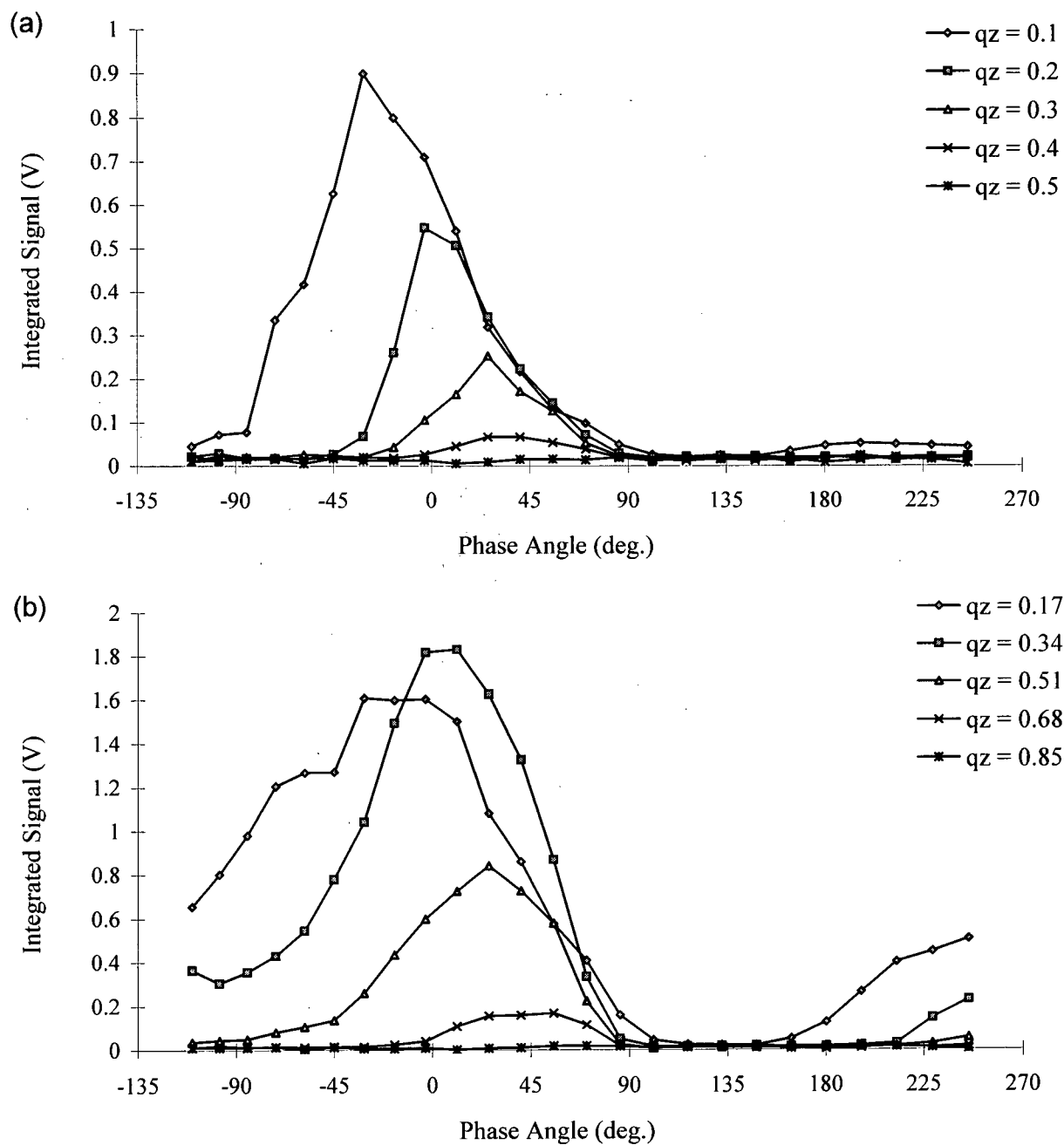


Figure 4.2 Integrated signal for TBA ions as a function of phase and their respective q_z values. (a) TBA molecular ion (q_z calculated for m/z 242) (b) TBA fragment with m/z 142 (q_z calculated for m/z 142).

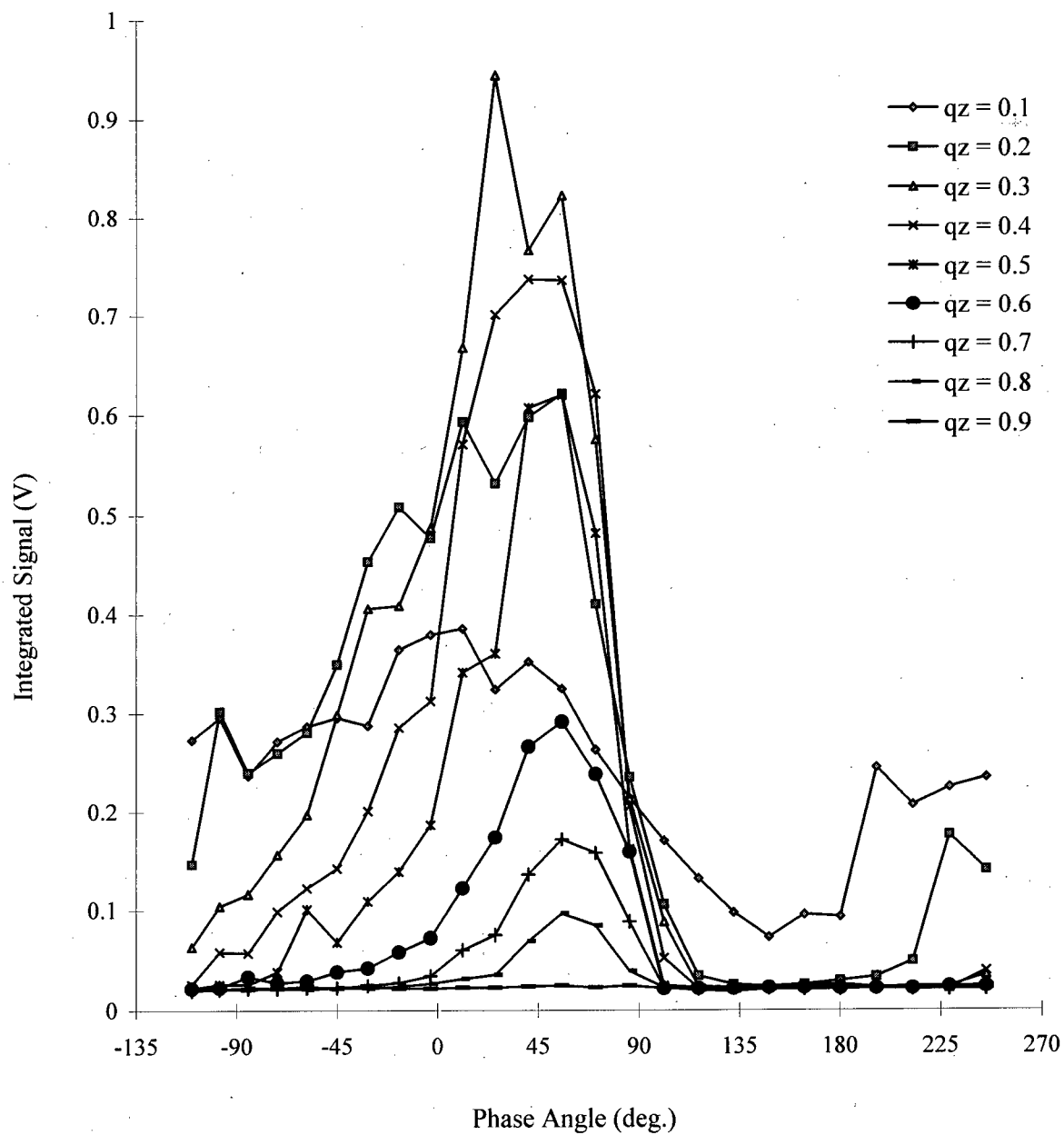


Figure 4.3 Integrated signal for the TBA fragment ion m/z 142 as a function of phase and q_z calculated for m/z 142.

the same q_z . If this simple model is accurate, then ions of similar m/z at identical values of q_z will have to overcome similar "barriers" and thus should show roughly equivalent trends in signal intensity as a function of q_z . To test this theory, an experiment was performed in which TEA, molecular ion m/z 130, was substituted for TBA in the sample film. The raw data for this experiment is presented in Figure 4.4, while Figure 4.5 is a summary of the dependence of two TEA ions on the phase of the RF potential and their respective q_z values. The trend for the TEA molecular ion closely matches that of the TBA molecular ion, even though their masses are dissimilar. Since TEA has a lower mass than the TBA fragment with m/z 142, the decrease in molecular ion signal with increased q_z cannot be attributed to a mass dependent trapping effect, as suggested by the "potential barrier" model. A more tenable explanation for the experimental results is that fragmentation results in a loss of molecular ion signal intensity at higher q_z , as described in the introduction of this chapter. At higher q_z , collisions with the helium bath gas will become excessively energetic, resulting in fragmentation instead of cooling. This conclusion neatly accounts for the decrease in molecular ion signal intensity observed at higher RF potentials, but the increase in fragment ion signal remains to be explained.

The intensity gain of the fragment ion signals at higher q_z may be due to increased production within the trapping volume as a result of collisional decomposition of larger m/z precursor ions, or it may be that the fragment ions produced during the laser pulse are trapped more efficiently than their molecular ions. To interpret fully the LD-ITMS results, it is thus necessary to discover whether the fragments observed were created through energetic collisions within the trap, or from thermal degradation during the laser pulse. To this end, complementary electrospray ionization (ESI) quadrupole mass filter and laser desorption ionization time-of-flight (LDI-TOF) mass spectrometric data were acquired (results not shown). Collisional decomposition of the electrosprayed ions was controlled by varying the accelerating potential

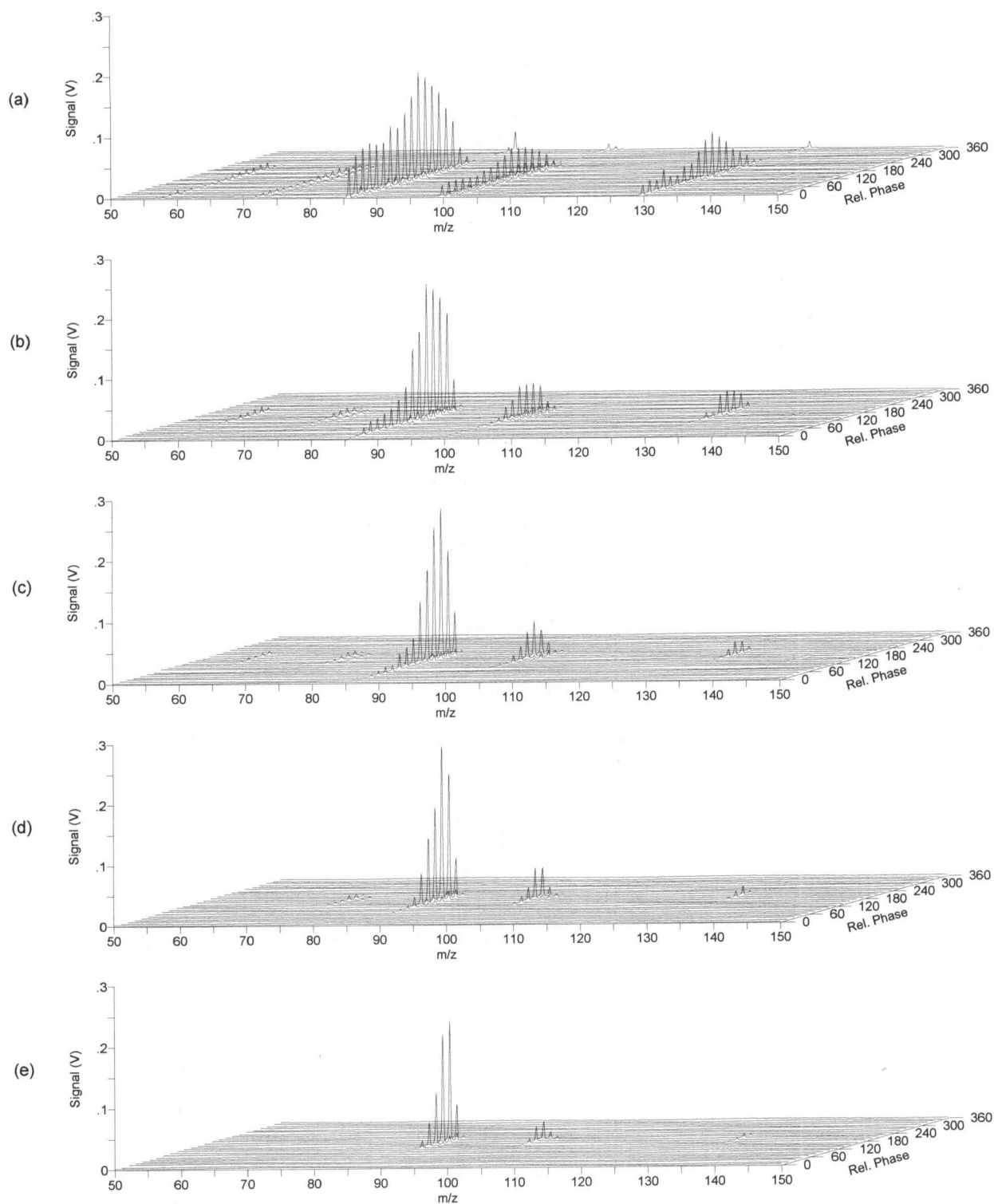


Figure 4.4 Laser desorption mass spectra of tetraethylammonium (TEA) acquired as a function of the phase angle at the time of the laser pulse and q_z for the molecular ion (m/z 130). Plots (a)-(e) correspond to $q_z = 0.1$ - 0.5 , respectively, and the step size is 0.1. The calibration of the z -axis is relative.

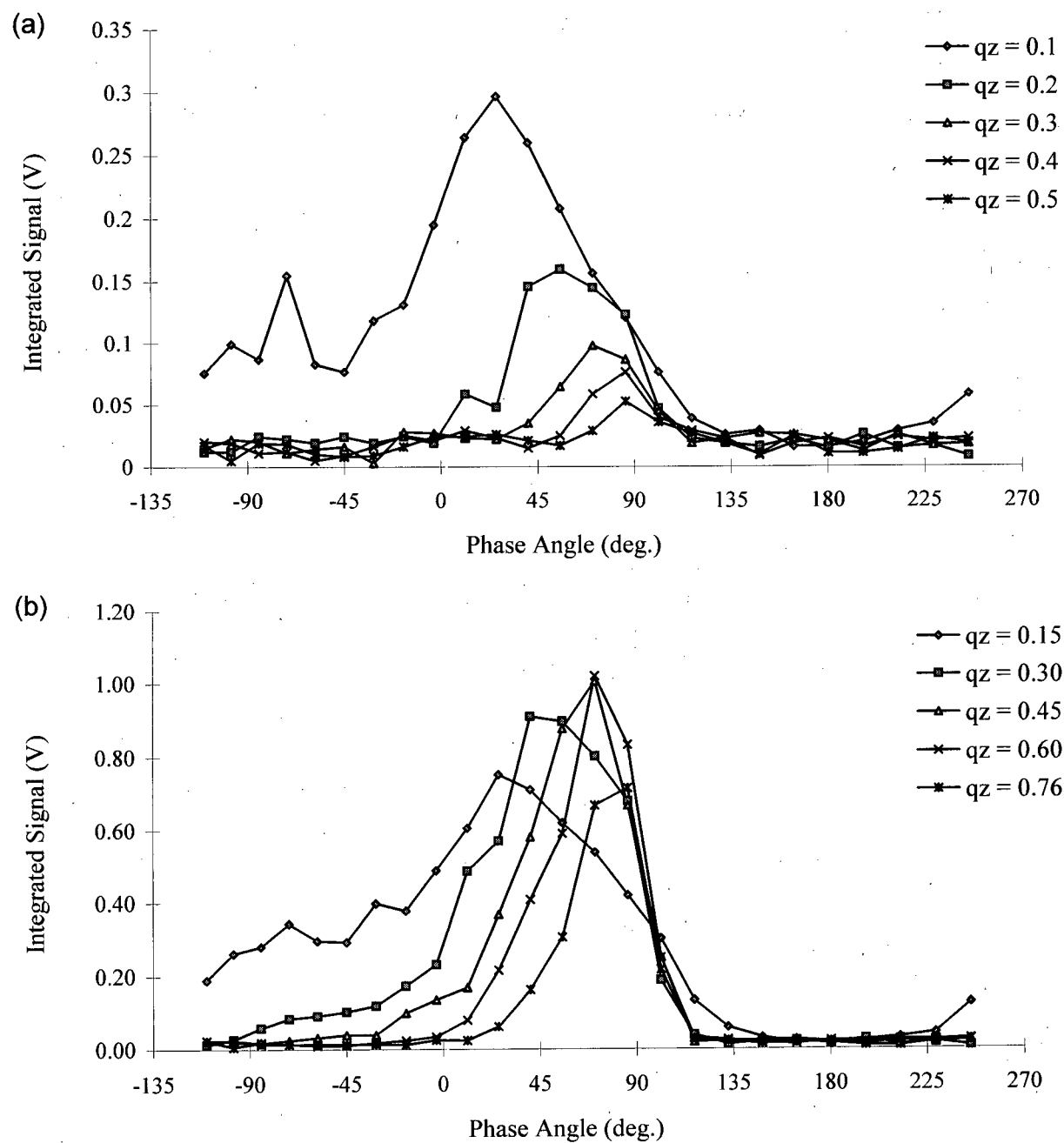


Figure 4.5 Integrated signal for tetraethylammonium (TEA) ions as a function of phase and their respective q_z values. (a) TEA molecular ion (q_z calculated for m/z 130) (b) TEA fragment with m/z 86 (q_z calculated for m/z 86).

between the skimmer plate and the quadrupole rods. Fragmentation in the LDI-TOF instrument was governed by the laser pulse energy. The major TBA decomposition products observed from both methods were identical, indicating that in this case fragment ions produced during the laser pulse are indistinguishable from those created as a result of collisional dissociation. It is known, however, that the ion trap will be more sensitive to fragment ions created inside the trap because they will be formed with smaller displacements from the trap center and will have a greater likelihood of adopting stable trajectories. Assuming that the fragment ions are not significantly more stable to dissociation than their respective molecular ions, and are thus also susceptible to collisional decomposition, it appears that the increase in fragment ion signals at higher RF levels is primarily due to extra production within the trap.

