ABSTRACT

We report on the development of a novel electrostatic ion trap for high-resolution mass spectrometry. The ion trap works on purely electrostatic fields, thereby allowing simultaneous trapping and studying of multiple mass species, over a large mass range. Ions are trapped and stored as a bunch between two collinearly placed electrostatic ion mirrors and oscillate continuously. The oscillatory signals are fourier-transformed to produce the frequency spectrum, wherein each frequency corresponds to a particular mass of the trapped ions. From the initial experiments a mass resolving power ($m/\Delta m$) of about 20,000 and a storage lifetime of about 100ms is observed. This unique feature and several other important characteristics of this ion trap are presented, along with its application as a high resolution mass spectrometer.

Introduction

Since the invention of Ion trapping techniques about 50 years ago [1], ion traps have been utilized for mass spectrometric purposes. These ion traps range from small tabletop size to large ion storage rings. In general, in most of the small ion traps, ions are trapped and confined to a small region of space using a combination of magnetostatic or time-dependent (RF) fields [2]. The motion of the ions under the influence of such fields is usually a complex function of these fields and in general has been well understood. Another method of trapping and storing ions is the storage-ring technique, where ions with high kinetic energy are kept circulating with the help of magnetic steering and focusing systems. These are large systems and are particularly advantageous when used with electron-cooler inside, which the circulating ion beam can be merged with the electron beam, in nearly zero relative velocity conditions. The storage rings require external injection followed by acceleration either externally [3] with a linac or within the ring itself using synchrotron-type acceleration capabilities [4,5].

Several techniques have been put forward for time-of-flight mass spectrometry such as time-lag focusing [6] and compensating mirrors [7]. Piyadasa, et al [8] reported on a multireflecting instrument where a resolution of about 31,000 for bovine insulin was obtained. Later, Benner [9] using a similar instrument could trap and study DNA molecules. Ring et al [10] demonstrated the fourier transform capabilities of a similar ion trap using a MALDI-type source.
In this paper, we present an electrostatic ion trap, similar to the one originally reported by Zajfman et al [11], which is somewhere in between the small ‘table-top’ devices and large ‘storage rings’ and its application for mass spectrometry. The principle of working of this ion trap and its application to radiative lifetime measurements has already been established [12,13] hence only a brief description is presented here.

**Design of the ion trap**

‘Photon-storage’ devices such as ‘optical resonators’ have long been used in optical devices such as lasers, and their properties have been well studied. In such devices, photons can be trapped between two focusing mirrors and the stability condition is given by [14]:

$$0 \leq \left(1 - \frac{D}{\rho_1}\right) \left(1 - \frac{D}{\rho_2}\right) \leq 1$$

(1)

where D is the distance between the mirrors and $\rho_1$ and $\rho_2$ are the radii of curvature of the mirrors. In the case of a symmetric resonator ($\rho_1 = \rho_2$) and using the relationship for focal length $f = \frac{D}{2}$ the above equation can be simplified to:

$$\frac{D}{4} \leq f \leq \infty$$

(2)

The ion trap presented here, works on a similar principle in which the photon mirrors are replaced by ‘electrostatic ion-mirrors’ and the photon beam is replaced by a well-defined ion-beam. The main advantage with electrostatic ion mirrors is that, they are not mass limited unlike ‘magnetic mirrors’, which means, very massive ions can also be trapped and stored along with lighter ions provided they have the same kinetic energy.

The design of the ion trap closely follows the original design of Zajfman et al [11,12]. A photograph of the actual ion trap is shown in Fig. 1. The ion trap consists of two collinearly placed electrostatic ion mirrors, each consisting of 5 electrodes. The mirrors are arranged on an optical bench with suitable tie-rods that ensures that they are collinear. In order to have lateral confinement, an einzel lens is added before each mirror. Together with the einzel lens, the ion mirrors have both reflecting and focusing properties that obey Eqn.(2). The inner most electrodes on each mirror are grounded, thereby keeping the region between the two mirrors field-free.

In order to have reflecting properties, the ion mirrors need to have a potential which is high enough to stop the ions i.e. $V_0 \geq \frac{E_k}{q}$ where $E_k$ is the kinetic energy of the ion beam and $q$ is the charge of the ions. The performance of the ion trap was simulated with SIMION v7.0 software [15]. The initial set of voltages on the ion mirrors and the einzel lenses could
be obtained from the simulation, in order to determine stable conditions of trapping. However in order to perform mass spectrometry with the ion trap, it is important that the trapped ions remain bunched for a long period of time. In order to achieve this, the voltages on the ion mirrors and the einzel lenses were adjusted such that the energy spread in the ion beam which translates into velocity spread could be compensated, by determining the turnaround points inside the ion mirror. It should be noted that this procedure only reduces the time-spread in the arrival of the ion bunch due to the energy spread in the ion beam at the centre of the ion trap, where the image charge detector is located.

