An ion trap storage/time-of-flight mass spectrometer

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An ion trap/time-of-flight (TOF) mass spectrometer combination has been developed in order to combine the storage capabilities of an ion trap with the speed and resolution of a time-of-flight device. The ion trap is an rf quadrupole trap which operates in the total storage mode, i.e., with the dc voltage=0 on the end caps and rf voltage on the ring electrode. The trap has an ion storage time of >2 s at an rf potential of 310 V_{pp}. The stored ions are ejected into the time-of-flight device using a -150 V dc pulse on the exit end cap which causes the ion trajectories in the trap to become unstable. The ions are mass analyzed using either a linear or reflectron TOF. In the linear mode the resolution is 240 while in the reflectron mode a resolution of 1300 at m/z 93 is achieved. The storage capabilities of this device may have important applications towards enhancing sensitivity, the study of very slow metastable decay, and photodissociation mass spectrometry and spectroscopy.

I. INTRODUCTION

In this work we have developed an ion trap/time-of-flight (TOF) mass spectrometer combination which potentially includes some of the best features of each of these instruments. The time-of-flight mass spectrometer in particular has become widely used because of several distinct advantages.[1-15] These advantages include the fact that TOF devices can rapidly measure an entire mass spectrum on every ionization pulse. This property of time of flight is particularly important in experiments where the ionization source has a low duty cycle as in laser ionization[3,5,8] or in experiments where rapid monitoring of transient species may be required. Other advantages include the potentially high resolution that can be achieved with TOF devices. A number of methods including supersonic jet cooling[5,6,8] and an ion reflecting mirror, i.e., a reflectron,[7-11] have been used to achieve resolution well in excess of several thousand using a variety of ionization sources, including laser ionization and electron impact. An increasingly important property of TOF devices has become the ability to measure high mass with high transmission, which arises since the TOF is a device which consists of a flight tube and several grids. In recent experiments masses in excess of 200 000 u have been detected using TOF mass spectrometers with high-voltage acceleration (i.e., 30 kV).[14] In addition, TOF devices are relatively simple, rugged and inexpensive and require only dc power supplies with essentially no current load to bias the acceleration region. There are no moving parts, scanning electric fields or slits to limit the throughput.

A major limitation of TOF devices is that there is no storage of ions in the acceleration region. Ion storage is particularly important in studies involving ion-molecule chemistry, for studies of very slow formation of metastables, and for enhancing the detection limits by integration of the signal. Although there have been several attempts to store ions using dc fields, the ion storage time via this method is limited.[15] However, a more versatile method for achieving ion storage and tandem MS is the ion trap mass spectrometer.

The quadrupole ion trap is a powerful tool for mass analysis and storage of ions over a wide mass range with excellent sample detection limits.[16-21] The ion trap has been used with numerous ionization sources, including electron impact,[17] chemical ionization,[22] and photoionization,[23] which can create ions directly inside the trap. Alternatively, techniques which require ion introduction from an external source into the trap such as atmospheric pressure sampling glow discharges and electrospray[24] have been interfaced to ion traps. The trap has been used to analyze ions in excess of 70 000 daltons and recently has been able to achieve extraordinarily high resolution.[19] In addition, an important feature of the trap is its ability to perform multiple stages of tandem mass spectrometry in combination with collisional or photodissociative fragmentation techniques.[19] A key feature of the ion trap is its ability to obtain high sensitivity through ion storage and integration of the signal over an extended period of time.[21]

The ion trap also has several inherent disadvantages. Although the trap can store high-mass ions, it is often difficult to scan the radio frequency to a sufficiently large value of the voltage in order to scan out high-mass ions. A technique has been developed known as axial modulation to scan out high mass; however, this usually occurs at the expense of the accuracy of the mass calibration.[19,21] In addition, very high-mass resolution can be achieved in the trap by scanning the rf voltage or the rf frequency very slowly.[25,26] Cooks and co-workers have achieved resolution in excess of 100 000 using this technique[25] while Goeringer and co-workers have achieved a resolution up to 45 000.[26] However, the rate at which the mass range is scanned, i.e., 4 m/z per second in the latter work, is impractical for many applications. On the other hand, the commercial Finnigan ion trap at this time has a resolution of 185 at m/z 69 and 1700 at m/z 502 and can only scan to m/z 650 at a scan rate of 5000 amu/s.[21]

The goal of this work has been to interface an ion trap storage device as a front end source for a time-of-flight
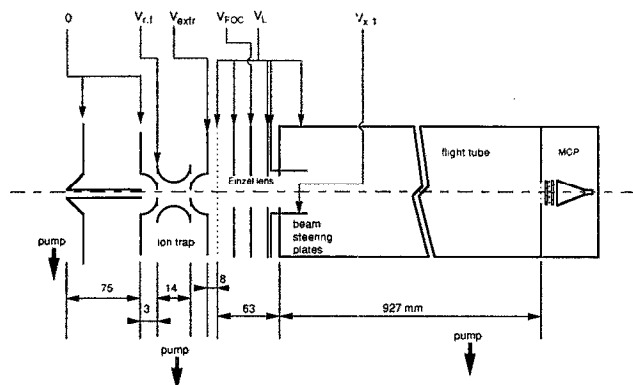
FIG. 1. Ion trap/linear time-of-flight mass spectrometer. See Fig. 2 for details of the sample introduction region. Where V_{rf}=radio frequency voltage. V_{extr}=dc extraction voltage, V_L=flight tube liner voltage, V_{FOC} =focusing voltage, V_{X1}=beam steering voltage.