The "potential barrier" model is unable to account for the trends in signal intensity versus q_z data presented thus far. Again, the model is further discredited by its failure to describe the effects of the theoretically predicted and experimentally recorded phase relationship. The data presented in Figures 4.1-4.5 confirm that synchronization of the laser firing time with the RF phase is indeed an important factor determining sensitivity in LD-ITMS. For all q_z values, there is a peak phase angle that allows for the largest signal. As q_z increases, for the molecular and fragment ions alike, the phase dependence becomes more critical, as the range of phases that lead to successful trapping narrows considerably. Also of note is that the upper limit of acceptable phase values is mostly independent of q_z for the same species. The position of this upper limit is approximately 90° ; however, there is variability in the position of both the maximum and the upper limit phases. This variability is the subject of Chapter 5.

Fortified with new insight of the trapping process, it is now appropriate to reflect upon other notable inconsistencies found in the literature. To begin with, in one commonly referred to early study,⁹⁸ perfluorotributylamine (PFTBA) ions were created in an external EI source, and

injected into the trap. Mass spectra were recorded as a function of the RF amplitude on the ring electrode for steady-state ionization conditions. For the PFTBA ions studied ($m/z = 69, 131, 264,$ and 502), an inverse relationship between m/z and the maximum q_z value that yielded signal was noted (e.g., ions of $m/z = 69$ were observed up until the exclusion limit of $q_z = 0.9$, whereas, for $m/z = 502$, the signals had tailed to zero before $q_z = 0.2$). This behavior was rationalized with a mass-dependent collisional model which presumed that, for a given q_z , higher m/z ions would be less likely to reach the center of the trap and ultimately be confined. However, the data presented here contradict this model as well, because the trend in ion signal with increasing m/z appears to be an artifact of fragmentation and not a mass-dependent trapping effect. Moreover, in the same study, it was experimentally demonstrated that collisional dissociation of the higher m/z (precursor) ions could in fact lead to increased signals for the lower mass ions. The evidence now suggests that this latter mechanism is the more accurate for explaining the observed trends.

The “dynamic trapping” method deserves further scrutiny, as well, now that the “potential barrier” model used to explain its effectiveness has been discredited. Since it is apparent that the ability of ions to penetrate the quadrupole field depends as much upon the RF phase as the potential, there is no basis for the claim that a low potential is necessary to introduce ions into the trapping volume. It is possible, though, that the dynamic method may be suitable for reducing the amount of fragmentation immediately after injection. By injecting ions when the RF field is very weak, ions may be able to initially penetrate the trapping volume without being accelerated greatly. The closer the ions are to the center of the trap before the RF potential is substantial, the less violent will be the collisions that lead to either trapping or dissociation. The potential must be raised to a level sufficient to effect ion containment, however, before the ions travel completely through the trap and are lost. It is possible then, that dynamic trapping

may provide enhanced sensitivity for fragile species by allowing for reduced fragmentation upon injection.

Although all practitioners of dynamic trapping cite a sensitivity enhancement, there has been only one report of a quantitative comparison between the various methods.¹⁸ This experiment involved the trapping of matrix-assisted laser desorbed ions created externally then injected through one end-cap. Due to the usual fluctuations in ion production between laser shots and between samples, these researchers were unable to obtain reliable data that showed absolutely which of the various trapping methods was most efficient, i.e., it was not possible to acquire a set of data for one set of trapping conditions, then compare absolutely the signal intensity obtained with that from another trapping method. During the period immediately following the laser pulse in which ions were injected, though, a signal was produced whenever ions that were not contained struck the detector behind the opposing end-cap. By using this signal from untrapped ions as an internal standard, the problem of reproducible ion production was believed to have been circumvented. Effectively, a measure of the trapping efficiency for each trial was taken from the ratio of the successfully trapped ions detected during the analytical ramp to the combined total signal from both the trapped and untrapped ions. Their calculations, however, overestimate the trapping efficiency because of at least one consequential error: it is assumed that all the injected ions that are not successfully contained pass directly through the trap and are detected.

Firstly, the assumption that all untrapped ions can be accounted for neglects to consider the effects of collisions within the trapping volume. Molecular ion loss due to collisional dissociation will occur to a varying extent depending on the q_z value upon injection. Also, scattering due to collisions with background particles may cause injected ions to deviate from strict axial trajectories, so that they strike the opposing end-cap off axis and are not transmitted

to the detector. The second factor omitted from the trapping efficiency calculations, and likely the most significant, is the phase relationship. As discussed in the introduction, depending upon the phase at which an injected ion first experiences the quadrupole field, it will be either accelerated into the trapping volume, or it will be repelled before it can penetrate the trap. Ions injected axially at phases such that they are repelled will not be detected at the opposite end-cap. As is also the case for the collisional processes, the extent to which inopportune phase synchronization contributes to unaccountable ion loss has yet to be determined. Furthermore, for the reasons stated above, these unrecorded ion losses will be affected by the RF potential applied during the injection. Without prior knowledge of the effects of RF potential on the fate of all the untrapped ions, this method can therefore not even accurately describe the relative efficiencies of the trapping methods, let alone provide an absolute measure, as suggested.

Based solely upon the suspect calculations of trapping efficiency described above, one method of dynamic trapping ("Matched Dynamic Trapping") has been described as "improved," relative to other methods, including the constant amplitude technique utilized here.¹⁸ This claim is unsubstantiated by the available evidence. Significantly, the instrument cited as yielding the best trapping efficiency uses an external ion source which adds considerable spread in the time over which ions are injected into the trap. This eliminates the possibility of synchronizing the injection period to the narrow optimum phase angle of the RF potential. The data provided here and elsewhere indicate that if ions are introduced at random phase angles then the trapping efficiency will suffer drastically. However, since the phase relationship is less significant at lower potentials, it may be that phase synchronization is at least partially obviated for dynamic trapping methods where ions are created at times when the quadrupole field is very weak. To date, though, there is no proof that dynamic trapping methods of any description are more sensitive than an appropriately phase locked constant amplitude technique. Even if the method

of calculating trapping efficiency described above were correct, the comparison between trapping techniques is not valid because the constant amplitude method was not optimized (there was no phase-locking).

Before closing this discussion, it is appropriate to address the issue of non-linear resonances and higher-order fields. In quadrupole ion traps, especially commercial instruments incorporating a “stretched” geometry (see Chapter 2), the electric fields generated contain higher-order components as well (hexapole, octapole, etc...) The presence of higher-order fields gives rise to non-linear resonances that are manifested by a diminished capacity for ion confinement at particular values of q_z . These “black holes” have been investigated and are known to occur at predictable locations within the stability diagram.⁹⁹ The q_z values used for the trapping studies documented in this thesis do not correspond to known black holes. In addition, the results obtained do not contain any deviations that cannot be explained. Hence, there is no reason to expect that higher-order fields are in any way responsible for the results reported in this chapter, or elsewhere in the thesis.

4.4 Conclusion

All future models of the trapping process must include fragmentation as a factor in determining the trapping efficiency for injected ions created by laser desorption or other techniques. Furthermore, the effects of the phase of the RF potential at the time at which ions are injected cannot be ignored. Discussions regarding the relative efficacy of the various trapping methods will remain conjectural until such time that reliable quantitative data is available to make meaningful comparisons. There is presently no evidence that indicates definitively that dynamic trapping is more or less sensitive than suitably phase locked constant amplitude techniques.

CHAPTER 5

DEPENDENCE OF THE OPTIMUM PHASE ANGLE FOR EFFICIENT TRAPPING OF LASER DESORBED IONS ON THE QUANTITY OF IONS PRODUCED AND THE LOCATION OF THE LASER FOCAL AREA ON THE SAMPLE PROBE

5.1 Introduction

The data presented earlier in this thesis confirm that the phase angle at which injected ions first experience the RF field is a critical parameter governing trapping efficiency for quadrupole ion traps. Although several laser desorption studies report measurements of sensitivity for ions injected into an ion trap as a function of phase angle, there is no consensus regarding what the value for optimum trapping is.^{9, 13, 38, 100-102} The results of simulations performed by the author (see Chapter 6), as well as those reported in the literature,^{34, 35} indicate that the optimum phase angle for trapping ions is a function of the RF amplitude (q_z), and the kinetic energy of each injected ion. Kinetic energy of injected ions is a variable which is not readily controlled in LD-ITMS experiments, so it comes as no surprise that researchers employing unique experimental arrangements have reported different results. Significantly, to the best of the author's knowledge, there have been no published attempts to correlate the real LD-ITMS experimental data with the results of the ion injection simulations. Hence, it has not been shown that the variation between experimental results is due solely to differences in q_z , or the kinetic energies of the ions, as could be surmised from the simulations. It may then be that any number of heretofore unconsidered factors contribute to the trapping process, and thus

influence the value of the optimum phase angle for confining injected or desorbed ions.

In this laboratory, with the advent of polythiophene films for laser desorption samples,⁹⁷ many experiments were undertaken seeking to better understand the trapping process, including the phase dependence of LD-ITMS sensitivity. Although initial results clearly demonstrated the dependence of the ion signal intensity on the phase of the RF potential and q_z , there were some troubling inconsistencies in the data. Specifically, it was found that for seemingly identical experimental conditions (same sample type, q_z , buffer gas pressure, and laser irradiance) the optimum phase angle varied widely between repeats of the same experiment, often by 90° or more. It was at first believed that these inconsistencies stemmed from imperfect calibration of the electronics governing the timing of the experiments, but repeated measurements always confirmed that this was not the case. The only significant source of uncertainty in the calibration scheme is the jitter in the laser firing time, which, at no more than ± 30 ns, corresponds to a maximum uncertainty in the phase calibration of $\pm 10^\circ$. The idea that the variation could be due to a real ion trapping effect was originally dismissed with little thought. It was assumed that trapping behavior for a given set of experimental conditions was as inviolate as Newton's Laws that determine the trajectories of the ions. Because the laws of physics are not to be disproved, at least not here, then the assumption that trapping behavior is consistent for a given set of conditions must hold. In retrospect, it is clear that, because the experimental apparatus was sound, the discrepancies between the results of repeats of the same experiments must have been due to real variables that were left unaccounted.

After several months of futilely attempting to resolve this problem, two previously overlooked experimental variables were empirically determined to be responsible, at least in part, for the observed inconsistencies. Firstly, the optimum phase angle for a given value of q_z was found to depend on the quantity of ions desorbed during the laser pulse. Based upon new data

presented in this chapter, and related evidence in the laser desorption mass spectrometry literature, a plausible mechanism for this dependence may be inferred. In the discussion below, it will be argued that trends observed in the present investigation are due to the collective ability of the desorbed ion plume to provide shielding of the ions within the plume from the applied electric field used to confine the ions. This phenomenon, known as Debye shielding, is typically associated with plasmas consisting of positive ions, electrons, and neutral species.¹⁰³ In the past, Debye shielding has been demonstrated to allow laser desorbed atomic ions generated from metal surfaces to penetrate retarding potential barriers greatly exceeding the initial kinetic energy of the ions.⁹⁶ For instance, it was found that Debye shielding exhibited by quasi-neutral populations was sufficient in some cases to allow ions on the order of 1 eV to penetrate retarding potentials as high as 500 V. Evidence from another early study suggests that the effects of Debye shielding in laser desorption are not limited to plasmas generated from metal targets, but may also be observed for ion plumes generated from ionic substances by thermal processes,⁷⁴ such as those resulting from the low irradiance laser desorption technique used here.

Quite unexpectedly, the optimum phase angle for trapping was also found to vary with the lateral position of the lens used to focus the laser energy onto the sample surface. The origins of this dependency are not well-understood, though a tentative explanation is offered in the discussion. An additional experiment demonstrated that the phase relationship does not depend on the pressure of the helium buffer gas; however, the effects of buffer gas pressure on fragmentation and sensitivity in LD-ITMS are noteworthy and will be discussed in brief.

5.2 Experimental

The home-built instrument described previously was used for the experiments presented in this chapter. For these experiments, laser desorption mass spectra were collected as a function

of the phase angle of the RF potential used to trap the ions. Calibration of the laser firing time with respect to the RF phase angle was performed as described in Chapter 2. As before, zero degrees is defined to be the phase angle at the positive going zero-crossing of the RF potential. The amplitude of the trapping potential was constant for all the trials, and was calculated from $q_z = 0.1$ for the tetrabutylammonium (TBA) molecular ion (m/z 242). An experimental sequence began with the RF potential being set by computer. Following a 5 ms delay to allow for the RF amplitude to stabilize at the level for trapping, a trigger was sent to the zero-crossing detector. Subsequent to the detection of the next positive going zero-crossing, a trigger was sent to the laser at a small variable delay. After the laser firing event, the trapping potential was held constant for 10 ms to allow for any trapped ions to collisionally cool. The mass-selective instability mode of operation⁴² was employed next by ramping the potential from the value determined by $q_z = 0.1$ for m/z 242 to the maximum amplitude of the supply (~ 3000 V_{o-p}). The ejected ions were detected using the electron multiplier held at -1.7 kV. During the ramp, the signal from the detector was amplified and sampled as detailed in Section 2.2. The RF amplitude was then set to zero to clear the trap, and the data was saved by the computer. For each series of data collected, spectra were acquired for 25 phase angles spanning one RF cycle. To compensate for random fluctuations in ion production between laser shots, 30 spectra were acquired and averaged for each phase angle at a rate of five spectra per second.

All the data presented in this chapter came from a polythiophene film prepared as described in Chapters 3 and 4. Tetrabutylammonium (TBA) perchlorate was the supporting electrolyte used for the preparation for the film that provided the ions to be analyzed in these studies. Since TBA ions are not involved in the mechanism of the polythiophene electrodeposition process,⁸³ some other means must be considered to account for their presence in the films. Observations reported in Chapter 3 suggest that electrolyte enriched solution is

entrained into the sample film during the electrodeposition process. Upon drying, a residue of the electrolyte ions remains intermixed with the polythiophene; thus, the sample films are impregnated with both TBA and perchlorate ions from the electrolyte solution. (Note: perchlorate ions are likely present in greater amounts than TBA ions in the polythiophene sample films; this is because, in addition to the contribution from the electrolyte residue, incorporation of negative electrolyte into the polymer structure is an integral part of the electrodeposition mechanism, since "anion holes" that form in the polymer as a result of oxidation during the electrodeposition process must be filled to maintain electrical neutrality.⁸³⁾

The laser and optical components were described in Section 2.3. Here, the neutral density filters were used to attenuate the nitrogen laser energy output at 337 nm to $\sim 30 \mu\text{J}$. The lens focused the laser pulse to an ellipse of approximately $400 \mu\text{m} \times 200 \mu\text{m}$, leading to a calculated irradiance of $\sim 5 \times 10^6 \text{ W/cm}^2$ at the surface of the sample. The lens was mounted on an x-y-z translation stage, and one experiment involved collecting data with the lens position set to different lateral positions. By translating the lens from side-to-side, the focal spot of the laser beam could be positioned at varying locations on the probe tip surface. The spatial arrangement of the ion trap relative to the laser is such that lateral translation of the lens causes the focal spot of the laser to move along the axial direction of the trap, with the radial position remaining constant. Initially, the lens position was adjusted such that the laser impinged on the outermost region of the probe tip (1.8 mm diameter). Ion production thus was achieved from a position on the probe that was displaced slightly towards one of the end-caps from the axial origin of the trap. Several sets of spectra were collected with the lens set to this position, then the lens was shifted 0.5 mm back towards the laser beam axis and additional data were acquired with the laser focussed to an area near the center of the probe. The distance from the lens to the sample along the laser beam axis was not varied, so the focal area and the laser irradiance were constant.

The pressure of helium in the manifold was held at 1 mtorr for all the experiments, except for the final study where it was varied over a range of 0.5 mtorr to approximately 8 mtorr. The pressure in the manifold was directly measured with the Balzers cold cathode gauge and meter, then the reading was corrected as described in Section 2.4.

5.3 Results and Discussion

5.3.1 Dependence of the Phase for Optimum Trapping Efficiency on Ion Production

Figure 5.1(a) displays a series of LD-ITMS spectra of TBA collected as a function of the phase angle at which the laser fired, with q_z held constant. The dependence of signal intensity on phase is clear from the data. The peaks at m/z 242 are due to the TBA molecular ion, and the other major peaks in the spectra are due to TBA fragments, for which structural assignments have been made elsewhere.^{84, 85} The spectra displayed in Figure 5.1(a) were collected from 750 of the first laser shots on the sample surface, when the ion production per laser shot was relatively high. To evaluate the effect of the ion yield per laser shot on trapping behavior, the sample was subjected to thousands of laser shots so that ion production was gradually diminished, while additional spectral series were acquired periodically. The series of spectra in Figures 5.1(b)-(d) were collected at increasing stages of decay of the laser desorption ion yield, with the final series shown being acquired after more than 28,000 shots on the same sample position. Eleven such series were acquired in all; the results of this study are summarized in Figures 5.2(a) and (b).