Experimental setup and results

A. Storage Lifetime Measurements

A schematic of the experimental setup is shown in Fig. 2. The setup consists of an electron impact ion source followed by suitable acceleration and focusing elements. An electrostatic chopper is utilized, to pulse the DC beam with pulse widths ranging from 0.5 to 5 microseconds. In order to remove the energetic neutrals that are produced along the beamline, a zeman type 90° electrostatic deflector [16] is employed. The pulsed ion beam is allowed to enter the ion trap through a 1mm aperture with the help of suitable XY deflectors and einzel lenses. The entire beamline is kept at a very low base pressure of about 5 x 10⁻⁹ mbar with the help of triode sputter ion pumps, while the ion trap is pumped with the help of a 1000 l/s cryopump and a base pressure of about 7 x 10⁻¹⁰ mbar could be achieved which rises to about 1 x 10⁻⁹ mbar with the ion source operating. DC ion beam currents of about 50 nA could be injected into the ion trap with every injection, or about 80,000 ions equivalent per microsecond pulse.
The voltages on the entrance mirrors are lowered to zero while injecting the ion bunch into the ion trap and the voltages on the exit mirror are kept high all the time. The voltages on the entrance mirror are switched ON (identical to the exit mirror), as the bunch enters the image charge pickup tube, located at the center of the ion trap. This reduces any interference due to the high voltage switching. Fast high voltage switches (Behlke GmbH, Germany. HTS Series) with rise times of less than 100ns are utilized to effect the high voltage switching. The ion bunch is now trapped between the two mirrors and oscillates with a frequency that is inversely proportional to the square root of the mass of the ions. Once the ion bunch is trapped, the ions can decay either by a charge transfer type of reaction (the ions are neutralized by colliding with a residual gas molecule and are no longer trapped) or by elastically scattering off a residual gas molecule and no longer within the realm of stability condition of the trap.

The storage lifetime of the ions is given by: \( \tau = \frac{1}{\eta \sigma \nu} \)

where \( \eta \) is the number density of residual gas molecules in the ion trap, \( \sigma \) is the charge transfer cross section and \( \nu \) is the velocity of the ions. The storage lifetime is measured by monitoring the energetic neutrals, that leave the trap (roughly about a quarter of the stored particles at any given time) detected by a Microchannel plate detector and counted by a PC-based Multichannel scaler (FAST ComTec, Germany. Model P7887) which histograms the data given the bin sizes. The start of the multichannel scaler is slightly delayed, with respect to the start of the trapping cycle. The entire timing cycle is controlled by a specially designed 6-channel, <5ns jitter timer, whose pulse widths and delay could be adjusted for individual channels in 100ns steps. Storage lifetimes measured for different ions are shown in Fig. 3. Storage lifetimes of about 100ms or greater could be achieved routinely which was only limited by the base pressure in the ion trap. Under these conditions, an argon ion bunch oscillates with a frequency of about 332 KHz, which when measured for 50ms turns out to be 16,500 oscillations or the equivalent of a 6 Km long time-of-flight tube when unfolded.

**B. Mass Spectrometry**

The oscillation of the ions is detected with the help of an image charge detector (a small metallic tube of 18mm length and 12mm diameter) located at the center of the ion trap. A proportional image charge is induced on the detector every time the ion bunch passes through it. This charge is then amplified with a suitable low noise charge sensitive preamplifier and the output signal of the preamplifier is digitized by a PC-based high speed digitizer card [CompuScope 82G, Gage Inc.]. A fourier transform operation is performed on the digitized signal, to obtain the frequency spectrum.

Two types of ion trapping modes were employed to optimize the oscillation signals of the ions. In the first case, the dispersive case, the potentials on the ion mirrors were chosen to be linear which made the mirror a ‘hard’ mirror. In the second case, the self-bunching case, a velocity compensated approach was applied to the potentials on the ion mirrors, which made the ion mirror function as a ‘soft’ mirror.
Fig. 4 shows an FFT spectrum obtained in the ‘dispersive mode’ from the oscillations of a $^{40}$Ar$^+$ ion bunch, which was used to calibrate the mass spectrometer. The sensitivity of the ion trap was limited by the capacitance of the image charge detector, the capacitance of the ultrahigh vacuum electrical feedthrough used to transfer the signal out of the vacuum chamber and the input capacitance and the noise levels of the pre-amplifier. Thus in the present setup, we could not observe $^{36}$Ar$^+$ due to its very low natural abundance. The FWHM ($\Delta f$) of the fundamental harmonic is 50Hz and using $R = m/\Delta m = f/2\Delta f$, we obtain a mass resolution of about $\sim 3320$. The FFT spectrum was averaged for about 100 injection cycles.

Fig. 5 shows an FFT spectrum obtained from the same $^{40}$Ar$^+$ ion bunches trapped in the self-bunching mode. In this case, the oscillatory signals decayed much slower than in the dispersive mode, which contributed to a better FFT spectrum. The FWHM ($\Delta f$) of the fundamental harmonic is now 20Hz and using $R = m/\Delta m = f/2\Delta f$, we obtain a mass resolution of about $\sim 8300$. The FFT spectrum was averaged for about 100 injection cycles.

Fig. 6a shows an ‘as recorded’ Xe$^+$ frequency domain spectrum obtained in the ‘self-bunching’ mode averaged for about 100 injection cycles. The peak amplitudes closely match the known natural abundances of the various isotopes. Further, even higher harmonics could be detected for longer observation times in the self-bunching mode, indicating that a very high mass resolution is possible with this type of mass spectrometer.

Fig. 6b shows a 5th harmonic from which the mass resolution is calculated as $R = m/\Delta m = 21,000$. This is mainly because the oscillations of the ion bunches in the ion trap are not affected by the usual factors that affect normal TOF instruments such as trigger jitter, time response of the MCP detector, etc. These and other interesting features such as its ability to be coupled with multiple ion sources such as MALDI ion source, Electrospray ion sources, etc., make this ion trap, a versatile instrument for mass spectrometry.

Conclusion

We have demonstrated a novel electrostatic ion trap which traps and stores ions as a well defined beam that works on the principle of an optical resonator. Storage lifetimes of about >100ms for various ions could be achieved. We have also demonstrated the capabilities of the ion trap as a high resolution mass spectrometer with mass resolutions over 20,000.
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References

15. SIMION V.7.0, Ion Source Software.
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