mass spectrometer. This device combines the storage capabilities of the ion trap with the relatively high resolution, speed, and high-mass capabilities of the TOF to potentially produce a hybrid instrument with unique capabilities. This article describes the design of an ion trap/time-of-flight device in which ions are initially produced by resonance-enhanced multiphoton ionization (REMPI) in the ion trap, stored for several hundred μs up to several seconds and then pulsed out into a time-of-flight device for mass analysis. This ejection method utilizes a dc pulse which is applied to the exit end cap. This dc pulse destabilizes the trap and the entire contents of the trap are simultaneously ejected for analysis into a reTOF. Pulsed dc ejection of ions from traps has been performed previously by a number of investigators and has been used to interface ion traps to quadrupole and sector mass spectrometer detectors.[27-29] These studies have mainly focused on the fundamental aspects of dc ejection. Other studies have used TOF analysis to study the energy distribution and mean kinetic and translational energy of the ion cloud combined in the trap.[30] More recent hybrid devices have seen ion traps interfaced to other ion traps and hybrid BEQ type devices.[31]

In the present work ions from the trap are ejected into a TOF device and a resolution of up to 240 is demonstrated in a linear device while a resolution of nearly 1300 at m/z 93 is demonstrated with the use of a reflectron TOF. The reflectron enhances the resolution by correcting for the spatial and energy spread of ions produced in the trap. In addition, it is demonstrated that ion storage enhances the resolution and sensitivity of the device.

II. EXPERIMENTAL

The experimental setup is shown in Figs. 1–4. It initially consisted of a differentially pumped linear time-of-flight mass spectrometer interfaced to a quadrupole ion trap ionization region and a liquid injection sample introduction source (R. M. Jordan Co., Grass Valley, CA). After experimental confirmation that the ion trap was working, the linear flight tube was replaced with an ion reflector in order to take advantage of its enhanced reso-

lution capability. All other parts of the experiment remained unchanged upon conversion of the ion trap/linear time-of-flight mass spectrometer to the ion trap/reflectron time-of-flight mass spectrometer. A liquid injection sample source was used to deliver the sample, dissolved in a solvent, through a heated stainless-steel tube to the first vacuum chamber. In this chamber, pumped to $\sim$150 mTorr, the sample and solvent are vaporized, most of the solvent is removed and the sample passed through a skimmer cone to the ion trap region. In the ion trap, the sample is ionized via 266 nm radiation generated by a Quanta Ray DCR-3 Nd:YAG laser which passes directly through the trap. The resulting ions are then stored in the trap until the trapping potential is shut off and subsequently an extraction pulse is applied to the exit endcap of the ion trap. The timing and characteristics of the ionization/trapping/extraction processes are described in detail below. This extraction pulse triggers the start for the TOF mass analysis. Upon leaving the trap, in the linear instrument, the ion packet enters a field-free drift region $\sim$1 m long and the ions are detected by a triple-layer 18 mm microchannel plate detector. In the reflectron, as the ion packet leaves the trap it enters a field-free drift region also $\sim$1 m long at the end of which its velocity is slowed and reversed by the ion reflector. The newly focused ion packet then retraverses the drift region and is detected by a dual 40 mm microchannel plate detector (R. M. Jordan Co.).

A. Sample injection system

An ISCO model μLC-500 micropump LC syringe pump was used to deliver the sample through a 50 μm fused silica capillary directly to the vaporization chamber. The flow rates were typically 50 μl/min and the solvent used was methanol degassed in an ultrasonic bath. The 50 μm fused silica capillary was inserted through a zero-dead-volume tee into a 1-in.-long, 1/16-in.-diam stainless-steel tube with 0.02 in. i.d. A tightly fitting 1/8 in. copper tube was placed over this SS tube and was tightly wound with 1/16 in. thermocoax cable heater. This copper tube was added to the sample introduction assembly to reduce the stress on the wound thermocoax cable heater. The working temperature of the nebulizer was controlled by a thermocouple and a temperature controller. Working temperatures were generally 90–110 °C; however, actual sample temperature is expected to be much lower due to the expansion and heat carried away by solvent vapor. This assembly is directly inserted and o-ring sealed to the back of the vaporization chamber (Fig. 2). The vaporization chamber is pumped to a pressure of $\sim$150 mTorr by a 650 l/min mechanical pump. The sample vapor is injected from the vaporization region through a skimmer fitted with a 3-in.-long stainless-steel tube (0.04 in. i.d.) into the ion trap region via the pressure difference.