There are two trends that are immediately conspicuous in Figure 5.2: as the ion production from laser desorption diminishes (evidenced by a decrease in signal intensity over all phases), the peak phase angle for trapping becomes more positive, and the distribution of phases for which ions are successfully trapped narrows. As well, for each series of spectra there is a

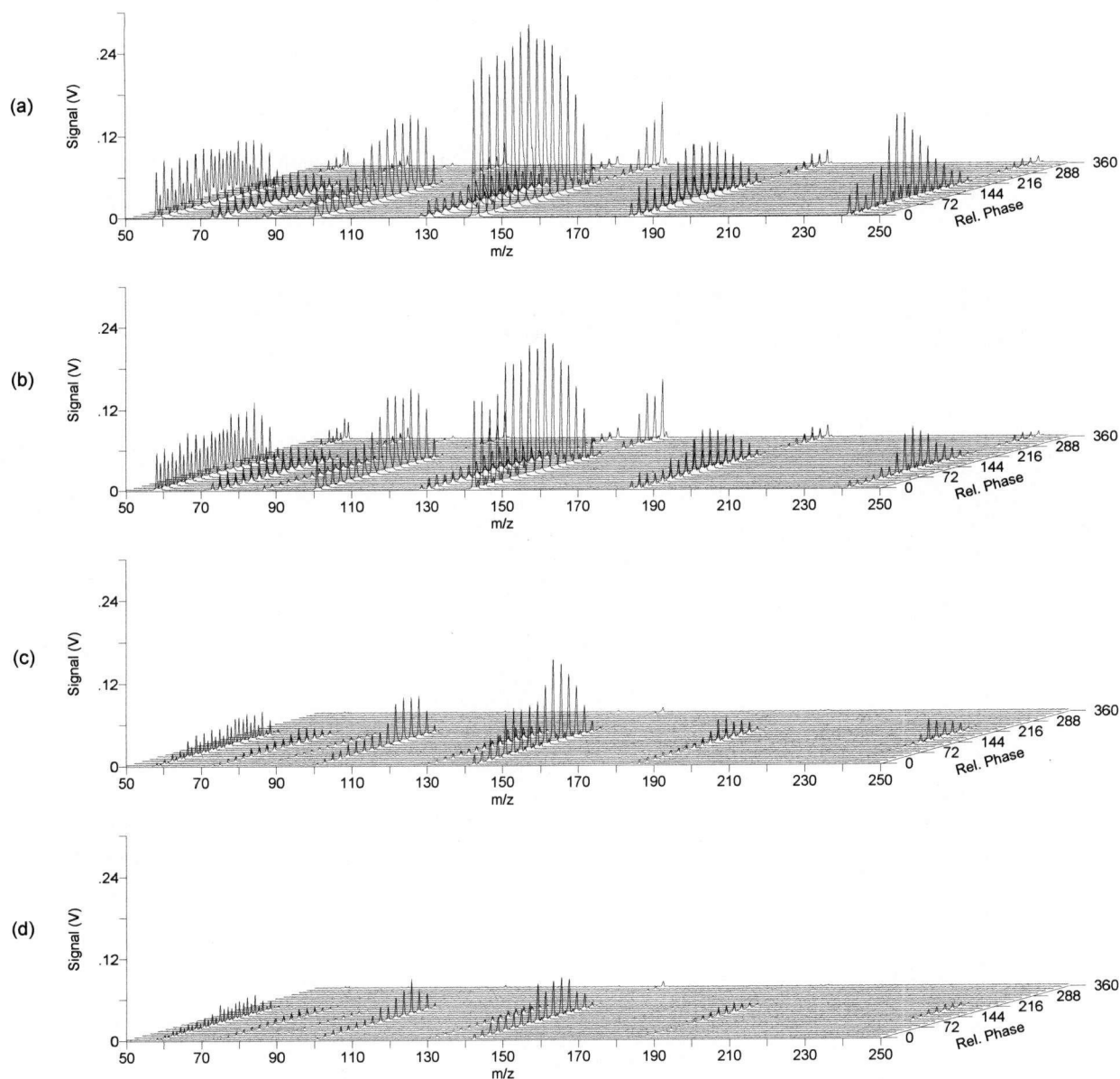


Figure 5.1 Series of laser desorption mass spectra of tetrabutylammonium (TBA) acquired as a function of the phase angle at the time of the laser pulse. The data in plots (a)-(d) were collected at increasing stages of decay of the ion production per laser shot from the sample film. The calibration of the z-axis is relative. Unless indicated otherwise, all other plots with a phase axis are calibrated absolutely.

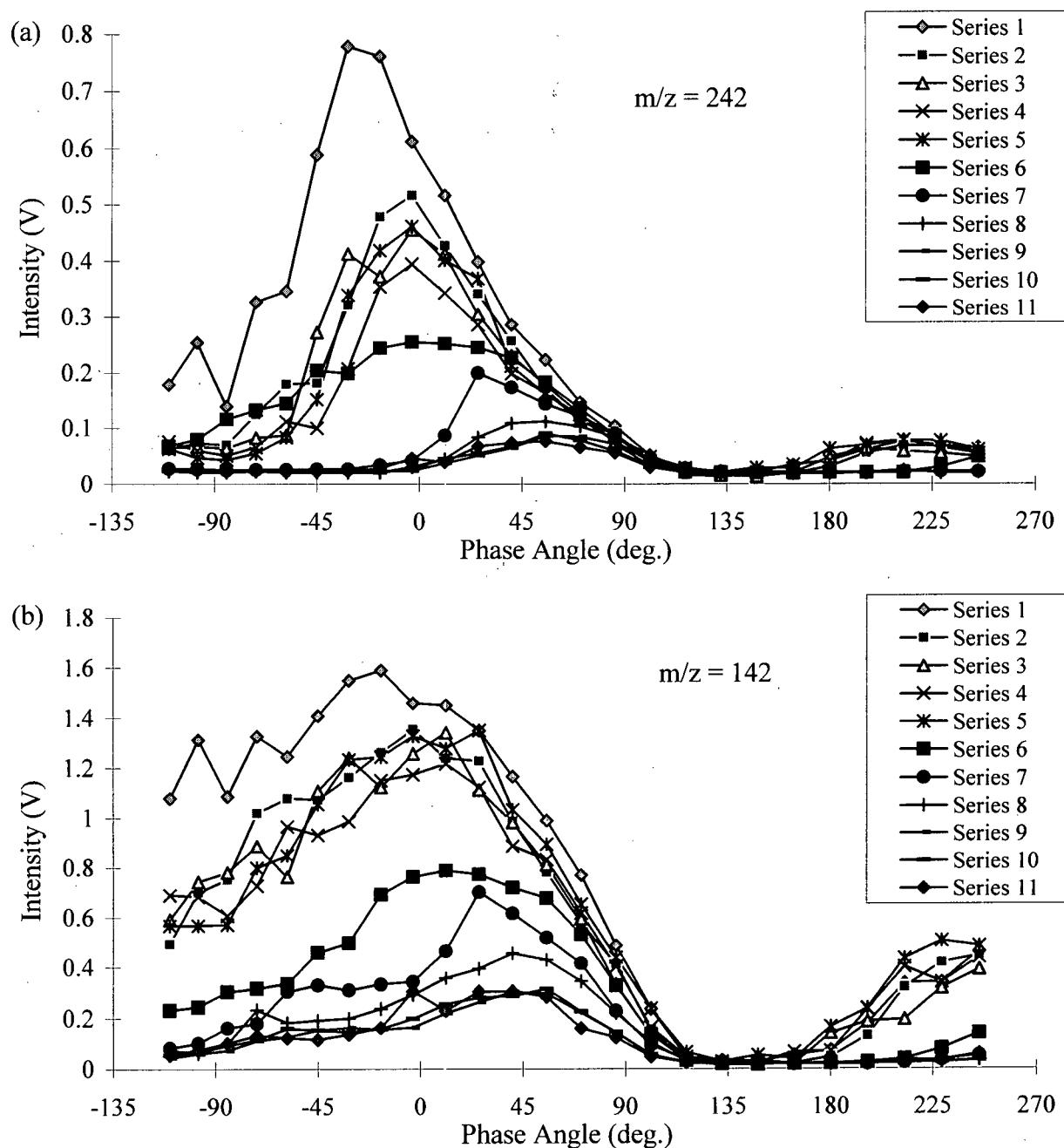


Figure 5.2 Integrated signal for the (a) TBA molecular ion (m/z 242) and (b) one of the TBA fragment ions (m/z 142) collected as a function of phase angle and the total ion yield per laser pulse. Series 1 was acquired from 750 of the first laser shots on the film. The other series were acquired at increasing stages of decay of the ion production. Series 11 was collected after the film had previously been subjected to 28,000 shots on the same position.

cut-off phase at which no more ions are trapped. The cut-off phase has a constant value of just greater than 90° for all the trials. A comparison between Figures 5.2(a) and (b) shows that this behavior is followed by both the TBA molecular ion and its fragment at m/z 142. It is apparent that if the two trends were to continue, as fewer ions are produced, the distribution of acceptable phases would continue to narrow and the optimum phase for trapping would increase until it eventually equaled the unvarying cut-off phase. This is evident from Figure 5.3, a summary plot of the peak integrated m/z 242 signal intensity for each series versus the phase angle at which the data was acquired. This plot plainly illustrates the positive shift that occurs in the optimum phase angle as the quantity of ions produced by each laser pulse decreases.

Before discussing the probable causes of the trends observed in the experimental data, it is first necessary to review a model of the trapping process which has developed from the simulations cited above. The two simulation studies published recently considered the problem of trapping positive ions injected from an end-cap electrode.^{34, 35} The mechanisms arising out of each investigation for the dependence of trapping efficiency on the initial phase of the RF potential are consistent with each other. The results of both studies indicate that, for ions with zero initial velocity, the ions may only penetrate the trapping volume if they are created when there is a negative potential on the ring electrode (phase angles from 180° to 360°). For all values of q_z , successful trapping may only occur when the phase upon injection is around 270° , at which the ions accumulate a minimum of kinetic energy upon reaching the trap center. The motion of the ions that are ultimately trapped is oscillatory, bounded in the axial dimension by the opposing end-caps, while the limits of displacement are much narrower in the radial dimension. Regarding the fate of ions created during the remainder of the RF cycle, positive ions introduced at phases when there is a positive potential on the ring (from 0° to 180°) are excluded entirely from the inner volume of the ion trap, because they initially face an uphill

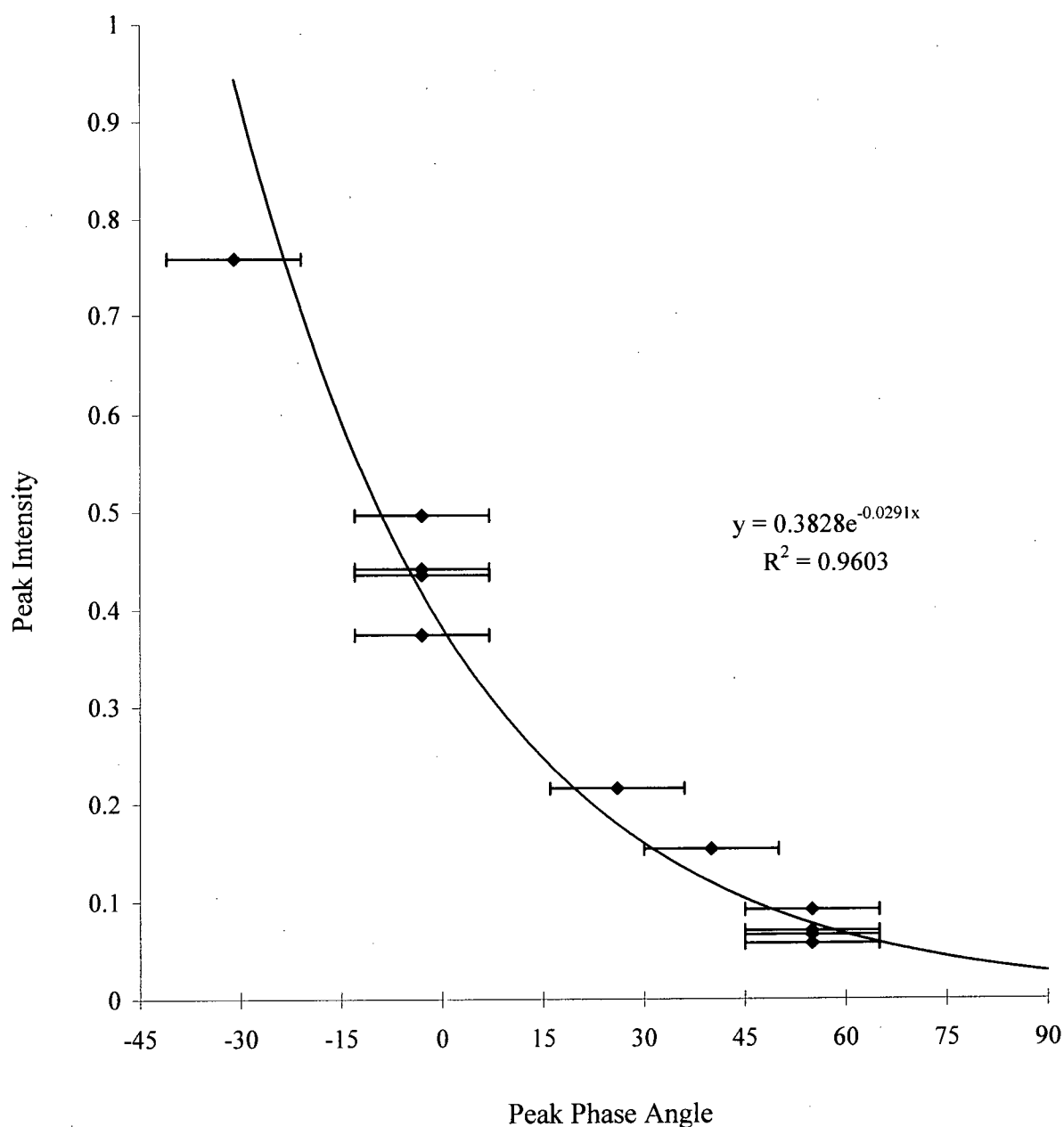


Figure 5.3 Summary plot of the peak integrated m/z 242 signal intensity for each series versus the phase angle at which the data was acquired. The optimum phase for trapping for Series 1-11 depends on the mean number of ions produced from the sample by the laser. The error bars on the x-axis correspond to the uncertainty in the phase angle calibration, $\pm 10^\circ$.

potential barrier. Ions introduced to the quadrupole field at phases less than 270° , but greater than 180° , experience excessive acceleration during the negative portion of the RF cycle, have too much energy upon crossing the trap center, and are lost at the opposite end-cap. Ions created at phases greater than 270° , but less than 360° , are also initially accelerated towards the trap center, but are repelled back into the electrode that they originated from when the potential on the ring electrode becomes positive.

Another key finding of the simulations is that as the velocity initially possessed by the injected ions increases, the optimum phase angle for trapping increases from 270° , because less acceleration is required for the ions to penetrate sufficiently far into the trap so that they will not be pulled back into the end-cap when the RF potential switches polarity. Ions created at 270° with non-zero initial kinetic energy are lost at the far side of the ion trap, because the combination of their initial energy and the velocity gained due to acceleration during the next quarter of the RF cycle is excessive.*

Results from the simulations performed in this laboratory are also consistent with those of the two described above. One key difference between the simulations is that, in this instance, the investigation considered ions injected from the ring electrode instead of an end-cap. The results for the dependence of the trapping mechanism on the initial RF phase angle were shifted by 180° from those discussed above, because, relative to the potential at the trap center, the potentials on the ring and on the end-caps are out of phase by 180° . Hence, the optimum phase angle for trapping ions injected from the ring electrode was 90° for ions created with zero kinetic

* Note that none of the simulations considered thus far have been able to accurately account for the effects of ion-ion interactions, one of which may be Debye shielding. It is plain to see, then, that the results of the simulations are only meaningful for the ideal case of a single ion unaffected by other charged particles, acting under the exclusive influence of the electric fields generated by the potentials applied between the trap electrodes.

energy, or slightly greater for those with some small initial velocity.

Returning to the earlier analysis of the LD-ITMS experiments, it is now profitable to compare the results from these with those of the simulations. Reiterating, if the experimentally observed trends were to continue, then, in the limit of only one ion being produced, the data suggest that the ion may only be trapped when created at a phase slightly greater than 90° . This finding agrees exactly with the results predicted by the simulations for one ion injected with nominal initial kinetic energy, a starting condition that may reasonably be assumed to hold for an ion created by a thermal laser desorption process. For the problem of trapping ions created outside of the central volume of the quadrupole ion trap, this is the first reported instance of congruence between the results obtained from real experiments and those from simulation studies. The evidence thus suggests that the simulations accurately reflect ion trapping behavior, albeit only for the seemingly unrealistic situation where there are no significant effects resulting from ion-ion interactions. The problem remains to explain the effects that are experimentally observed to accompany the production of substantial quantities of both positive and negative ions.

The variance observed in Figure 5.2 with the number of ions produced indicates that the ions themselves affect the trapping process. Other studies have shown that ions within quasi-neutral plumes resulting from laser desorption may be shielded from the influence of external electric fields.^{74, 96} If it is assumed that this phenomenon, Debye shielding, also contributes to the process governing the trapping of the TBA ions analyzed here, then it is possible to describe a mechanism that accounts for the discrepancies between the results of the experiments and the simulations. The principal effect that can be ascribed to Debye shielding is an added delay between the time that ions are formed and when they experience the full amplitude of the applied RF field. To understand how this may come about, one must consider the processes that

accompany the arrival of the laser pulse. First, a plume consisting of TBA and perchlorate ions is desorbed as a result of rapid heating of the sample by the laser pulse. The immediate collective action of the particles within the quasi-neutral ensemble is to arrange themselves such that Coulombic repulsion is minimized. One of the ensuing effects is that ions within the plume are shielded from external electric fields; only the outer shell of the plume is left unshielded. The thickness of this layer is specified by the Debye length, which depends upon the density of the plume, among other factors.¹⁰³ Those ions within the plume that are shielded from the RF field will diffuse away from the probe tip, into the trapping volume, at the velocities imparted to them during the desorption event (typical reported velocity values range from 400-1000 m/s.¹⁰⁴⁻¹⁰⁶) Ions which are affected by the external electric field will be accelerated away from the rest of the ions, at a rate dependent upon the instantaneous magnitude of the applied RF potential. We thus have a system characterized by an inner core of shielded ions diffusing in a field-free manner, that will ultimately be dispersed due to the normal expansion of the plume and the invasive effects of the quadrupole field.

A predictable consequence of the processes described above is that there will be a distribution in time over which desorbed TBA ions first experience the full effects of the RF field. The shape of this distribution will depend upon the rate at which de-shielding of ions within the plume occurs as it is dispersed. The rate of dispersal can be expected to be directly related to the instantaneous magnitude of the RF potential. As well, the dispersal rate must be inversely related to the density of the plume, because the Debye length specifying the depth of penetration of external electric fields into the plume is reduced for higher charged particle densities. Both the instantaneous magnitude of the applied potential and the density of the plume vary over time, so the dispersal rate of the plume cannot be easily predicted. In short, the factors governing the rate at which the ion plume is dispersed are complex, and it is currently impossible

to predict the delay subsequent to the laser firing event at which the greatest number of ions will be de-shielded.

The measured dependence of the TBA signal intensity on the phase at the time of the laser firing is a function of the distribution in time over which the desorbed ions first experience the RF field. If the pre-supposition is valid that unshielded ions at the ring electrode are only efficiently trapped when introduced at a phase angle of around 90° , then, from the data displayed in Figure 5.2, it is possible to infer what the distribution for each series was likely to have been. For example, the peak ion signal for Series 1 was obtained when the laser fired at $\sim -30^\circ$, a negative shift of 120° (equivalent to roughly 350 ns) from the theoretical optimum phase for trapping unshielded ions. We can therefore infer that the greatest number of ions were de-shielded at approximately 350 ns after the laser fired. Signals observed at phases less than the optimum ($< -30^\circ$) came from ions that had been de-shielded at delays greater than 350 ns. Conversely, those observed at phases greater than the optimum value came from ions de-shielded at delays less than 350 ns. The cut-off phase can also be explained: when the laser fired at a time such that the RF phase was just greater than the cut-off value, for all the data series collected here, no ions were trapped because all the ions were de-shielded and lost in a period less than the time it took for the RF phase to cycle through again to the optimum value of $\sim 90^\circ$.

A key factor that must be considered in evaluating the accuracy of this model is the distance into the trap that the ions penetrate while they are shielded. This is because the assumption that ions are most efficiently trapped when de-shielded at 90° may only hold if they start at the outer edge of the quadrupole field (i.e. at the ring electrode). Assuming an average velocity of 700 m/s (probably high for a strictly thermal desorption process), ions drifting for 350 ns before experiencing the quadrupole field will have traversed only 0.24 mm during the shielding period. This displacement is likely insignificant insofar as it affects the value of the

phase angle for which ions are most likely to be trapped.

The delay between when the laser fires and when the peak number of ions are first influenced by the quadrupole field is a function of the quantity of ions produced during the laser shot. Shielding has a lesser effect if either the plume volume or density of ions within the plume is diminished; therefore, if there are fewer ions available to provide shielding, there will be on average a lesser delay between when the ions are desorbed and when their motion is significantly affected by the quadrupole field. It is believed that this is the effect responsible for the trends evident in Figures 5.1-5.3. For Series 1 the phase was optimized for maximum signal intensity when the laser fired at -30° , whereas for Series 7-11 an insignificant number of ions were trapped when the laser fired at this phase. The ions were then not shielded for as long when the ion production was lowest. Consequently, when produced at -30° , the majority of the ions began to be influenced by the quadrupole field at a phase angle less than 90° and were not trapped, as predicted by the simulations.

Corroboration of the mechanism proposed above can be had if it can be successfully applied to interpret the results from other LD-ITMS studies, such as several of the observations described in Chapter 4 that have yet to be fully explained. Referring back to Figure 4.2(a), it can be seen that that the peak phase angle for $q_z = 0.1$ is approximately -30° , the same value as for Series 1 in Figure 5.2. In fact, the signal versus phase plots are nearly identical for these two trials that were acquired for similar experimental conditions (including the total ion yield—observe the correspondence between the integrated signal intensities for each series). Moreover, as q_z increases, the same trends that accompany decreased ion production in Figure 5.2 are evident in Figure 4.2: the phase angle of peak trapping efficiency shifts towards larger values, the width of the distributions of acceptable phases narrow, and there is a constant cut-off phase value around 90° . It is known, though, that the trends in Figure 4.2 are not artifacts of decreased

ion production at higher q_z values.** Therefore, the trends must be due to the effects of the increasing RF amplitude, which mimic the effects that accompany a reduction in the quantity of ions desorbed.

The close similarity of the two experiments is readily interpretable: the trends in both cases are believed to stem from a reduction in the effects of Debye shielding. The delay between when the laser fires and when the ions experience the quadrupole field is reduced not only if fewer ions are produced, but also if the ions are dispersed at a faster rate. As stated previously, the rate of de-shielding is directly related to the magnitude of the electric field, which is in turn proportional to q_z . Thus, we can expect that the distribution of delays will be shifted towards lower values as the RF amplitude increases, which is exactly the effect observed.

5.3.2 Dependence of the Phase for Optimum Trapping Efficiency on the Location of the Laser

Focal Area on the Sample Probe

When performing any of the various methods of laser desorption mass spectrometry, it is frequently desirable to translate either the focussing lens, or the sample itself, so that the laser light impinges on different areas of the sample surface. This is because many samples are quickly depleted after only a few laser shots, or else they may have uneven surface distributions. In order to attain sufficient ion production from the samples, both of these eventualities may then require that new portions of the sample surface be exposed to the laser at regular intervals. Compared to most other sample types, the polythiophene films used here as laser desorption standards provide ion production that is superior in terms of both longevity and consistency; however, even polythiophene samples are imperfect. This means that occasionally the probe

** Recall from Section 4.2 that the data was acquired in order of high to low q_z values to ensure that any decrease in ion production after many laser shots did not overemphasize the increase in signal intensity observed at low q_z .

must be turned to expose a new surface to the laser, or alternatively the focussing lens can be translated slightly so that the laser focal spot impinges on a new position on the probe. Significantly, for laser desorption from a probe inserted through the ring electrode of a quadrupole ion trap, it has heretofore been assumed that this type of adjustment does not affect the relationship between trapping efficiency and the phase angle at which the laser fires.

To investigate the possibility that the inconsistencies described earlier stemmed in part from deviation in the location of the laser focal point, series of signal versus phase data were acquired with the lens set to two different lateral positions. Initially, the lens position was set so that the laser impinged on the outer edge of the probe tip. Since the diameter of the tip is 1.8 mm, and the width of the focal spot at the sample surface is 0.4 mm, it is believed that for the first lens position the desorbed ions originated from an area that was offset 0.5-0.9 mm towards one end-cap in the axial dimension. The intensity of the focussed beam is not homogeneous over its 0.4 mm length, though, so ion production may have been concentrated from localized spots within the broader focal area. The initial radial (r) and axial (z) coordinates of the ions when they are desorbed at this position are thus $r = r_0 = 10$ mm and somewhere between $z = 0.5$ -0.9 mm. Figure 5.4 displays a summary of the signal versus phase data that were acquired with the lens at this position. After collecting several series of data, the lens was translated to a new position 0.5 mm towards the trap center axis. All the data summarized in Figure 5.2 came from this spot on the sample ($r = 10$ mm and $z = 0.0$ -0.4 mm). In order to compare the results from each position, a data series collected at the second position has been included in Figure 5.4. The signal intensities from the various series have not been normalized; rather, those series selected for comparison between the positions were chosen on the basis of their similar intensities, so that differences in ion production between series could be eliminated as a variable.

Examining the results displayed in Figure 5.4, there is a striking phase shift evident in the

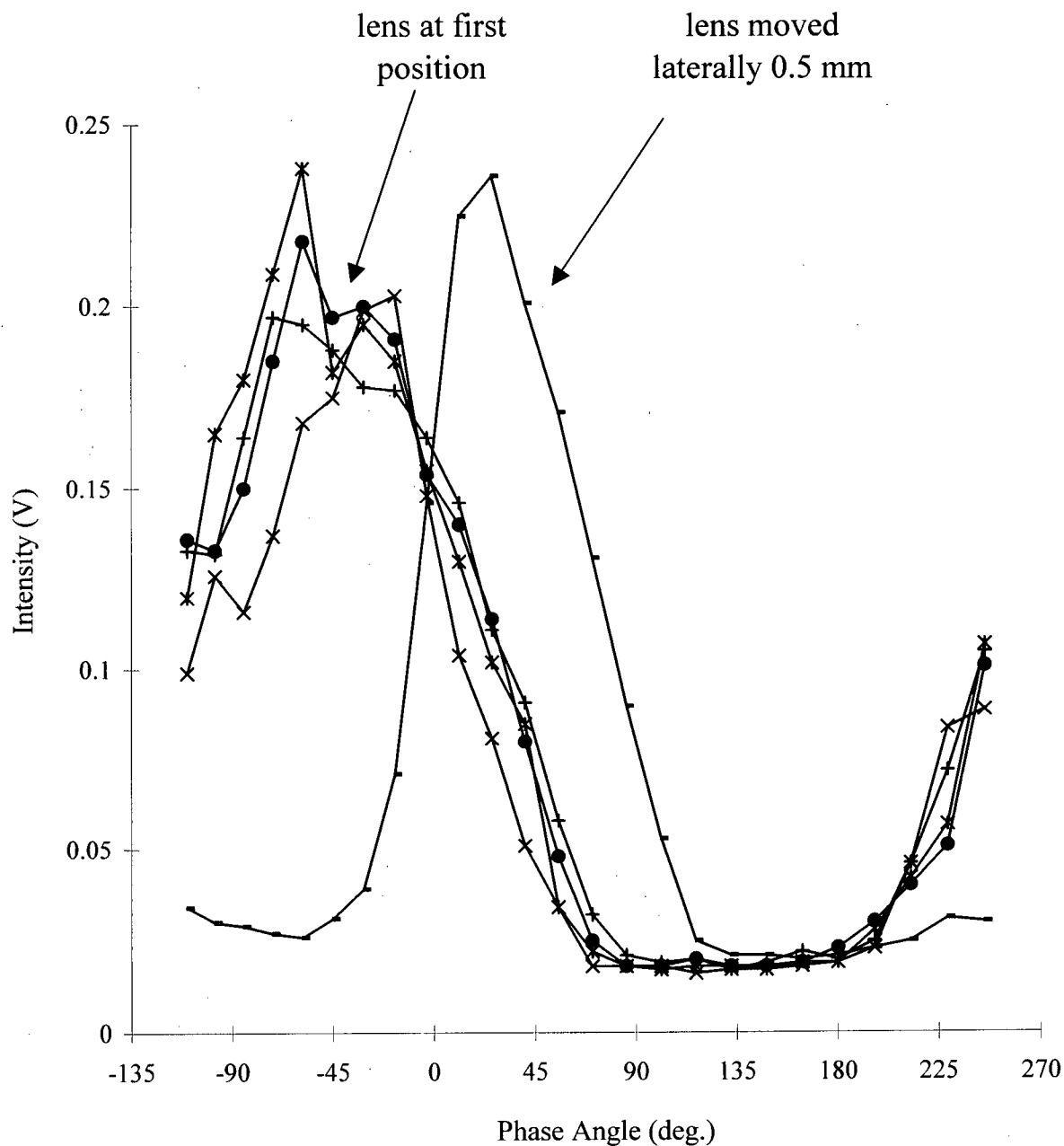


Figure 5.4 Integrated signal for the TBA molecular ion acquired as a function of phase angle. Series of data were collected with the laser focal area situated at two different positions on the probe tip. The first position was located at the edge of the probe tip. The second position was translated over 0.5 mm, so that ion production came from near the probe tip center.

data for the two lens positions. All the series acquired for the first lens position have similar values for the phase for best trapping ($\sim 45^\circ$), as well as for the cut-off phase where ions are no longer trapped ($\sim 70^\circ$). The series displayed for the second position has an optimum phase value of $\sim 25^\circ$ and a cut-off phase of $\sim 115^\circ$, results which are entirely consistent with those summarized in Figure 5.2. The discrepancy between the cut-off phases is especially important, because it suggests that, in the absence of ion-ion interactions, the optimum phases for trapping will still be substantially different. This indicates that the relationship between trapping efficiency and phase depends strongly on the position of the probe from which the ions originate.

To date, there is insufficient information available to elucidate the mechanism responsible for this dependence. Ion injection simulations have been run where the ions were injected from positions that were displaced from the axial origin of the trap, but in no case was a shift in the peak phase for trapping observed. The only difference noted in the simulations was an increase in the axial displacement of the ions over the course of their trajectories.^{***} Some other factor is then probably responsible for the variation observed in Figure 5.4. One possibility is that the effect is due to irregularities in the quadrupole field caused by the spatial configuration of the probe tip: the probe tip is flat across its surface, and there is a separation between the edge of the tip and the ring electrode (the gap is 0.35 mm all the way around the probe tip). At the edge of the probe tip the strength of the electric field may be very high, so ions created there may experience different conditions than those formed near the center of the probe. In any event, it is impossible to state with certainty what the cause of this effect is; the results indicate, however, that the area from which the ions are created from the probe is another important parameter for

^{***} In the absence of scattering effects, ions injected from the ring have large trajectories in only the radial dimension—ions injected with zero initial displacement or velocity in the axial dimension experience no acceleration toward the end-caps, and thus the axial component of their trajectories is zero.

laser desorption in the quadrupole ion trap.

5.3.3 Study of the Effects of the Helium Bath Gas Pressure on LD-ITMS

Thus far in the discussion, the effects of the helium buffer gas on the trapping mechanism have been ignored. It has long been recognized that to trap ions injected with some energy from the trap periphery, some means of damping the motion of the ions must be employed (although some researchers employing special trapping methods appear to have obviated this requirement.¹⁴⁾ Typically, a bath gas of helium at approximately 1 mtorr is utilized to effect this damping. For the simple trapping method under consideration here, no signal is observed for laser desorbed ions if a bath gas is not present. In the search to discover the factors responsible for the fluctuation in the phase dependence of trapping efficiency, an experiment was performed to see if variations in the pressure of helium were somehow responsible for the discrepancies noted.

Figure 5.5 displays three series of signal versus phase data acquired for three different pressure conditions. The first series was collected when the pressure of helium was extremely high, approximately 8 mtorr. This was the highest pressure that could be maintained in the vacuum chamber before the turbo pump switched off (which did in fact occur immediately after this series was collected). The spectral series acquired at high pressure is characterized by prominent TBA molecular ion peaks, with relatively small signals from the fragment ions. At lower pressures, Figures 5.5(b) and (c), fragmentation of the desorbed ions becomes increasingly prominent, as the molecular ion signal is greatly reduced and the intensity of the peaks due to lower mass fragments increase. This type of behavior has been observed in the past by McLuckey et al.,⁶⁶ who presumed that higher pressures limit the kinetic energies that the ions acquire from the RF field, thereby reducing the energy of collisions between the injected ions

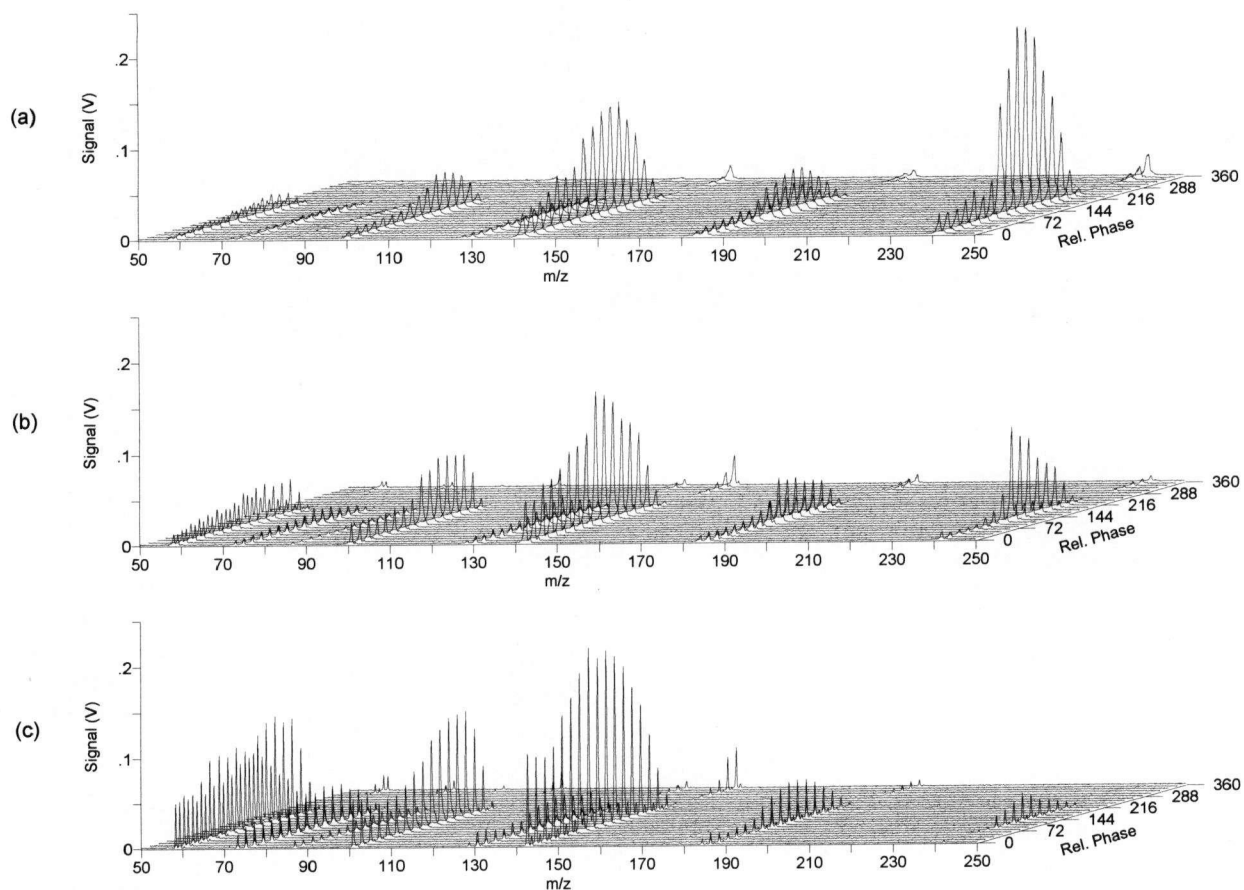


Figure 5.5 Series of laser desorption mass spectra of tetrabutylammonium (TBA) acquired as a function of the phase angle at the time of the laser pulse. The pressure of helium within the manifold was varied between the series shown. The data in plots (a)-(c) were collected for helium pressures of 8, 2, and 0.5 mtorr, respectively. The calibration of the z-axis is relative.

and the background gas. Apparently, at high pressures, the reduction in collision energy more than compensates for the increased collision frequency, because the diminishment of fragmentation is indicative of a decrease in the average internal energy deposited into the ions as they are injected, or desorbed in this case.