B. Ionization and trapping

The sample vapor present in the ion trap is ionized by UV laser radiation (λ=266 nm) which is directed through 3.1 mm holes in the ring electrode of the ion trap as shown in Fig. 3. Ions which are selectively produced by laser-
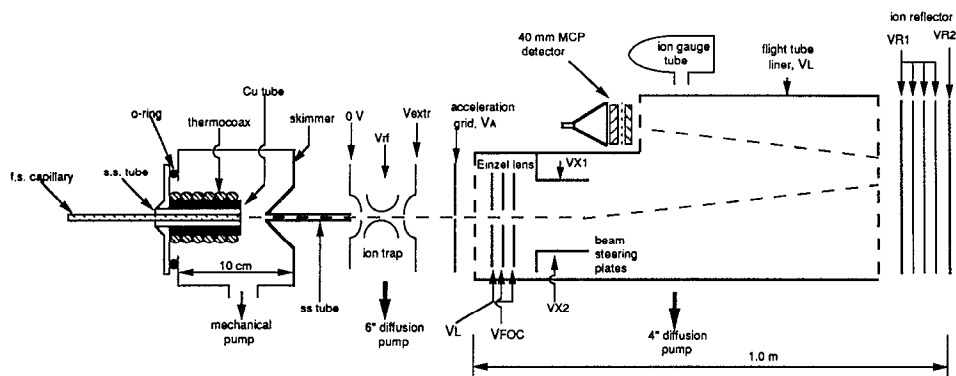
FIG. 2. Ion trap/reflectron time-of-flight mass spectrometer with sample introduction region shown. Where V_{rf}=radio-frequency voltage, V_{extr}=dc extraction voltage, V_A=acceleration voltage, V_L=flight tube liner voltage, V_{FOC}=focusing voltage, V_{X2}=beam steering voltage, V_{R1}=ion repeller voltage, V_{R2}=ion reflector voltage.

induced REMPI are trapped by the applied rf potential, while other ions and unionized sample and solvent vapor are pumped away by the 6 in. diffusion pump located directly below the ion trap.

The ion trap consists of two endcap electrodes with a ring electrode between them. These electrodes have hyperbolic surfaces and are configured as shown in Fig. 3. In initial work, the ion trap was not entirely enclosed. However, Teflon spacers were placed between the ring and endcaps to produce a trap that was completely enclosed except for an inlet and exit aperture 3.1 mm in diameter, two apertures (3.1 mm) for the laser beam to enter and exit, and an extra inlet tube into the Teflon spacer for addition of a buffer gas if desired. During operation, both end caps are held at 0 V while an rf signal of constant frequency (1.19 MHz) and variable amplitude (0–500 V_{pp}) is applied to the ring electrode. This applied rf field serves to trap ions present within the volume of the trap. Varying the rf amplitude varies the m/z range of ions that are stable within the trap. Ions with appropriate m/z for a particular

rf amplitude have a stable trajectory within the trap and, therefore, are trapped.[21] The mass range of the ions that will be trapped were approximated by computer simulation.[32] After a selected m/z range has been trapped, a dc pulse was applied to the exit endcap to simultaneously extract all ions from the trap for TOF analysis as detailed below.

The ionization, trapping, extraction, and detection processes were timed as follows: the Q-switch output pulse of the laser was used to trigger a Systron-Donner Corp. Datapulse 100A pulse generator (PDG) and a California Avionics Laboratories, Inc. model 112AR (MOD) digital delay generator (DDG). The PDG output pulse was used to trigger the rf power supply (which provided the trapping potential to the ion trap). The DDG output pulse triggered the extraction pulse supply and the LeCroy model 9400A digital oscilloscope (DOSC) data collection system.

In Fig. 5 a typical experimental cycle is depicted: the Q-switch output pulse (+11 V, 2 ns baseline width) from the Nd:YAG laser triggered the PDG and the DDG. After a 50 ns internal delay the laser pulse fires (7 ns FWHM at
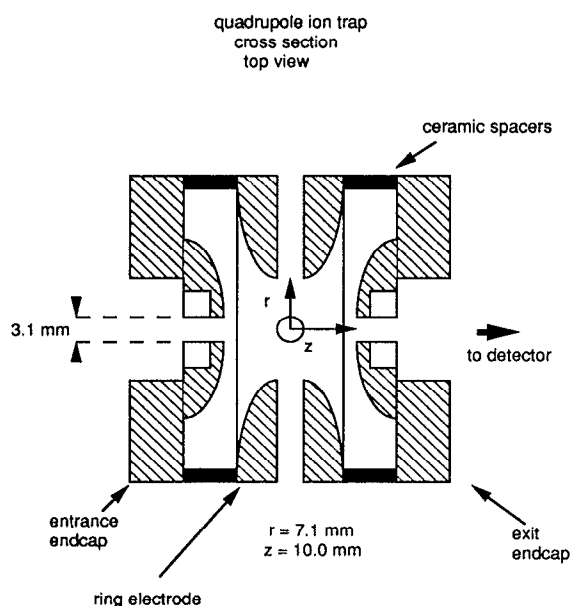