Figure 5.6 displays the integrated intensity for the m/z 242 molecular ion signal, as well as the integrated signal for the entire mass spectra (total ion current), plotted as a function of phase for the three different pressures. The total ion currents do not increase nearly as much with pressure as do the TBA molecular ion signals. As shown in Figure 5.5, the reduction of the TBA molecular ion signal at lower pressures is at least partially matched by the substantial increase in the signal intensities of the fragment ions. This suggests that much of the apparent increase in trapping efficiency commonly associated with high pressure ion trap operation may in fact be due to reduction of fragmentation upon injection/desorption, rather than simply more effective containment. As well, close inspection of Figures 5.5(a) and (b) reveals that the resolution of the peaks is severely degraded at the higher pressures. Clearly, though, the presence of helium does improve LD-ITMS performance, because as the pressure is lowered beyond 0.5 mtorr, the molecular ion signal disappears altogether for TBA, followed soon after by the signal from the fragment ions.

Returning to the original problem of the variation in the phase relationship, the data summarized in Figure 5.6 indicate that there is no significant deviation in the dependency of TBA signal on phase, so the pressure of the background gas is not a factor in this regard.

5.4 Conclusion

The data presented within this chapter illustrate how the phase dependence of LD-ITMS signal intensity is a function of the number of ions produced during the laser pulse, as well as on

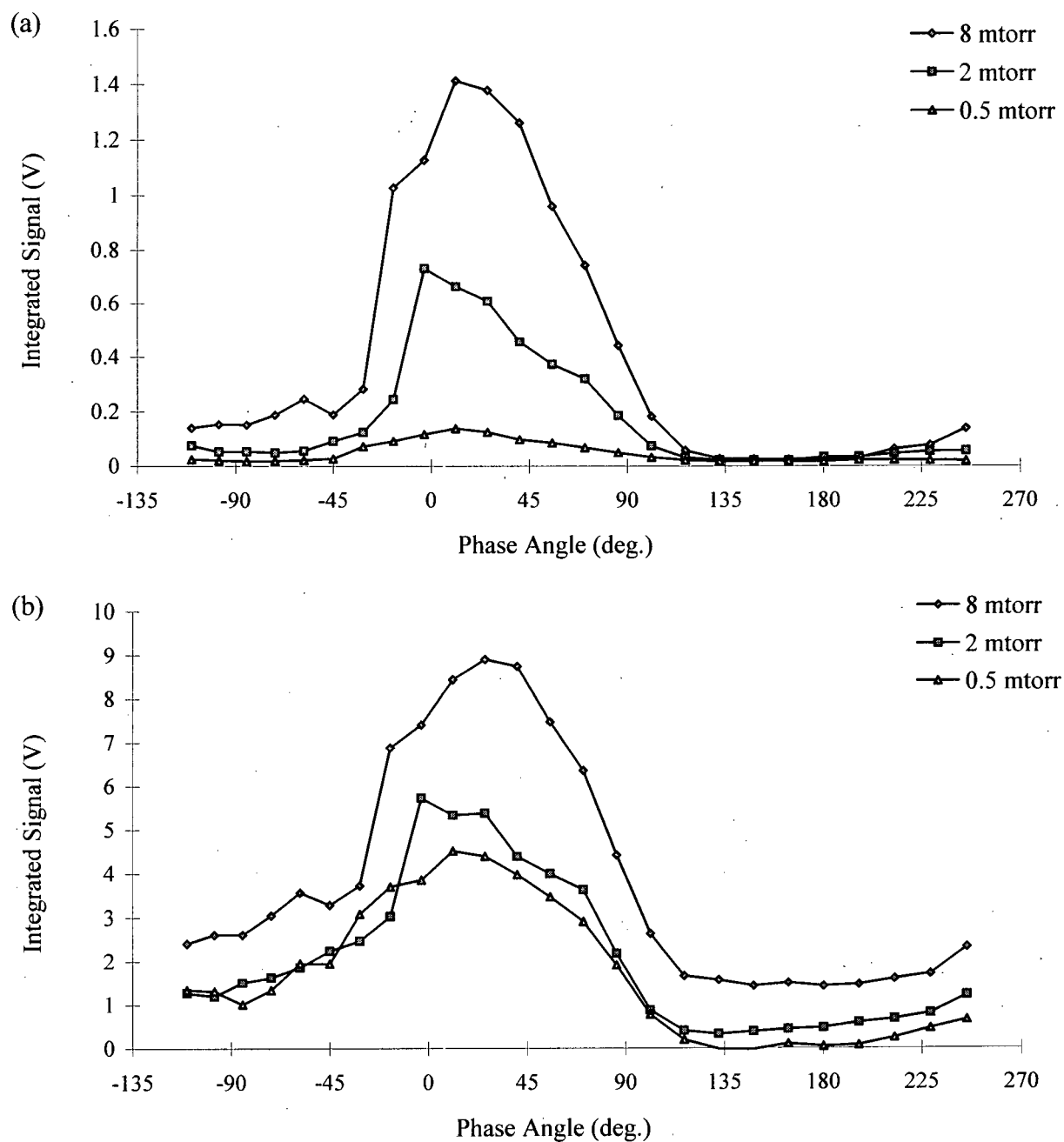


Figure 5.6 (a) Integrated signal for the TBA molecular ion plotted as a function of phase from the three series displayed in Figure 5.5. (b) Total ion current plotted as a function of phase for the same three data series. The decrease in signal intensity for the TBA molecular ion as pressure lowers is partially compensated by the increase in the fragment ion signals.

the position of the probe from which the ions originate. The mechanisms proposed to explain the experimentally observed trends rely upon conjecture regarding phenomena accompanying ion production from laser desorption. Before the trapping process for laser desorbed ions can be described with complete certainty, it will be necessary to successfully elucidate specific details of the laser desorption process that remain unknown. Nevertheless, the effects observed are real enough, and the mechanisms proposed to explain them, while speculative, are plausible and consistent with the information available to date.

The effects discussed in this chapter portend real problems that will complicate practical applications of LD-ITMS, especially those requiring quantitative information. First and foremost, the strong dependency of the optimum phase value for trapping on total ion yield and on the location of the laser focal area make it impossible to predict what the best phase will be for a given experiment. Moreover, even if a pre-experiment is performed to learn the optimum phase, there is no guarantee that the value selected will remain the optimum value. When a continuous series of data is collected, the ion signal will eventually disappear, and there may be no sure method to determine the extent to which this is due to loss of ion production or to the advent of an unfavorable shift in the optimum phase for trapping. Adjusting the phase at which the laser fires may temporarily increase the signal intensity, but this will also eliminate any possibility of employing calibration curves for quantitative analysis. Summing up, in order to optimize the signal for LD-ITMS, it is presently necessary to empirically discover the best phase angle for trapping not only at the beginning of each experiment, but also at periodic intervals throughout the experiment.

Regarding the best pressure of helium to use for LD-ITMS, evidently a relatively high pressure (> 1 mtorr) is best to minimize fragmentation and to optimize trapping efficiency, but these benefits come at the expense of overloading the vacuum system, increased risks of arcing,

and severe losses of resolution. Accordingly, it is not possible to state an optimum value for routine use, because a trade-off will need to be made depending on the relative importance of these factors.

CHAPTER 6

COMPUTER SIMULATION STUDIES OF THE TRAPPING PROCESS USING SIMION 6 SOFTWARE

6.1 Introduction

When studying complicated systems such as quadrupole ion traps, many instances arise where it is difficult to elucidate the mechanisms that are responsible for observed effects. In these situations it is often desirable to incorporate simulations based upon sound theoretical principles into the investigations. Simulations performed on fast computers permit the investigator to verify prior experimental results or to quickly test the effects of many variables without having to devise and assemble elaborate experimental systems. Furthermore, simulations offer a degree of flexibility that is difficult to attain experimentally. In real experiments, for instance, it may be impossible to completely isolate one particular variable for study, whereas this is trivial for a properly designed computer simulation. By undertaking a series of related simulations, the effects of a host of variables can be examined in a short period, and insight into a particular process can be gained that may be not be attainable through experiments alone. A cautionary note, however, must always be included in any discussion regarding simulations: the results of simulation experiments are only as valid as the accuracy with which the model in question mimics the real system. Great care must therefore be taken when devising a simulation experiment to ensure that accuracy is maintained and that every facet of the model is well-understood; failure to adhere to this principle when studying a complicated system will inevitably lead to faulty interpretation of results.

SIMION 6 is a commercially available software package that has been developed to

facilitate studies of all manner of problems involving ion and electrode systems. Produced by David A. Dahl at the Idaho National Engineering Laboratory, SIMION 6 was obtained from Scientific Instrument Services (Ringoes, NJ). For a full description of SIMION 6, the reader is referred to the manual that accompanies the software.

When designing a simulation to be run on SIMION 6, the first step that must be taken is to specify the dimensions and geometry of a model electrode system in a three-dimensional grid to be stored in the computer's memory. Elements of the grid are designated as either part of an electrode set to a given potential, or as free space through which charged particles may move. The force on a charged particle located at a specific grid point is governed by the strength of the electric and magnetic fields present at that point. Since the magnitude of the electric field is determined not only by the potentials on the electrodes, but also by the electrode separation, a scaling factor is used to assign the distance that each grid unit is equivalent to. Magnetic fields were never included in the simulations described here, so no further mention will be made of how SIMION 6 accounts for these. A very large number of grid units may be used in the simulations, allowing for fine resolution of electrode structures; however, excessive numbers of grid units may not provide a significant increase in accuracy of the calculations, and they add extra time to the runs.

It is possible to simulate the motion of large numbers of ions simultaneously. The practical limit to the number of ions that may be included in each run is set by the speed of the CPU and the RAM of the host computer, in conjunction with the time and patience available to the investigator. At the start of each simulation, the program assigns a set of initial values to each ion that is to be "created." Some characteristics of each ion that are specified by the user include its mass, charge, initial kinetic energy, initial coordinates, and the delay after time zero (the start of the run) at which it is created. Subsequent to initialization, at small time intervals,

the program repeatedly calculates values for the following properties: the potential on each electrode, the electric field strength at each grid unit, the distance traveled by each ion since the last calculation, and the new spatial coordinates and velocity of each ion. The maximum time interval that may elapse between each set of calculations is also set by the user. Small intervals provide the greatest accuracy, but the additional calculations required increase the time necessary to complete each run of the program. By continuously recalculating the potential on the each electrode after each time interval, the program allows for devices employing AC potentials to be modeled. Other factors may also be taken into consideration, such as the effects of collisional dampening and ion-ion repulsion on ion motion, although the accuracy of the latter is not highly regarded. At the end of each time interval, the program checks the new position of each ion; if an ion is located in a grid unit assigned to electrode space, then the ion is destroyed ("splat," in SIMION 6 parlance) and is removed from further calculations. The program keeps running until either all the ions have been lost at electrode surfaces or a pre-set maximum time-of-flight has been reached. To prevent quadrupole ion trap simulations from running indefinitely while ions with stable trajectories oscillate between the trap electrodes, it is advisable to assign a low value to the time-of-flight, such as 50 μ s. After this period, the number of ions within the trap stabilizes: all ions that have unstable trajectories will have already been lost.

SIMION 6 is especially useful because it provides for a visual display of the motion of charged particles in response to the electric fields within the model electrode system. This feature helps the investigator to gain an intuitive understanding of the effects caused by modifications to the simulation parameters. As well, procedures are available to expedite data collection during the runs. For instance, the position and kinetic energy of each ion may be recorded at each time interval, or when they cross a particular region in space (such as the trap center). These features are made all the more useful because user-written programs are easily

incorporated into the main SIMION 6 program, adding a high degree of flexibility to the simulations. The user programs also facilitate the automation of repetitive parametric simulations.

The remainder of this chapter is concerned with SIMION 6 simulation studies that were devised and implemented to study the containment process for ions injected into the trapping volume from the trap periphery. This problem is the main concern of this thesis, and has already been discussed at length in previous chapters. The results from the simulations will be discussed with respect to the real experimental data presented earlier, and conclusions will be drawn where appropriate.

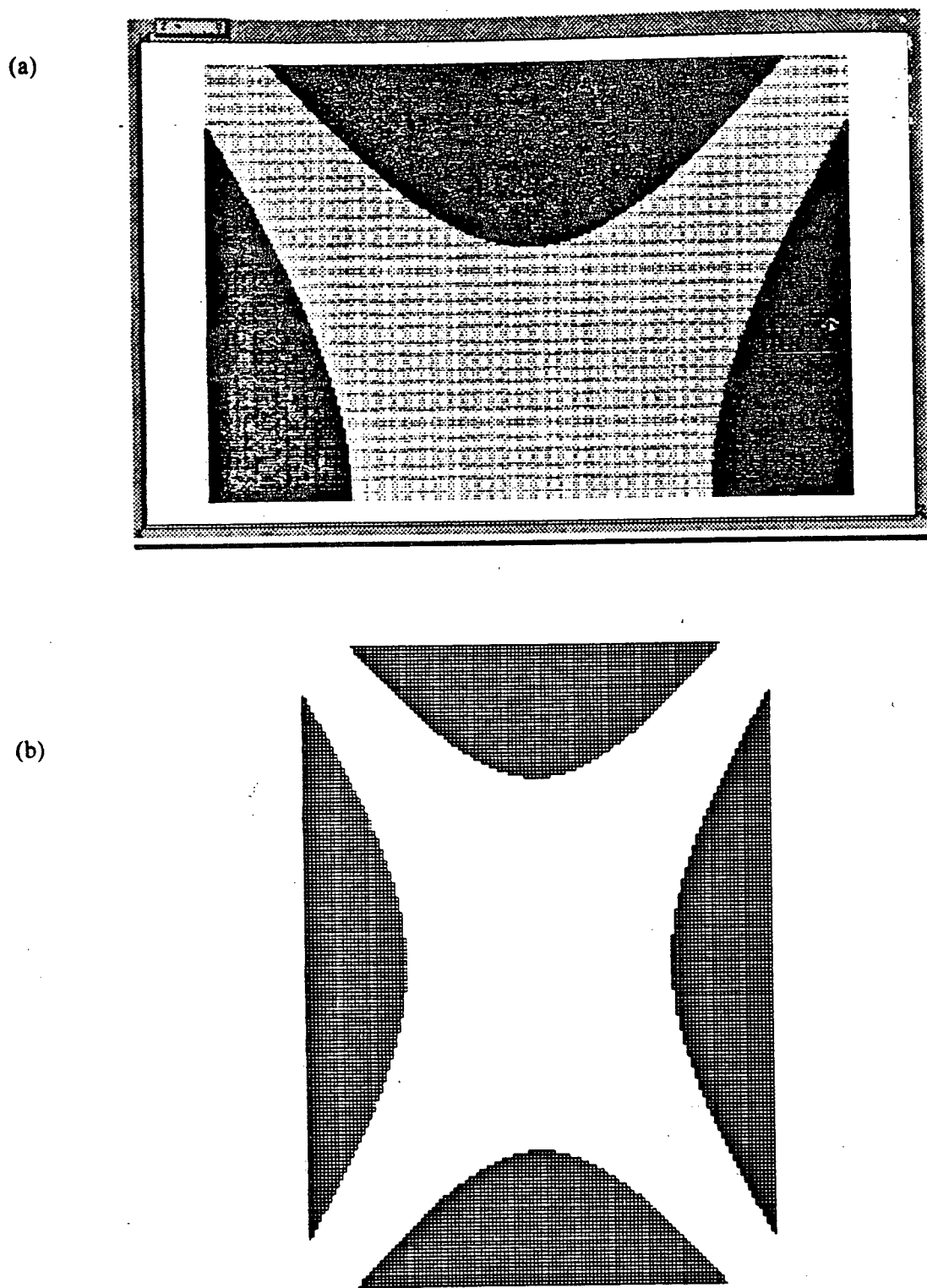
6.2 Experimental

All the experiments described in this chapter were quadrupole ion trap simulations run on a 133 MHz Pentium equipped computer utilizing SIMION 6 software. Figure 6.1(a) is a picture of the array of grid units used to define the ion trap electrodes. The array was programmed to have cylindrical symmetry about the x-axis of the SIMION “workbench,” and it consisted of 251 grid units in the x dimension, 173 grid units in the y dimension, and one grid unit in the z dimension.* The ring electrode geometry was determined from equation (6.1):

$$\frac{r^2}{r_0^2} - \frac{z^2}{z_0^2} = 1 \quad (6.1)$$

where r_0 is the ring electrode radius, equivalent to 100 grid units here; z_0 is one half the minimum separation of the end-cap electrodes, 71 grid units. Similarly, the end-caps were

* The x-axis in the SIMION workbench corresponds to the axial dimension of the ion trap, normally specified to be the z-axis. The y and z dimensions for SIMION, accordingly, are equivalent to the radial dimensions of the ion trap, normally specified as x and y.



SIMION

Figure 6.1 (a) Array of grid units used to construct 3-D model ion trap electrode structure for SIMION 6 ion injection simulations. (b) Cross-sectional view of cylindrically symmetric ion trap electrode model obtained by rotating the array in (a) around its x-axis.

specified by equation (6.2):

$$\frac{r^2}{r_0^2} - \frac{z^2}{z_0^2} = -1 \quad (6.2)$$

Figure 6.1(b) is a cross-sectional view of the resulting cylindrically symmetric electrodes.