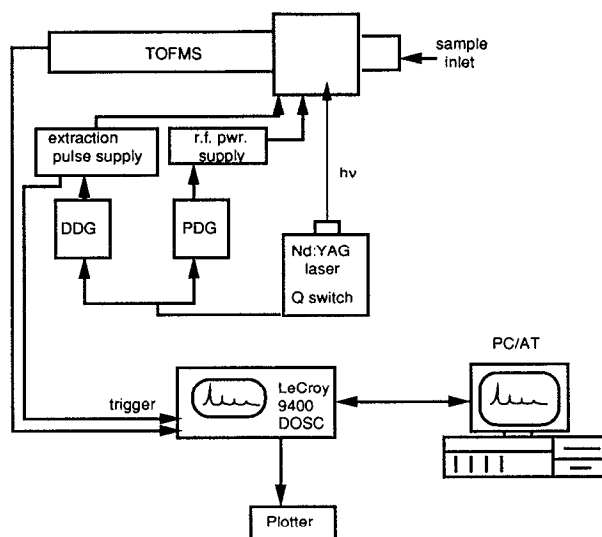FIG. 3. Detailed construction of the quadrupole ion trap.

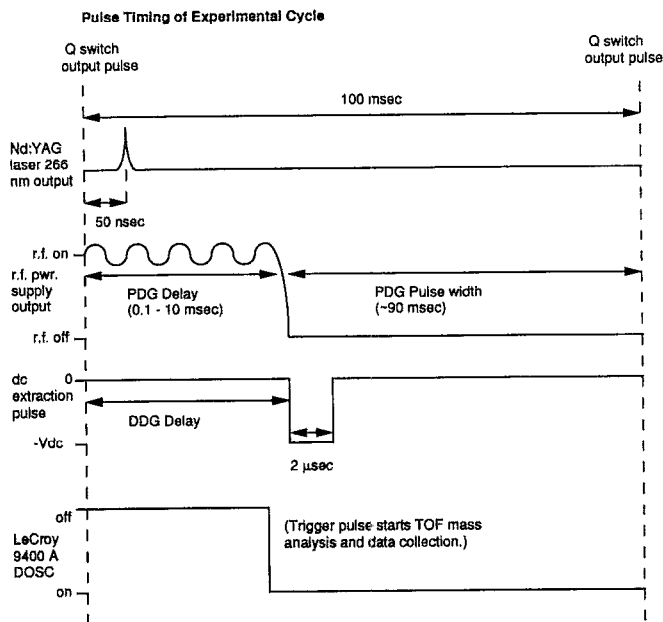FIG. 4. Schematic of the experimental setup.

FIG. 5. Diagram of the timing of an experimental cycle.

266 nm) and ionizes the sample vapor in the ion trap. The rf trapping potential (1.19 MHz, 310 V_{pp}) remains on while this sequence occurs, thus trapping the ions produced by the laser beam. The rf potential remains on until the PDG pulse triggers the rf power supply. Then 2 μs (internal delay of rf power supply) after the rising edge of the PDG pulse arrives, the rf potential is shut off and remains off for the entire pulse width of the PDG pulse. PDG output pulses were typically delayed 0.1–5.0 ms after triggering and were of 88–90 ms pulse widths, 40 ns rise time, +5 V amplitude square-wave pulses. Therefore, the delay of the PDG determined the duration of ion trapping, i.e., how long the ions could be stored in the trap. After its set delay, the DDG outputs a pulse (20 ns rise time, ~ +10 V amplitude, 10 μs FWHM) which triggers the extraction pulse supply. The extraction pulse supply serves the dual purpose of both providing a start time reference for the TOF mass analysis and providing an extraction pulse to the exit endcap of the ion trap, thereby ejecting the ions from the trap. Upon the arrival of the rising edge of the DDG pulse, the extraction pulse supply passes this trigger pulse, the DDG output pulse, to the DOSC's external trigger. This provides the start time reference for the TOF mass analysis. 1.5 μs after the arrival of the rising edge of the DDG output pulse, the extraction pulse supply sends the extraction pulse to the exit endcap of the ion trap. This extraction pulse was a dc square wave -150 V in amplitude and 2 μs in width with 10 ns rise and fall times. The delay of the DDG was set to coincide with the delay of the PDG, therefore, extraction of the ions occurred simultaneously with the rf trapping potential's triggering. The repetition rate of the laser was 10 Hz so that the Q-switch triggers a new experimental cycle every 100 ms.