To perform the ion injection simulations, a customized user program was developed from the sample ion trap programs included with the SIMION 6 software. Procedures were added to the new program to facilitate recording of data and automation of repetitive parametric studies. The program was designed so that the critical specifications of the model ion trap were the same as those of the real laboratory device. Accordingly, the frequency of the RF potential was set to 1 MHz. The amplitude of the RF potential on the ring electrode was calculated for each run from the q_z and the m/z that the trap was “tuned” to. No DC or supplementary AC potentials were included in the simulations, and the end-caps were considered to be earthed. Since the radius of the real trap ring electrode was 10.0 mm, and this distance was equivalent to 100 grid units in the SIMION 6 electrode array, each grid unit in the model was assigned a distance of 0.1 mm. A procedure was also included in the user program to simulate the cooling effects resulting from a bath gas of helium. The mean free path (fp) between collisions was set by the user. For each time step, depending upon the distance (d) that the ion had traveled since the previous calculation, the probability that each ion had of experiencing a collision was calculated from (6.3).

$$1 - e^{-d/fp} \quad (6.3)$$

At each time step, the probability of a collision was compared to a random number between zero and one, and a collision occurred if the random number was the lesser of the two. Each collision assumed a direct hit on a resting gas molecule (mass of 4 Da). The velocity of the ion was then

attenuated by a factor of

$$\frac{m-4}{m+4} \quad (6.4)$$

where m represents the mass of the ion.

The experiments selected for inclusion in this chapter illustrate phenomena that are significant to the model of the ion trapping process being developed in this thesis. They consist of a set of simulations testing the dependence of trapping efficiency on q_z , the phase at the time of injection and the initial kinetic energies of the ions injected from the ring electrode (as before, zero degrees corresponds to the positive zero-crossing of the RF potential.) The significance of these experiments will be described in the Results and Discussion section below.

Table 6.1 contains summary data for the simulation experiments described in this chapter. Each column of data in the table contains the values of parameters used for a particular simulation trial. Most of the parameters have names that are self-explanatory, including the “number of ions” injected for each trial and the “ m/z ” of each ion; others require additional explanation. “Initial kinetic energy,” for instance, refers to the center value of a rectangular distribution of initial energies that has a width specified by two times the “percent kinetic energy variation.” Using simulation trial 2 as an example, where the injected ions had a mean kinetic energy of 3 eV with 67% variation, each ion thus had an equal chance of starting with any energy between 1-5 eV. For all the runs where the ions had some initial velocity, there was also a distribution of directions over which they were injected. In the absence of external electric fields, the injected ions fanned out from their point of origin into a cone of width governed by the “cone angle off the velocity axis.” The center axis of the cone was always oriented directly towards the center of the ion trap. The next two parameters have already been introduced: the “mean free path” refers to the average distance that an ion traveled between collisions with a

Parameter	Experiment		
	1	2	3
number of ions	200	200	100
m/z	250	250	250
initial kinetic energy (eV)	0	3	10
% kinetic energy variation	0	67	25
cone angle off velocity axis (deg.)	10	10	5
mean free path (mm)	20	20	20
random time of birth (ns)	14	10	10
maximum time-of-flight (μs)	50	50	50
initial axial position (mm)	0	0	0
initial radial position (mm)	9.99	9.9	9.9
random displacement, height (mm)	0.05	0.05	0.05
random displacement, width (mm)	0.2	0.2	0.2
start q _z	0.1	0.1	0.1
final q _z	0.9	0.9	0.9
delta q _z	0.1	0.1	0.1
start phase angle (deg.)	0	0	0
final phase angle (deg.)	355	355	350
delta phase angle (deg.)	5	5	10
Comments:	Number of trapped ions is determined as a function of phase and q _z for 3 different mean kinetic energies (KE).		
Constants			
collision gas mass (a.m.u)	4	<i>italics</i> indicates changed variable of minor importance	
RF frequency (MHz)	1	bold indicates primary variable	
ring electrode radius (mm)	10		
a _z	0		

Table 6.1 Parameters for the SIMION 6 quadrupole ion trap simulation experiments.

helium atom, and the “maximum time-of-flight” specified the time that each simulation trial was allowed to run before termination. For all the experiments, the population of ions within the trap stabilized in a (simulated, not real) period of less than 50 μs , for $q_z \geq .01$. The “initial axial/radial position(s)” specify the initial spatial coordinates of the ions when they were injected. Ions were created very near to the electrode boundaries to simulate real desorption/injection conditions. Again, the initial positions of the ions were considered to be randomly distributed (rectangular distribution) about a mean value. The rectangular area over which ions were formed was programmed to have dimensions and alignment similar to those of the laser focal spot of the real experiments. For the simulations of ions injected from the ring electrode, the ions originated from a 400 μm x 100 μm strip that was aligned lengthwise along the axial dimension of the trap. The center of the distribution had zero axial displacement from the trap origin, and radial displacement approximately equal to r_0 . The remaining parameters in the table were used to dictate the q_z and phase values for each simulation run during the automated experiments.

Close inspection of the table will reveal that there were occasions where more than one parameter was varied over the course of an experiment. The explanation for this is that the simulations here were selected from a larger group of studies that were not necessarily acquired in a systematic fashion. Rather, they were designed and implemented in a manner perhaps best described as exploratory. Experience has shown, though, that differences in trapping performance between the experiments are due primarily to the variables indicated, and that the extra variables do not significantly alter the results obtained.

6.3 Results and Discussion

Figures 6.2-6.4 display the results of three separate sets of trials of an experiment

studying the effects of phase and q_z on trapping efficiency of ions injected from the ring electrode. The principal difference between the conditions that each set of data was acquired under was the initial kinetic energy of the ions. The data depicted in Figure 6.2 show the number of ions trapped, out of 200 created with zero kinetic energy. The relationship between the phase of the RF field at the time of ion creation and the number of ions trapped is the most prominent feature of the data. For q_z values between 0.1 and 0.9, the best phase for trapping ions is largely independent of q_z and is around 90° . Significantly, no decrease in trapping efficiency is noted at high q_z ; this evidence directly contradicts the potential barrier model, as was discussed at length in Chapter 4 and elsewhere.¹⁰² The simulated data suggest, in fact, that the trapping efficiency at the optimum phases improves somewhat as q_z is raised. Recall, though, that the model ion trap system used to generate this data did not consider the effects of collision induced fragmentation or ion-ion interactions.

A summary was provided in Chapter 5 of the knowledge gained from the simulations regarding the dependence of the trajectories of ions on the phase at which they are injected. Further discussion will be presented here on this topic, firstly for the case of ions created at the ring electrode with zero initial kinetic energy. One of the findings is that the ions will not be able to enter the trapping volume if they are created at times such that they initially face a potential barrier. This is the case for positive ions created when the phase of the RF potential applied to the ring electrode is between 180° and 360° . Indeed, Figure 6.2 shows that no ions were trapped for these phases. Ions may thus only enter the trapping volume if they are initially accelerated outwards, towards the trap center, which occurs in this case for phases between 0° and 180° . The data in Figure 6.2 illustrate how ions with no initial energy are only trapped at phases around 90° , in the absence of complicating effects, such as fragmentation and ion-ion interactions. Those ions that are successfully contained by the quadrupole field undergo

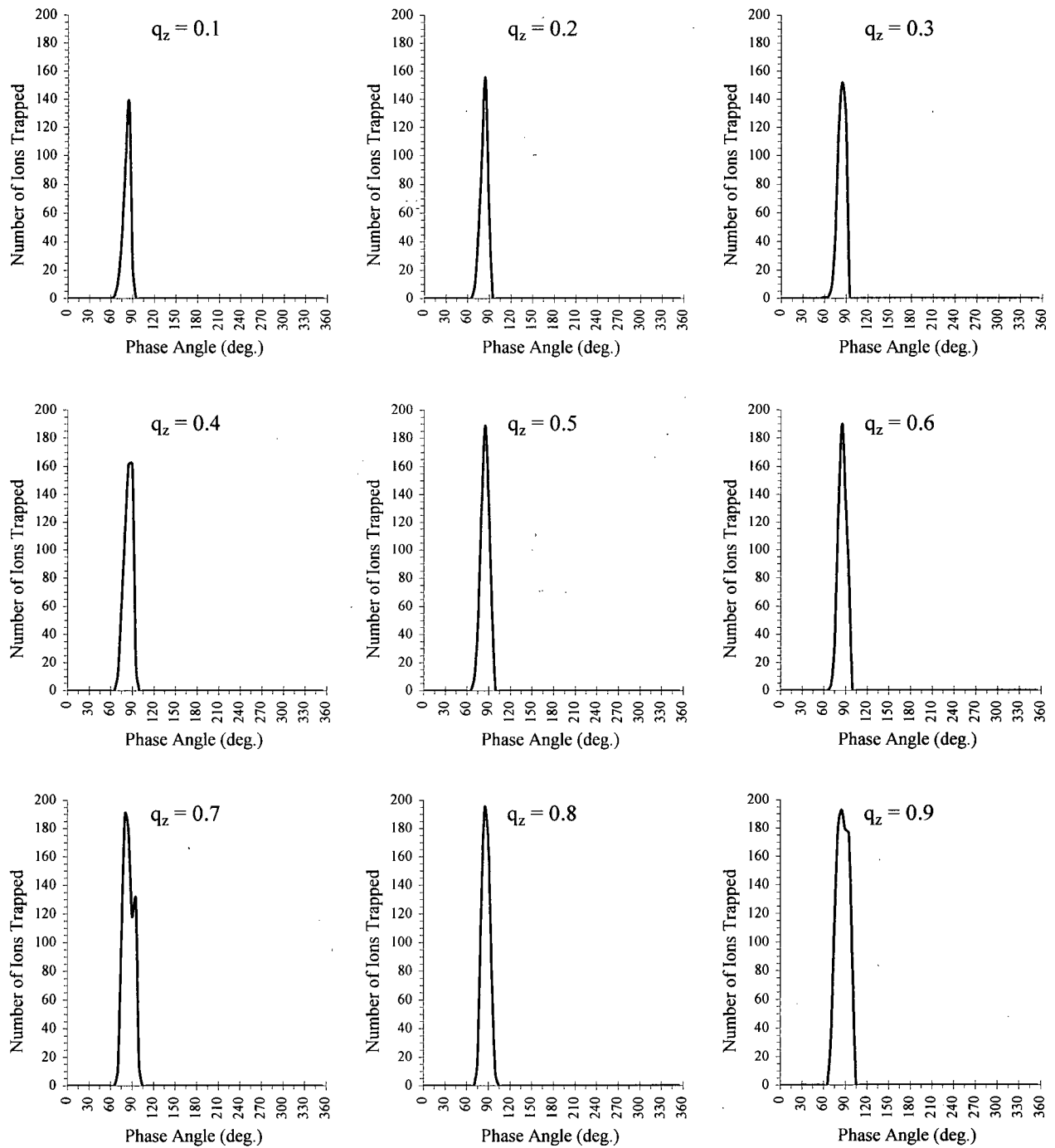


Figure 6.2 Number of ions trapped versus the phase angle at which they were injected from the ring electrode for q_z values 0.1 to 0.9. For each phase and q_z value, two hundred ions were injected with zero initial kinetic energy. See Table 6.1 for a full description of the simulation parameters.

oscillatory motion between the trap electrodes, with the limits of their displacement being very near the ring electrode surface. Ions created at phases such that they penetrate the trapping volume, but at values less than 90° , are initially accelerated outwards for an excessive period, and are lost at the side of the trap opposite whence they originated. Conversely, those positive ions entering the trapping volume that have been created at phases greater than 90° do not penetrate sufficiently far into the trap before the direction of the RF electric field reverses. These ions are pushed back towards their place of origin during the half cycle of the RF period that follows when the potential on the ring is negative. As expected, Figure 6.2 shows that no ions are observed to be trapped over the range of phases between just past 90° and 180° .

The description of the dependence of ion trapping on phase provided above suggests that ions with zero initial kinetic energy may only be trapped when introduced at exactly 90° ; however, the results in Figure 6.2 indicate that some ions can be trapped over a range of phases encompassing roughly 70° to 90° . This broadening may be explained by cooling effects due to the helium buffer gas included in the simulations. Ions created at phases just less than 90° would normally be lost at the opposite side of the trap, because they would gain too much energy in the initial cycle of the RF field. Depending on the mean free path, there is a certain probability that collisions will occur during the traversal of the ions across the trap. Collisions remove some of the kinetic energy that the ions acquire from the quadrupole field, but the number of collisions that ions are likely to experience in their first traversal of the trap is minimal. The cooling effect of each collision is also small. Collisional cooling is thus sufficient only to increase the trapping efficiency for those ions that have very little extra kinetic energy, such as those that are injected at phases slightly less than 90° .

It is believed that collisional cooling may be a real factor for LD-ITMS that affects the width of the range of phases over which ions may be trapped. Collisional cooling effects,

however, cannot account for the q_z dependence on the phase relationship discussed in Chapter 4, where the width of the distribution of appropriate phases narrowed as q_z increased (Figures 4.2 and 4.5). This trend is not evident in Figure 6.2. Moreover, the shift of the phase relationship in response to variation in the total ion current, discussed in Chapter 5 (Figure 5.2), cannot be explained by cooling effects. Perhaps the most convincing evidence that collisional cooling does not have a major role in determining the signal versus phase relationship for LD-ITMS is the fact that no variation was observed in the phase dependence when the pressure of helium within the manifold was itself the variable (Figures 5.5 and 5.6).

Figure 6.3 depicts data gathered in the same fashion as those in Figure 6.2, the difference being that the two hundred ions created for each phase and q_z value in this experiment each had some initial kinetic energy between 1-5 eV. The drastic decrease in trapping efficiency at $q_z = 0.1$, and to a lesser extent $q_z = 0.2$, is the most notable feature of this figure. This suggests that there is a minimum q_z value required to trap ions that have some initial kinetic energy. One general observation that has been made in the simulations is that, for all phases, if the amplitude of the RF field is too low to significantly affect their trajectories, ions injected with substantial energies will pass directly across the trap and not be trapped. Another interesting feature of the data is the shift towards higher values for the optimum phase angle for trapping ions. This occurs because less initial acceleration is required for the ions to penetrate sufficiently far into the trapping volume in order to avoid being pulled back into the ring when the polarity of the RF field reverses.

Figure 6.4 shows data obtained for similar conditions as Figures 6.2 and 6.3. Only one hundred ions were injected this time, and the energies of the ions was randomly distributed between 7.5-12.5 eV. Plainly, the decrease in trapping efficiency at lower q_z values is more pronounced when the ions are injected with relatively higher energies. No ions are trapped at all

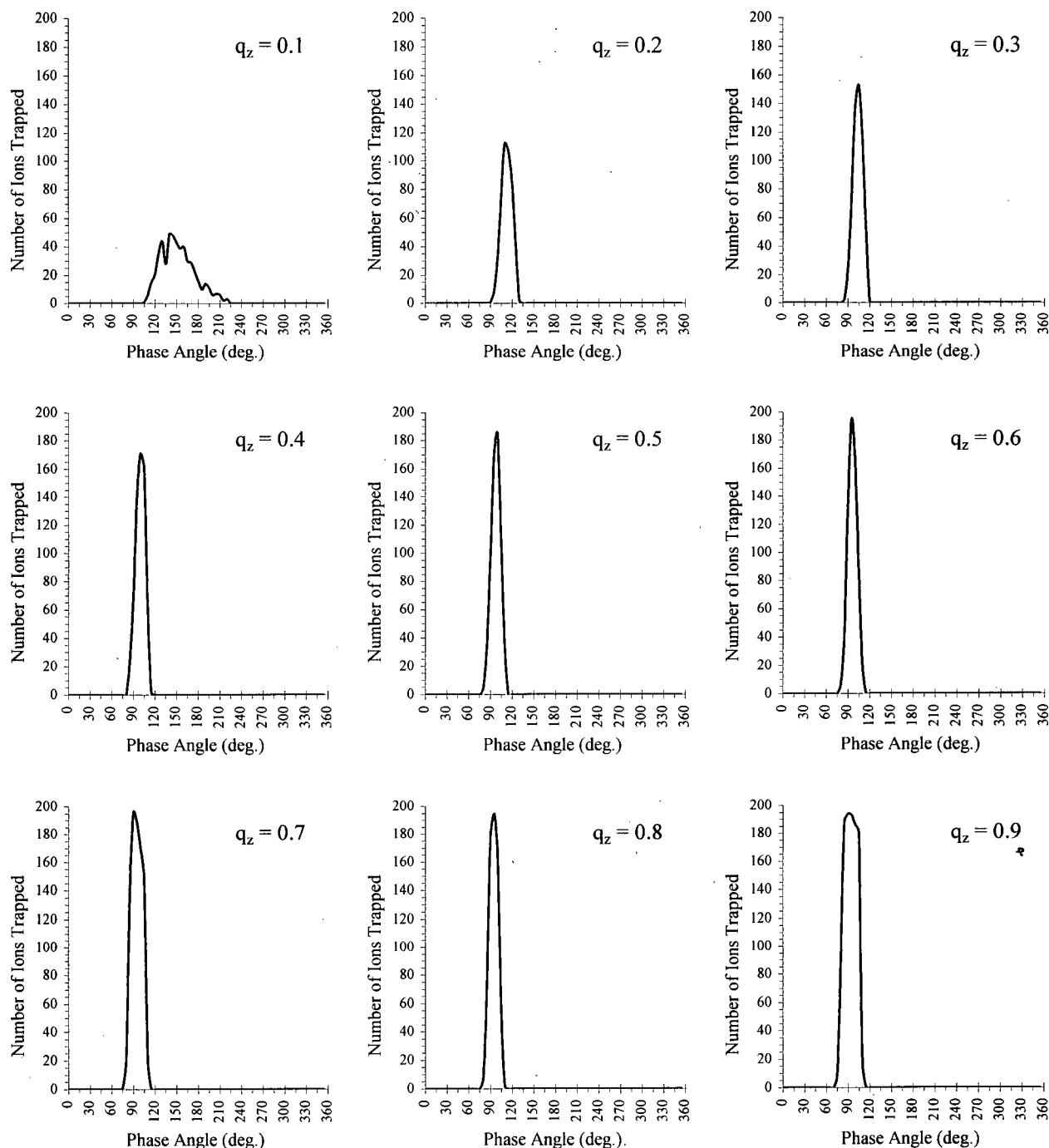


Figure 6.3 Number of ions trapped versus the phase angle at which they were injected from the ring electrode for q_z values 0.1 to 0.9. For each phase and q_z value, two hundred ions were injected with initial kinetic energies between 1–5 eV. See Table 6.1 for a full description of the simulation parameters.

at $q_z = 0.1$, and the efficiency is low for $q_z = 0.2$, as well. Comparing the results in Figure 6.3 with those of Figure 6.4, it can be seen that the optimum phase angle for trapping continues to shift towards higher values as the kinetic energies of the ions are raised. It noteworthy that the trapping efficiency at the optimum phase for the higher q_z values remains quite high, so the initial kinetic energies of the ions do not have a great effect on trapping efficiency, except for when the amplitude of the RF potential is too low.