C. TOF operation

In the linear configuration of the experiment, once the ions exit the ion trap, they are focused using a set of Einzel lens. A pair of beam steering plates are then used to steer the ions onto the microchannel plate detector. The flight tube uses a liner which is typically at a voltage of -1300 V to pull the ions down the flight tube. The use of a liner in the flight tube allows the extraction process to function at relatively low voltage. The detector is a triple-layer microchannel plate (18 mm diameter) with a gain estimated from previous work of 5×10^7–5×10^8.[33] The face of the first plate is operated at ~ -4.1 kV instead of the usual -2.2 kV in order to achieve additional postacceleration and to increase the sensitivity for detection of ions. The flight tube is pumped by a Varian VHS 4 diffusion pump while the main chamber is pumped by a Varian VHS 6 diffusion pump. A restriction of 1 in. tubing is placed between the flight tube and the main chamber. Typical operating pressures were 2×10^{-6} and 6×10^{-7} Torr, respectively. The actual pressure in the ion trap during sample introduction though was between 5×10^{-4} and 10^{-3} Torr.

In the ion trap/reflectron TOFMS configuration of the experiment, the ions, upon exiting the ion trap, pass through a set of accelerating plates and Einzel lens which serve to focus the ion packet and accelerate it into the field-free flight tube region through a potential difference of about -1100 V. A pair of beam deflecting plates are then used to steer the ions towards the ion repeller/reflector assembly, where the ion packet is more tightly focused, reversed in direction, and reaccelerated through the flight tube (with angular displacement from its initial axis of trajectory) onto the 40 mm dual microchannel plate detector. The reflectron flight tube also had a 1 in. tubing restriction between it and the main chamber and was pumped by a Varian VHS 4 diffusion pump. The reflectron version of the instrument was operated at the same typical pressures as the above mentioned linear instrument.

The TOF of the extracted ion packets was measured on the DOSC. Signal averaging was used to enhance the signal-to-noise ratio and reported spectra are averages of 1000 single waveforms. In the experiment, the DDG simultaneously triggered the DOSC and the extraction pulse supply. The ion signals from the detector were sent to the input of the DOSC, and the time difference between various ion peaks and the trigger ($t=0$) reference provides the time of flight of each ion.

The TOF spectra in the DOSC can be plotted out by dumping the screen to a two-pen HP plotter. However, in order to store the data permanently for analysis, it was transferred to a computer. An RS232 interface bus was established between the DOSC and a PC/AT computer. A user written QUICKBASIC program was used to control the transfer processes. The size for each data point was 16 bit for our experiments. The raw data from DOSC were in ASCII form. It was converted into signed decimal form by a user-written program.
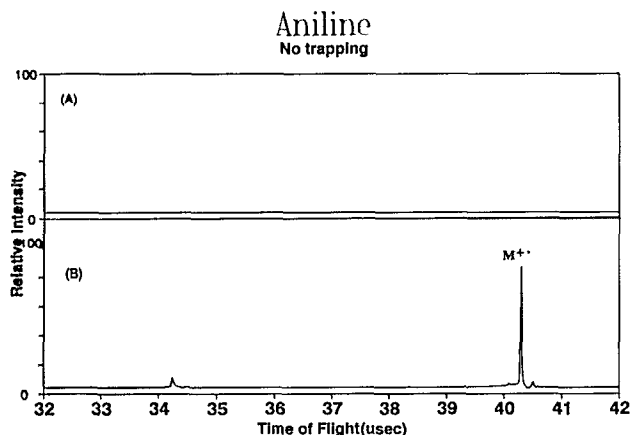
FIG. 6. IT/reTOF mass spectra of aniline with no rf trapping potential applied. (a) 20.10 μs delay before extraction, and (b) no delay before extraction. Both spectra were obtained with the following operating conditions. $V_L = V_{X1} = -1100$, $V_{X2} = -980$, $V_{FOC} = -400$, $V_A = -300$, $V_{extr} = -150$, $V_{R1} = +1200$, $V_{R2} = +1950$.

III. RESULTS AND DISCUSSION

A. Mass spectra

The capabilities of the ion trap/time-of-flight device are demonstrated in the mass spectra of Figs. 6, 7, and 9. These spectra were taken with 7×10^{-4} M aniline dissolved in methanol. Sample and solvent were pumped into the interface chamber via the syringe pump set at a flow rate of 50 μl/min. Vaporization, delivery to the ion trap region, and ionization occurred as described above. Figures 6(a) and 6(b) are mass spectra of aniline without ion trapping, i.e., no rf applied to the ring electrode of the ion trap. Figure 6(b) shows the extraction and TOF mass analysis of aniline ions by applying a -150 V dc pulse to the exit endcap of the ion trap 0.10 μs after laser ionization has occurred. The m/z 93 peak is assigned to the aniline molecular ion. The ^{13}C isotope peak is present at m/z 94 at ~6% of the molecular ion peak's intensity. The m/z 77 peak is the $C_6H_5^+$ fragment. Increasing the laser power

FIG. 8. Time-scale expansion of the aniline molecular ion spectrum of Fig. 7 showing the peak shape and peak width.

increases the relative intensity of the $C_6H_5^+$ peak. In Fig. 6(a) the spectrum is of the same sample and conditions as (b) except that the extraction pulse is delayed 20.10 μs. This spectrum shows that with no rf applied to the ring electrode of the ion trap, all ions produced are pumped away by the 6 in. diffusion pump, thus, only a flat line background was detected. Figure 7 shows a spectrum of the same sample with the rf potential applied to the ring electrode of the ion trap and an extraction delay of 100.10 μs (100.10 μs trapping time). This spectrum clearly illustrates that the ions are successfully trapped and the trapping results in an increase in resolution.