The results of the experiments just described are summarized in Figures 6.5 and 6.6. Figure 6.5(a) is a plot of the phase angle at which trapping efficiency was highest versus q_z , for the three ranges of kinetic energies. Again, for ions with zero kinetic energy, the best phase for trapping was around 90° , and this result was independent of q_z . As the kinetic energy was raised, for all q_z , the optimum phase for trapping increased. This effect was especially prominent for the lower values of q_z , but it became less significant as q_z was raised. Figure 6.5(b) is a plot of the trapping efficiency at the optimum phase angle versus q_z , again for all three experiments. It is interesting to note that the simulations indicate that trapping efficiency actually increases with q_z . This effect is greatest when the energies of the ions are the largest, as the trapping efficiency is markedly low at the smallest q_z when the ions have substantial energies. This plot also indicates that when the phase relationship is optimized, trapping efficiency plateaus at higher q_z values, near 100%. Presently, there is no reliable experimental data available to compare this figure with, so it is not known whether or not this high value is realistically attainable. As stated previously, it is important that the results of simulations only be accepted with reserve.

Figure 6.6 shows the overall trapping efficiency for the three experimental trials plotted as a function of q_z . Overall trapping efficiency was calculated for each run by dividing the number of ions trapped by the number of ions created, integrated over all phase values. The importance of synchronizing the timing of the ion creation event with the phase of the RF

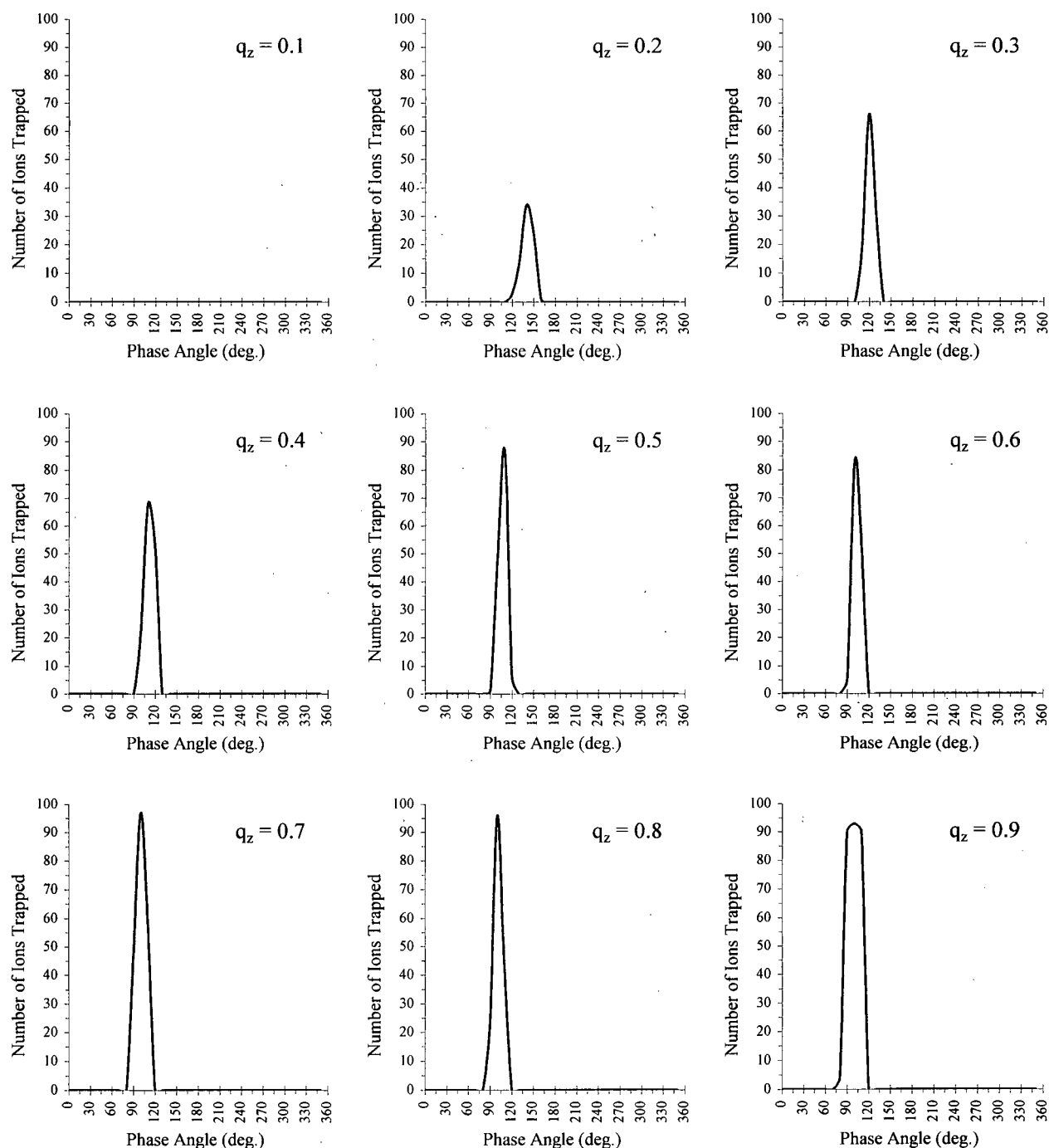


Figure 6.4 Number of ions trapped versus the phase angle at which they were injected from the ring electrode for q_z values 0.1 to 0.9. For each phase and q_z value, one hundred ions were injected with initial kinetic energies between 7.5–12.5 eV. See Table 6.1 for a full description of the simulation parameters.

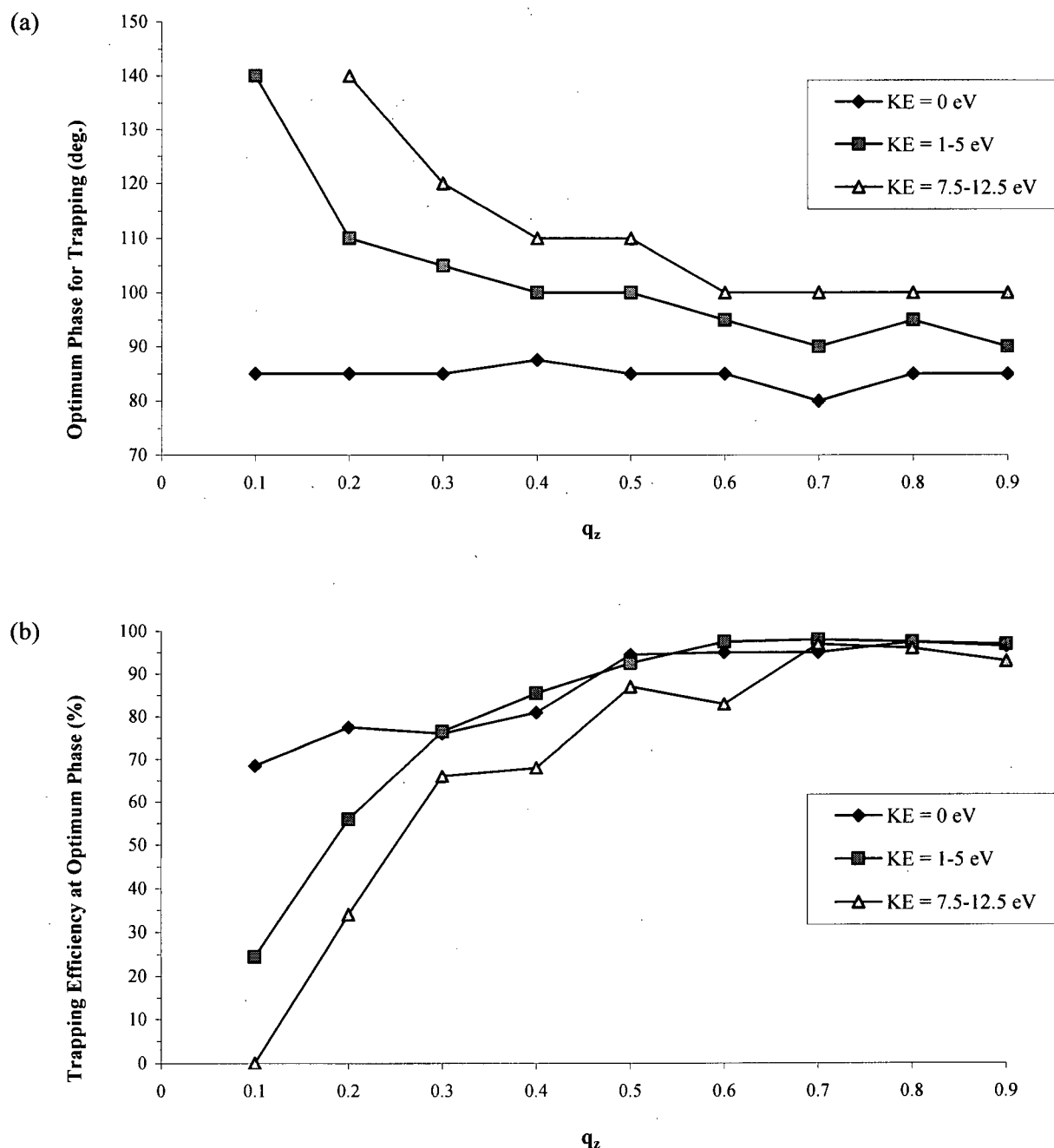


Figure 6.5 Summary of results presented in Figures 6.2–6.4. (a) Optimum phase for trapping injected ions versus q_z for three different ranges of initial kinetic energy. (b) Trapping efficiency at the optimum phase versus q_z for three different ranges of initial kinetic energy.

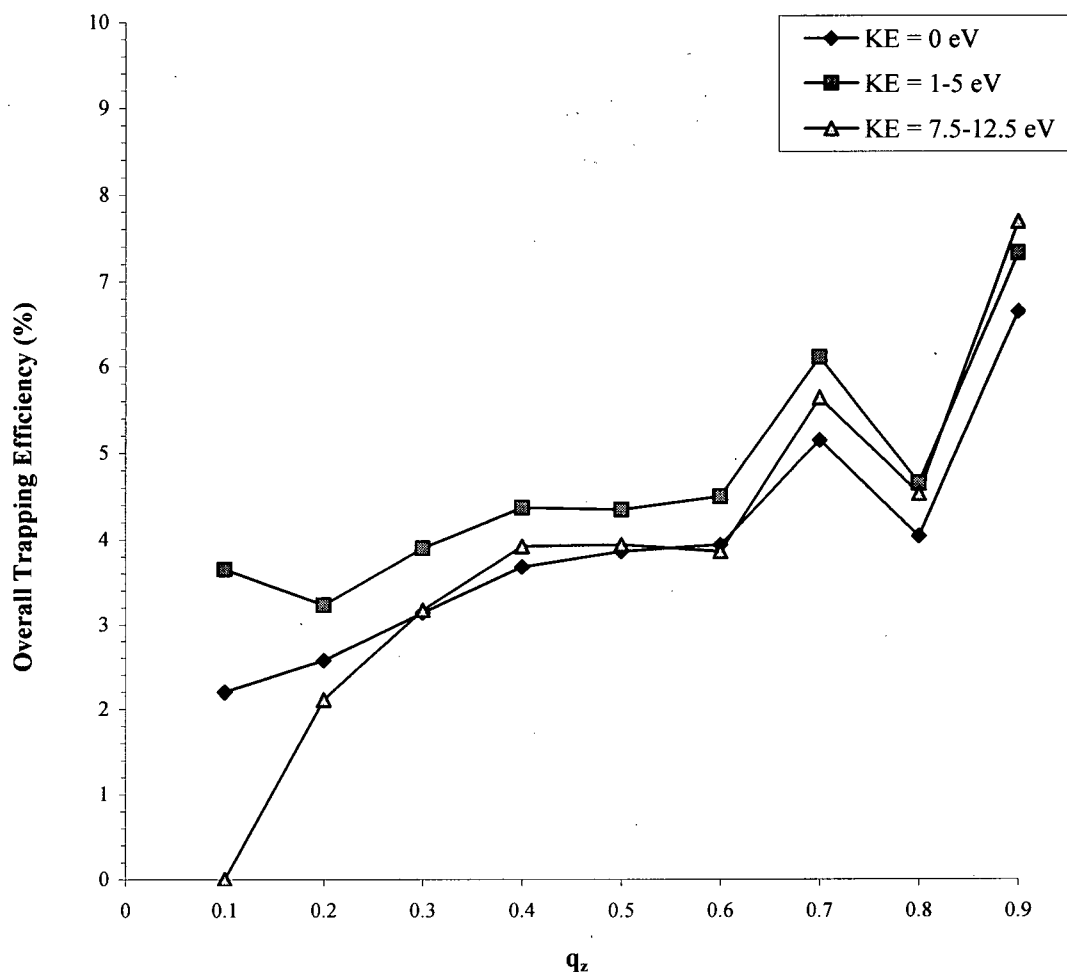


Figure 6.6 Summary of results presented in Figures 6.2–6.4. Overall trapping efficiency versus q_z for three different ranges of initial kinetic energy. Overall trapping efficiency is calculated by integrating the trapping efficiency over all phase angle values.

potential is emphasized by this plot, because when averaged over all phases, the trapping efficiency is quite low for each case. Thus, it can be expected that ion trap methods that utilize ion injection from continuous sources will suffer poor trapping efficiency.

Fragmentation due to collision induced dissociation was not considered as a possibility in the simulation model developed here. Had it been, because of the increase in kinetic energy of ions with q_z , it is clear that far fewer ions would have been trapped at the higher q_z values: ions whose trajectories would otherwise have been stable would have been destroyed upon colliding with elements of the background gas. This finding provides strong support for one of the conclusions of Chapter 4: fragmentation, more than any other factor, is responsible for the decrease in molecular ion signal intensity for LD-ITMS at high q_z .

CHAPTER 7

CONCLUSIONS

7.1 Summary of Thesis

This thesis has been concerned principally with the problem of how laser desorbed ions are confined by the electric field within the quadrupole ion trap. Prior to the investigations reported here, the efficiency with which laser desorbed ions are trapped by the quadrupole field was known to be related to the phase angle and the amplitude of the RF potential at the time of the laser desorption event. The exact mechanisms for these dependencies, however, were not well-understood, and the literature on the subject was remarkable in its inconsistency. Many details of the trapping process that had previously been poorly defined are believed to have been successfully elucidated in this thesis, the major findings of which are summarized below.

I. Polythiophene films are suitable standard samples for fundamental studies of laser desorption mass spectrometry. The consistency and longevity of ion production from this new sample type are superior to those of other commonly employed standard samples. Before the advent of polythiophene films as laser desorption samples, it was extremely difficult to obtain reliable experimental data regarding trapping efficiency in LD-ITMS. Polythiophene films were used to gather all the experimental data presented here.

II. The amplitude of the RF potential on the ring electrode, as specified by q_z for a particular m/z , is a critical parameter that governs signal intensity for LD-ITMS. For laser desorption of molecular species, it was found that the molecular ion signal intensity was inversely related to q_z . Contrary to previous assertions, this trend is not the result of the inability of the ions to penetrate

a static "potential barrier," that has a magnitude proportional to q_z . The experimental evidence indicates that this trend is not followed for lower mass fragment ions. Furthermore, the data indicate that the difference between the two cases is not a function of the mass of the ions, as has also been suggested. Rather, the evidence strongly suggests that the observed trends are the result of collision induced dissociation of molecular species subsequent to their injection into the quadrupole ion trap. Computer simulation studies utilizing SIMION 6 software demonstrate that trapping efficiency, in the absence of fragmentation, may in fact be enhanced at higher q_z values. This is not the trend observed experimentally, at least for molecular species. Therefore, for a model of the trapping process to be accurate, one requirement is that it must include a consideration of the effects of fragmentation.

III. It has long been known that the phase of the RF potential at the time of ion injection is an important parameter governing trapping efficiency, but the mechanism for this dependence has been poorly defined. The results from SIMION 6 based simulation experiments indicate that injected ions, in the absence of ion-ion interactions, may best be trapped at a phase of around 90° , or at a slightly greater value if the ions have appreciable initial kinetic energy. LD-ITMS data acquired from real experiments, however, demonstrate that there is range of phases for which ions may be successfully trapped. It is believed that this is due to the collective ability of the desorbed ion plume to prevent its core from being influenced by external electric fields; a process known as Debye shielding. The principal effect that may be attributed to Debye shielding is a delay added between when the ions are created and when they first experience the quadrupole field. The peak phase for trapping is shifted towards lower values when Debye shielding is a factor. Debye shielding effects are reduced if there are fewer ions produced during the laser pulse, or if the amplitude of the RF potential is raised. Accordingly, as the number of ions produced during each laser pulse diminishes, or as q_z is increased, the peak phase for

trapping shifts towards more positive values, and the width of the distribution of acceptable phases narrows. The data also suggest that if Debye shielding were not a factor, then the best phase for trapping injected ions would be just past 90° , in complete agreement with the results of the simulation experiments.

Some of the findings presented in this thesis have general applicability to all quadrupole ion trap methods utilizing external ion injection, whereas others are specific to laser desorption. Firstly, the finding that fragmentation is a factor of increasing importance at higher RF potentials is generally relevant, although the effect does not need to be considered for atomic ions, of course. Another finding of general applicability is that trapping efficiency *per se*, uncomplicated by fragmentation, is primarily a function of the phase at which the ions are introduced to the quadrupole field. The effects attributed to Debye shielding, however, will only be a factor for laser desorption, or other methods that produce substantial quantities of both positively and negatively charged particles. Hence, Debye shielding effects will not be observed for methods that involve the exclusive injection of either positive or negative ions.

7.2 Suggestions for Future Research

As discussed in Chapter 4, the trapping method investigated in this thesis is one of several that have been developed. There has yet to be an experiment performed that directly compared the relative efficacy of the various methods. The results of this thesis have shown, though, that trapping methods requiring synchronization of the laser firing time with the phase of the RF potential will have a disadvantage relative to those that do not. This is primarily because the relationship between trapping efficiency and the phase at which the laser fires is inconstant, a phenomenon which may be inherent to LD-ITMS. To increase the suitability of LD-ITMS for quantitative applications, some means must then be implemented to obviate the dependence of

sensitivity on phase. It is possible that the so-called “dynamic trapping” methods may meet this requirement. In addition, dynamic trappings may provide equal or better trapping efficiency than the method investigated here. Further investigations of the dynamic trapping methods are thus necessary to fully develop LD-ITMS as an analytical tool.

In the past, it has not been possible to make direct comparisons between the various trapping methods. The primary obstacle facing experimenters has been unpredictable fluctuations in the ion production from the various laser desorption samples used. The polythiophene films employed here, though, provide ion production that is much more stable than that of the previous sample types. These new samples can be used to better characterize the dynamic trapping methods. In order for the dynamic trapping methods to be investigated in this laboratory, however, the present ion trap instrumentation will need to be modified. Dynamic trapping methods rely upon the trapping potential being very low initially, so that ions can penetrate the space between the trap electrodes without being unduly accelerated, then it must quickly ramp up to a level sufficient to effect containment. The risetime of the RF potential for the present instrument is on the order of 1 ms, much too slow for effective dynamic trapping (10-20 μ s may be best.^{14, 35})

Future research may confirm that one or another of the several existing trapping methods is best suited for routine LD-ITMS operation, or perhaps all will be found to suffer some disadvantages. For the moment, this issue must await resolution.

BIBLIOGRAPHY

- (1) Vertes, A.; Gijbels, R.; Adams, F. In *Chemical Analysis*; Winefordner, J. D., Ed.; John Wiley & Sons, Inc.: Toronto, 1993; Vol. 124, pp 560.
- (2) Zenobi, R. *Fresenius J. Anal. Chem.* **1994**, 348, 506-509.
- (3) Glish, R. G.; Goeringer, D. E.; Asano, K. J.; McLuckey, S. A. *Int. J. Mass Spectrom. Ion Processes* **1989**, 94, 15-24.
- (4) Gill, C. G.; Daigle, B.; Blades, M. W. *Spectrochim. Acta* **1991**, 46B, 1227-1235.
- (5) Gill, C. G.; Blades, M. W. *J. Analyt. At. Spectrom.* **1993**, 8, 261-267.
- (6) Gill, C. G. Ph.D., University of British Columbia, 1994.
- (7) Alexander, M. L.; Hemberger, P. H.; Cisper, M. E.; Nogar, N. S. *Anal. Chem.* **1993**, 65, 1609-1614.
- (8) Eiden, G. C.; Cisper, M. E.; Alexander, M. L.; Hemberger, P. H.; Nogar, N. S. *J. Am. Soc. Mass Spectrom.* **1993**, 4, 706-709.
- (9) Eiden, G. C.; Garrett, A. W.; Cisper, M. E.; Nogar, N. S.; Hemberger, P. H. *Int. J. Mass Spectrom. Ion Processes* **1994**, 136, 119-141.
- (10) Chambers, D. M.; Goeringer, D. E.; McLuckey, S. A.; Glish, G. L. *Anal. Chem.* **1993**, 65, 14-20.
- (11) Jonscher, K.; Currie, G.; McCormack, A. L.; Yates III, J. R. *Rapid Commun. Mass Spectrom.* **1993**, 7, 20-26.
- (12) Schwartz, J. C.; Bier, M. E. *Rapid Commun. Mass Spectrom.* **1993**, 7, 27-32.
- (13) Doroshenko, V. M.; Cornish, T. J.; Cotter, R. J. *Rapid Commun. Mass Spectrom.* **1992**, 6, 753-757.
- (14) Doroshenko, V. M.; Cotter, R. J. *Rapid Commun. Mass Spectrom.* **1993**, 7, 822-827.
- (15) Doroshenko, V. M.; Cotter, R. J. *Anal. Chem.* **1995**, 67, 2180-2187.
- (16) Doroshenko, V. M.; Cotter, R. J. *Rapid Commun. Mass Spectrom.* **1996**, 10, 65-73.
- (17) Doroshenko, V. M.; Cotter, R. J. *Anal. Chem.* **1996**, 68, 463-472.

- (18) Qin, J.; Chait, B. T. *Anal. Chem.* **1996**, *68*, 2102-2107.
- (19) Qin, J.; Steenvoorden, R. J. J. M.; Chait, B. *Anal. Chem.* **1996**, *68*, 1784-1791.
- (20) Qin, J.; Chait, B. T. *Anal. Chem.* **1996**, *68*, 2108-2112.
- (21) Bristow, A. W. T.; Creaser, C. S. *Rapid Commun. Mass Spectrom.* **1995**, *9*, 1465-1469.
- (22) He, L.; Liu, Y.-H.; Zhu, Y.; Lubman, D. M. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 1440-1448.
- (23) McLuckey, S. A.; Van Berkel, G. J.; Goeringer, D. E.; Glish, G. L. *Anal. Chem.* **1994**, *66*, 689-696.
- (24) O, C. S.; Schuessler, H. A. *Int. J. Mass Spectrom. Ion Physics* **1981**, *40*, 53-66.
- (25) O, C. S.; Schuessler, H. A. *Int. J. Mass Spectrom. Ion Physics* **1981**, *40*, 67-75.
- (26) O, C. S.; Schuessler, H. A. *Int. J. Mass Spectrom. Ion Physics* **1981**, *40*, 77-86.
- (27) O, C. S.; Schuessler, H. A. *J. Phys. D: Appl Phys.* **1981**, *4*, 953.
- (28) O, C. S.; Schuessler, H. A. *J. Appl. Physics* **1981**, *52*, 1159.
- (29) O, C. S.; Schuessler, H. A. *Revue Phys. Appl.* **1982**, *17*, 83.
- (30) Todd, J. F. J.; Freer, D. A.; Waldren, R. M. *Int. J. Mass Spectrom. Ion Physics* **1980**, *36*, 371-386.
- (31) Chattopadhyaya, R.; Ghosh, P. K. *Int. J. Mass Spectrom. Ion Physics* **1980**, *36*, 365-370.
- (32) Chattopadhyaya, R.; Ghosh, P. K. *Int. J. Mass Spectrom. Ion Physics* **1981**, *41*, 1-6.
- (33) Kishore, M. N.; Ghosh, P. K. *Int. J. Mass Spectrom. Ion Physics* **1979**, *29*, 345-350.
- (34) Weil, C.; Nappi, M.; Cleven, C. D.; Wollnik, H.; Cooks, R. G. *Rapid Commun. Mass Spectrom.* **1996**, *10*, 742-750.
- (35) He, L.; Lubman, D. M. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 1467-1477.
- (36) Moore, R. B.; Gulick, S. *Physica Scripta*. **1988**, *T22*, 28-35.
- (37) Moore, R. B.; Lunney, M. D. N.; Rouleau, G.; Savard, G. *Physica Scripta*. **1992**, *46*, 569-574.

- (38) Vargas, R. R.; Yost, R. A. In *Practical aspects of ion trap mass spectrometry: Ion Trap Instrumentation*; March, R. E., Todd, J. F. J., Eds.; CRC Press, Inc., 1995; Vol. 2, pp 217-234.
- (39) March, R. E.; Hughes, R. J. *Quadrupole Storage Mass Spectrometry*; John Wiley & Sons: Toronto, 1989.
- (40) Cooks, R. G.; McLuckey, S. A.; Kaiser, R. E. *Chemical and Engineering News* **1991**, 26-41.
- (41) Dawson, P. H.; Whetten, N. R. *J. Vac. Sci. Technol.* **1968**, 5, 1.
- (42) Stafford Jr., G. C.; Kelley, P. E.; Syka, J. E. P.; Reynolds, W. E.; Todd, J. F. J. *Int. J. Mass Spectrom. Ion Processes* **1984**, 60, 85-98.
- (43) Nourse, B. D.; Cooks, R. G. *Anal. Chim. Acta* **1990**, 228, 1-21.
- (44) Griffiths, I. W. *Rapid Communications in Mass Spectrometry* **1990**, 4, 69-73.
- (45) Knight, R. D. *Int. J. Mass Spectrom. Ion Physics* **1983**, 51, 127.
- (46) Dawson, P. H.; Whetten, N. R. *J. Vac. Sci. Technol.* **1968**, 5, 11.
- (47) Dawson, P. H.; Hedman, J. W.; Whetten, N. R. *Rev. Sci. Instruments* **1969**, 40, 1444.
- (48) Dawson, P. H.; Whetten, N. R. *Naturwissenschaften* **1969**, 56, 109.
- (49) Bonner, R. F.; Lawson, G.; Todd, J. F. J. *Int. J. Mass Spectrom. Ion Physics* **1973**, 10, 197.
- (50) Lawson, G.; Bonner, R. F.; Todd, J. F. J. *Journal of Physics E* **1973**, 6, 357.
- (51) Bonner, R. F.; Lawson, G.; Todd, J. F. J.; March, R. E. *Adv. in Mass. Spectrom.* **1974**, 6, 377.
- (52) Lawson, G.; Todd, J. F. J.; Bonner, R. F. *Dynamic Mass Spectrometry* **1975**, 4, 39.
- (53) Bonner, R. F.; March, R. E.; Durup, J. *Int. J. Mass Spectrom. Ion Physics* **1976**, 2, 17.
- (54) Fulford, J. E.; March, R. E. *Int. J. Mass Spectrom. Ion Processes* **1978**, 26, 155.
- (55) Kaiser Jr., R. E.; Louris, J. N.; Amy, J. W.; Cooks, R. G. *Rapid Commun. Mass Spectrom.* **1989**, 3, 225-230.

- (56) Kaiser Jr., R. E.; Cooks, R. G.; Stafford Jr., G. C.; Syka, J. E. P.; Hemberger, P. H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *106*, 79-115.
- (57) Johnson, J. V.; Yost, R. A.; Kelley, P. E.; Bradford, D. C. *Anal. Chem.* **1990**, *62*, 2162-2172.
- (58) Louris, J. N.; Brodbelt-Lustig, J. S.; Cooks, R. G.; Glish, G. L.; Van Berkel, G. J.; McLuckey, S. A. *Int. J. Mass Spectrom. Ion Processes* **1990**, *96*, 117-137.
- (59) Soni, M. H.; Cooks, R. G. *Anal. Chem.* **1994**, *66*, 2488-2496.
- (60) Louris, J. N.; Cooks, R. G.; Syka, J. E. P.; Kelley, P. E.; George C. Stafford, J.; Todd, J. F. *Anal. Chem.* **1987**, *59*, 1677-1685.
- (61) Louris, J. N.; Brodbelt, J. S.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1987**, *75*, 342-352.
- (62) Kaiser Jr., R. E.; Cooks, R. G.; Syka, J. E. P.; Stafford Jr., G. C. *Rapid Commun. Mass Spectrom.* **1990**, *4*, 30-33.
- (63) Van Berkel, G. J.; Glish, G. L.; McLuckey, S. A. *Anal. Chem.* **1990**, *62*, 1284-1295.
- (64) Van Berkel, G. J.; McLuckey, S. A.; Glish, G. L. *Anal. Chem.* **1991**, *63*, 1098-1109.
- (65) McLuckey, S. A.; Goeringer, D. E.; Glish, G. L. *J. Am. Soc. Mass Spectrom* **1991**, *2*, 11-21.
- (66) McLuckey, S. A.; Glish, G. L.; Asano, K. G. *Anal. Chim. Acta* **1989**, *225*, 25-35.
- (67) Goeringer, D. E.; Asano, K. G.; McLuckey, S. A. *Anal. Chem.* **1994**, *66*, 313-318.
- (68) Asano, K. G.; Goeringer, D. E.; McLuckey, S. A. *Anal. Chem.* **1995**, *67*, 2739-2742.
- (69) Fenner, N. C.; Daly, N. R. *The Review of Scientific Instruments* **1966**, *37*, 1068-1070.
- (70) Kovalev, I. D.; Maksimov, G. A.; Suchkov, A. I.; Larin, N. V. *Int. J. Mass Spectrom. Ion Physics* **1978**, *27*, 101-137.
- (71) Conzemius, R. J.; Capellen, J. M. *Int. J. Mass Spectrom. Ion Physics* **1980**, *34*, 197-271.
- (72) Dutta, P. K.; Talmi, Y. *Analytica Chimica Acta* **1981**, *132*, 111-118.
- (73) Jansen, J. A. J.; Witmer, A. W. *Spectrochimica Acta* **1982**, *37B*, 483-491.

- (74) McCrery, D. A.; Ledford Jr., E. B.; Gross, M. L. *Anal. Chem.* **1982**, *54*, 1435-1437.
- (75) Novak, F. P.; Balasanmugam, K.; Viswanadham, K.; Parker, C. D.; Wilk, Z. A.; Mattern, D.; Hercules, D. M. *Int. J. Mass Spectrom. Ion Physics* **1983**, *53*, 135-149.
- (76) Dittrich, K.; Wennrich, R. *Prog. analyt. atom. Spectrosc.* **1984**, *7*, 139-198.
- (77) Hillenkamp, F.; Karas, M. *Anal. Chem.* **1991**, *63*, 1193-1203.
- (78) Karas, M.; Hillenkamp, F. *Anal. Chem.* **1988**, *60*, 2299-2301.
- (79) Williams, J. D.; Cox, K.; Morand, K. L.; Cooks, R. G.; Julian Jr., R. K.; Kaiser, R. E. 1991; 1481-1482.
- (80) Goeringer, D. E.; McLuckey, S. A.; Glish, G. L. 1991; 532-533.
- (81) Londry, F. A.; Wells, G. J.; March, R. E. *Rapid Commun. Mass Spectrom.* **1993**, *7*, 43-45.
- (82) Londry, F. A.; March, R. E. *Int. J. Mass Spectrom. Ion Processes* **1995**, *144*, 87-103.
- (83) Tourillon, G. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker, Inc.: New York, 1986; Vol. 1, pp 293-350.
- (84) Cotter, R. J.; Yergey, A. L. *Anal. Chem.* **1981**, *53*, 1306-1307.
- (85) Vaeck, L. V.; Waele, J. D.; Gijbels, R. *Mikrochimica Acta* **1984**, *III*, 237-257.
- (86) March, R. E.; Todd, J. F. J. In *Modern Mass Spectrometry*; Cairns, T., Ed.; CRC Press, Inc., 1995; Vol. 2, pp 320.
- (87) Kofel, P. In *Practical aspects of ion trap mass spectrometry: Ion Trap Instrumentation*; March, R. E., Todd, J. F. J., Eds.; CRC Press, Inc., 1995; Vol. 2, pp 51-86.
- (88) Boue, S. M.; Jones, J. A.; Yost, R. A. *42nd ASMS Conference on Mass Spectrometry*, Chicago 1994; 218.
- (89) Todd, J. F. J.; Waldren, R. M.; Freer, D. A.; Turner, R. B. *Int. J. Mass Spectrom. Ion Physics* **1980**, *35*, 107-150.
- (90) McLuckey, S. A.; Glish, G. L.; Asano, K. G. *Int. J. Mass Spectrom. Ion Processes* **1991**, *109*, 171-186.
- (91) Fountain, S. T.; Lee, H.; Lubman, D. M. *Rapid Commun. Mass Spectrom.* **1994**, *8*, 407-

416.

- (92) Qin, J.; Steenvoorden, J. J. M.; Chait, B. T. *42nd ASMS Conference on Mass Spectrometry*, Chicago 1994; 696.
- (93) Jonscher, K. R.; Yates III, J. R. *42nd ASMS Conference on Mass Spectrometry*, Chicago 1994; 216.
- (94) Lubman, D. M. , Chicago 1994; 698.
- (95) Lee, H.; Lubman, D. M. *Anal. Chem.* **1995**, 67, 1400-1408.
- (96) Beu, S. C.; Hendrickson, C. L.; Vartanian, V. H.; Laude Jr., D. A. *Int. J. Mass Spectrom. Ion Processes* **1992**, 113, 59-79.
- (97) Robb, D.; Blades, M. W. *J. Am. Soc. Mass Spectrom.* **1997**, 8, 1203-1205.
- (98) Louris, J. N.; Amy, J. W.; Ridley, T. Y.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Processes* **1989**, 88, 97-111.
- (99) Mo, W.; Langford, M. L.; Todd, J. F. J. *Rapid Commun. Mass Spectrom.* **1995**, 9, 107-113.
- (100) Blades, M.; Robb, D. , Providence, Rhode Island, October 26 - 30 1997; 196-197.
- (101) Robb, D.; Blades, M. W. , Palm Springs, CA, June 1-5 1997; 133.
- (102) Robb, D. B.; Blades, M. W. *submitted to Anal. Chem.*, **1998**.
- (103) Chen, F. F. *Introduction to plasma physics and controlled fusion*, Second ed.; Plenum Press: New York, 1983.
- (104) Yang, M.; Reilly, J. P. *The Journal of Physical Chemistry* **1990**, 94, 6299-6305.
- (105) Beavis, R. C.; Chait, B. T. *Chemical Physics Letters* **1991**, 181, 479-484.
- (106) Kinsel, G. R.; Russell, D. H. *J. Am. Soc. Mass Spectrom.* **1995**, 6, 619-626.