The ability of the IT/reTOF mass spectrometer to trap ions for an extended period of time is shown in Figs. 9 and 10. In Fig. 9 an aniline spectrum with 1.0 ms trapping time results in a similar mass spectrum with similar resolution as that with a 100.10 μs trapping time. Trapping times as long as 2 s have been observed using a laser repetition rate of 0.5 Hz. This is demonstrated in Fig. 10 where the aniline molecular ion is stored for at least 2 s and a mass spectrum very similar to that of Figs. 8 and 9 is obtained. Although the mass spectra in Figs. 9 and 10 are similar, the peak
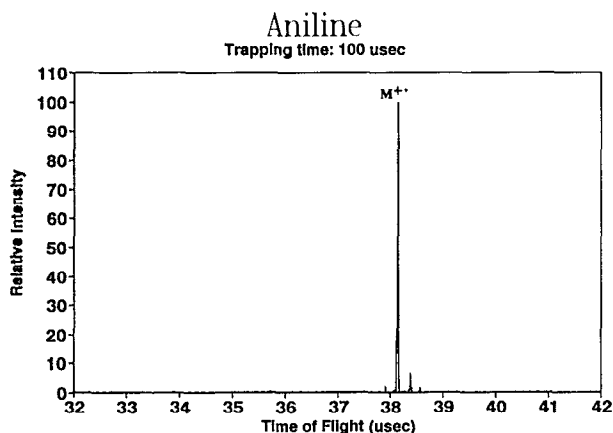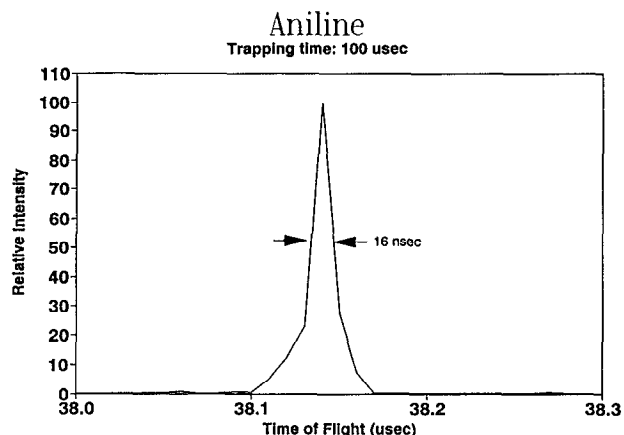

FIG. 7. IT/reTOF mass spectrum of aniline obtained by laser-induced REMPI at 266 nm with 100.10 μs trapping time. rf frequency = 1.19 MHz, rf voltage = 310 V_{pp}, and all other operating conditions the same as those of Fig. 6.
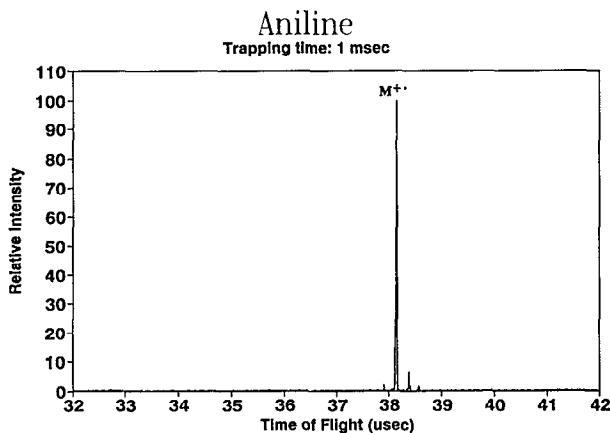

FIG. 9. IT/reTOF mass spectrum of aniline obtained by laser-induced REMPI at 266 nm with 1.0 ms trapping time. All operating conditions were the same as those in Fig. 7.
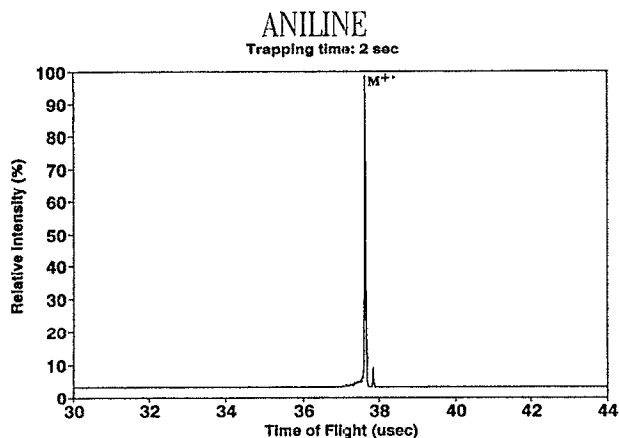
ANILINE
Trapping time: 2 sec

FIG. 10. IT/reTOF mass spectrum of aniline obtained by laser-induced REMPI at 266 nm with 2 s trapping time. All operating conditions were the same as those in Fig. 7 except the laser repetition rate was reduced to 0.5 Hz.

height after 2 s of storage typically decreases by a factor of 5–10 relative to storage after only 1 ms as ions are lost from the trap. In Fig. 11 is shown a laser REMPI mass spectrum of aniline obtained when the laser power is increased to produce extensive fragmentation. This mass spectrum demonstrates that the molecular ion and its accompanying fragments can all be stored for an extended time, i.e., 5 ms, by the trap and detected by the reTOF. The laser REMPI mass spectrum is essentially the same as that obtained without trapping. The resolution in this figure is slightly degraded compared to the other figures due to the extended mass range processed by the digitizer. An expanded view of any of these peaks reveals a resolution very similar to that obtained in Figs. 6–10.

The TOF spectra were plotted by a laser printer from the stored data files. These spectra were obtained by signal averaging over 1000 signal pulses at 32 000 data points per sweep and were taken in ~5 min limited by the rate at which the DOSC can accumulate the data.
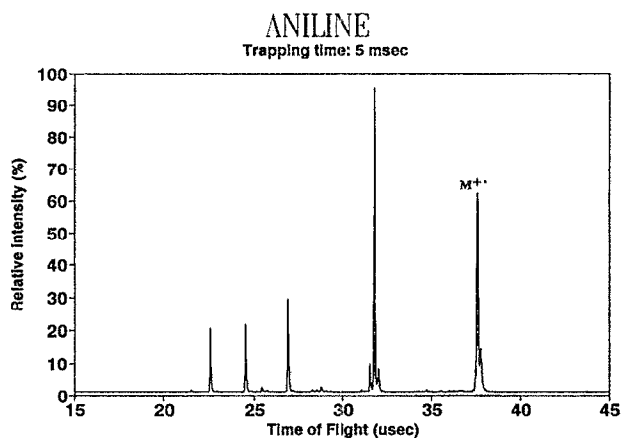
ANILINE
Trapping time: 5 msec

FIG. 11. IT/reTOF mass spectrum of aniline obtained by laser-induced REMPI at 266 nm. The laser power has been increased to induce fragmentation which is stored in the trap for 5 ms and detected by the reTOF. All operating conditions were the same as those in Fig. 7.

B. Experimental parameters

1. rf frequency and voltage

The rf potential applied to the ring electrode determined the m/z range that resulted in stable trajectories in the trap, that is, the applied rf frequency determined the m/z range trapped. Varying the rf frequency was experimentally determined to move the observed m/z range that was trapped. As the frequency was lowered, a region of lower m/z ions were trapped and as the frequency was increased this "window" shifted toward higher m/z. Other than a shift in m/z values over which the "window" was located, frequency variations showed no changes in instrumental performance in the experiment. The experimental results are reported with 1.19 MHz as the selected rf frequency, as this setting was compatible with our chosen m/z range (i.e., the "trapping window" roughly centered on $m/z = 93$). Frequencies in the range 800 kHz–1.19 MHz were studied. Varying the amplitude of the rf voltage applied at a fixed frequency also served to move the "trapping window." A limitation observed here was that rf voltage amplitudes less than 160 V_{pp} were too low to trap the ions studied in this work.

2. dc extraction pulse

The extraction voltage was varied from -50 to -350 V. It was found that -150 V provided both the best signal intensity and resolution. If the extraction voltage was increased significantly both the resolution and signal were degraded. This is due to the fact that the reflectron performance is very sensitive to the exact voltages used on the grids. Various extraction pulse widths were also attempted. A pulse width of ~0.5 μs or less was too short to allow significant extraction of ions from the trap, resulting in decreased signal intensity or no observed signal. A pulse width from >0.5 μs to ~5.0 μs resulted in the best signal intensities, with ~2.0 μs yielding the best resolution.

3. dc extraction with rf power applied

The effect of performing the dc extraction from the ion trap while the rf voltage remained on the ring electrode was examined. The advantage of not having to trigger off the rf voltage becomes evident when using higher rf voltage (>1000 V_{pp}) to trap increasingly higher mass. However, studies on dc ejection of ions from traps with the rf field on have been performed previously by Todd and co-workers[27-29] and there are several apparent problems that result as shown herein. In this study an EAI rf-dc generator rf power supply, which was modified to produce a variable amplitude, 0–2200 V_{pp}, 1.05 MHz rf wave, was used. Due to its high-voltage capabilities, this rf power supply can be used for higher-mass storage but cannot be triggered off.

The results of performing dc extraction of ions in the trap while an rf voltage of 740 V_{pp} is applied to the ring electrode are shown in Fig. 12. The resulting mass spectrum of aniline analyzed by the linear time-of-flight instrument shows a double peak with a high background between the two peaks. This double peak is a result of the 1.05 MHz
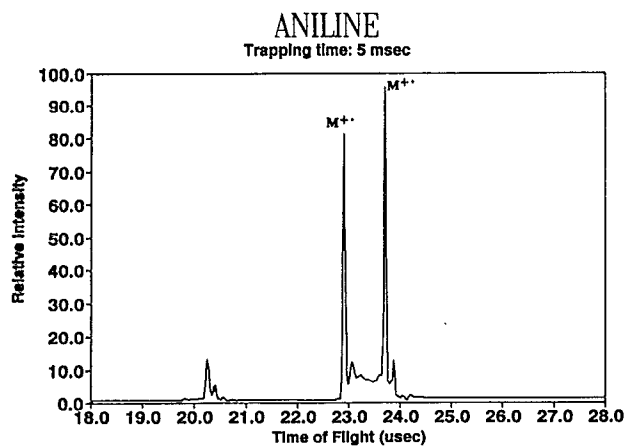
ANILINE
Trapping time: 5 msec

FIG. 12. IT/reTOF mass spectrum of aniline obtained by laser-induced REMPI at 266 nm with 5.0 ms trapping time. In this spectrum, dc extraction was performed while the rf potential was applied to the ring electrode and thus a double molecular ion peak is observed. Note that this spectrum was taken with the linear time-of-flight instrument.

rf trapping voltage and the 2 μs dc extraction pulse width. In this case extraction occurs over several cycles of the rf wave. When the rf wave reaches 0 V, the ions are efficiently extracted resulting in the first peak. However, the ejection of ions from the trap appears to be incomplete at this point and as the rf amplitude increases as a function of time the ions continue to be stored in the trap. During this rf cycle some ions are ejected, as the dc extraction pulse remains on, so that background ions are observed between the two peaks. As the rf voltage approaches zero on the next cycle of the rf wave the ions are efficiently extracted again resulting in the second observed peak. The ion ejection appears to be complete at this point as the dc extraction pulse ends. The second peak can be reduced significantly by increasing the dc drawout pulse. Indeed as the dc voltage is increased the second peak can be made to disappear almost entirely. The problem here though is that the TOF resolution is very sensitive to changes in the voltages used on the device. The drawout voltage of -150 V was chosen to provide the optimum resolution. An increase in the drawout voltage enhances the ability to eject ions from the trap but also significantly degrades resolution and signal intensity. This situation becomes even more critical in the case of the IT/reTOF where the reflectron is very sensitive to small changes in the voltages used and the results obtained when pulsed dc ejection is performed with the rf on are marginal at best. Thus, pulsed dc extraction into the TOF detector appears to work best when the rf voltage is shut off before extraction.

4. Resolution and sensitivity

The peak width (FWHM) of the molecular ion peak in Fig. 6(b), where there was no trapping, was 30 ns. This corresponds to a resolution of nearly 700. In Figs. 7 and 9 the molecular ion peak width was 16 ns, which is a resolution of 1300 at m/z 93, when the trapping capability is utilized. This enhanced resolution provided by the ion trapping is probably due to improved spatial resolution of the ions. As shown in recent computer simulations, the extended trapping of ions results in their accumulation in the center of the trap.[32] Upon dc ejection, this accumulation results in a marked improvement in the spatial resolution factor in the time-of-flight device, as opposed to the untrapped situation where the ions are produced over the diameter (~ 2 mm) of the laser ionization beam.

A measurement of the sensitivity was also performed in the IT/reTOF using laser-induced REMPI at 266 nm for benzene. The benzene was dissolved in methanol in a concentration of 10^{-5} M and a series of successive dilutions down to 10^{-7} M were made. The sample was injected as before using the microsyringe pump at a rate of 30 μl/min into the trap. The 266 nm radiation was used at a power density of 5×10^5 W/cm^2, which was the highest power at which ionization could be produced without significant fragmentation. In the case where no storage was used a lower limit of detection of ~ 600 fmole ($S/N = 3$) was obtained. If a storage time of 90 ms was used following a single laser pulse then the detection limit was ~ 200 fmole, i.e., at least a factor of $3\times$ improvement over no trapping. This is probably partially due to the smaller ion cloud following trapping which is more efficiently ejected along the z axis of the trap. However, if the ions are trapped for 1 s and the laser pulsed ten times during this period, then a detection limit of ~ 60 fmole is achieved. Thus the production and storage of ions over several laser pulses enhances the sensitivity by a factor of nearly $10\times$ compared to the situation where no storage is used. Of course during this storage time some fraction of the ions will be lost from the trap and at some point saturation of the trap with resulting space charge losses will result. Indeed it is found that a saturation point is reached after storage of ~ 4 pulses. Additional pulses do not appear to increase the detection limit while inducing space charge broadening at the given laser power. However, at lower laser power where less ions are produced per laser pulse or in a sample molecule where ionization is much less efficient than benzene, the use of additional laser pulses within a storage time interval will be increasingly important for enhancing the sensitivity for detection. Nevertheless, in the case illustrated herein, the use of ion trap storage with the reTOF can provide excellent sensitivity and may enhance the sensitivity even further where low signal levels are present.

ACKNOWLEDGMENTS

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