Miniature Ion Traps and Arrays for High Pressure Mass Spectrometry

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Progress in Miniaturization of Ion Trap Mass Spectrometry

Commercial ITMS, 45 Kg, 1800W

Battery-powered prototype, 10Kg, 60W

MGA ITMS array, 40-μm traps
Commercial Ion Trap Electrodes
1-mm Cylindrical Ion Trap

End-cap

Insulator

1.0 mm

Insulator

End-cap

0.9 mm

0.45 mm
Timing sequence

- Ion trapping
- Mass scan
- Electron gun on
- Detector on
- Ion signal

-t (ms)-

- Voltage - rf amplitude (V)
Mass spectrum of perfluorophenanthrene
Mass Spectrum of Xenon isotopes, 1-mm Trap

\[ \frac{\Omega}{2\pi} = 6.8 \text{ MHz} \quad f_{ax} = 1.7 \text{ MHz} \]
The equation of motion for an ion in a quadrupole trap is

$$\frac{d^2u}{dt^2} + c \frac{du}{dt} = \frac{\alpha e}{m(r_0^2 + 2z_0^2)} [V_{DC} + V_{AC} \cos(\Omega t)]u$$

where $\alpha = -2$ for $u = r$, $\alpha = 4$ for $u = z$ and we have added a drag term. The velocity-dependent term can be removed by changing to a new variable,

$$u = \exp\left(-\frac{c}{2}t\right)u'$$

To put the equation in the canonical form, we also change to a dimensionless time variable,

$$\xi = \frac{\Omega t}{2}$$
giving

\[
d^2 u' \frac{d^2}{d \xi^2} + \left[ a' - 2q' \cos 2 \xi \right] u' = 0.
\]

where

\[
a' = \frac{4 \alpha e}{m \Omega^2 (r_0^2 + 2z_0^2)} V_{DC} - \frac{c^2}{\Omega^2} = a - \frac{c^2}{\Omega^2},
\]

\[
q' = \frac{2 \alpha e}{m \Omega^2 (r_0^2 + 2z_0^2)} V_{AC} = q,
\]

with \( \alpha = -4 \) for \( u = z \) and \( \alpha = 2 \) for \( u = r \).

This reverts to the usual Mathieu equation for zero pressure, \( c = 0 \).

The only result of adding drag to the equation is to shift the value of \( a \).
Stability diagram for zero pressure
Stability diagram for $c^2/\Omega^2 = 0.1$
How large is $c$?

c is given by $2/\tau$ for oscillatory motion. Plass et. al. ([*J. Phys. Chem. A*] 104, 5059-5065 (2000)) found $\tau = 4$ ms for m/z 84 at a pressure of 0.43 mTorr, giving $c = 500$ s$^{-1}$. $c$ is linear in buffer gas pressure. At atmospheric pressure, $c$ will be approximately $10^9$ s$^{-1}$ for m/z 84.

c varies inversely with mass for heavy ions.

We can make $\Omega$ as large as we want as long as the stability requirements are met.

Although not included in the analysis, we need to maintain sufficient trap depth, given approximately by $D = q_z V_{AC}/8$, to preclude thermal detrapping.
There is an uncertainty relation between collision frequency and linewidth

\[ \Delta \omega = \frac{2(3)^{1/2}}{\tau} \]

Goeringer et al. and Marshall et al. have shown that the linewidth resulting from collisional relaxation is given by \( \Delta \omega = 2(3)^{1/2}/\tau \). The mass resolution will then be,

\[ \frac{m}{\Delta m} \leq \frac{\omega_0 \tau}{2(3)^{1/2}} = \frac{\omega_0}{((3)^{1/2}c)} \]

Since \( c \) is proportional to the pressure, the frequency \( \omega_0 \) must also increase with pressure to maintain the same resolution.
\[ r_0 = 0.3 \times 10^{-7} \sqrt{mVq_z \Delta m} \frac{\Delta m}{P} \]

\[ f = \frac{10.5 \times 10^{12} P}{q_z m \Delta m} \]

**Graph: Trap Size and Frequency vs Pressure**

- **Axes:**
  - X-axis: Pressure (Bar)
  - Y-axis 1: \( r_0 \) (cm)
  - Y-axis 2: Frequency (Hz)

- **Lines and Points:**
  - Blue line: ITD
  - Red line: ORNL 1-mm Trap
  - Green line: Diaphragm Pumps

- **Labels:**
  - Diaphragm
  - Pumps

**Conditions:**
- \( m = 100 \text{ amu} \)
- \( \Delta m = 1 \)
- \( V = 100V \)
- \( q_z = 0.4 \)
Array of 40-μm poly-Si ion traps fabricated at Bell Labs
Lucent has also fabricated a series of arrays of 250-mm diameter ion traps from micro circuit-board material. These arrays will be tested in both the ion drift experiment and the electron ionization experiment.
Mask for Fabrication

- Mask contains 33 chips to fit on 4-in Silicon wafer
- Each chip has 808 holes of the same diameter
  - 5 chips have 200-\(\mu\)m holes
  - 6 chips have 100-\(\mu\)m holes
  - 10 chips have 60-\(\mu\)m holes
  - 12 chips have 30-\(\mu\)m holes
A second generation array of 40-micrometer traps has fewer traps, lower capacitance. We can now detect trapped xenon ions at low pressure.

Ion signal (xenon) obtained with the array at left at low helium pressure ($10^{-4}$ Torr) Origin at 4.090 ms.

Scan function - electron gun on, 0-4 ms
Detector on 4-5 ms
Micro Ion Trap, Ionization Source And Detector

- Filament
- Focusing Electrode
- Mounting Plate
- End Caps
- Ground Plate
- Ring Electrode
- Electron Multiplier
- pump
Dual-chamber system for high-pressure MS

- Ion trap
- Detector
- Gate valve
- Turbo pump
View of mounting flange, ion trap array
View of detector assembly
Experiments with a single 1-mm ion trap at high pressure, using a detector in vacuum

- Instrumentation:
  - RF frequency: 6.5 MHz
  - RF voltage: ~120-140 V 0-p
  - Scan rate: ~5 amu/ms ~600 Xe ions detected/scan

- Mass spectrum of xenon isotopes with helium pressure of 0.46 Torr in chamber.
- Sticks show major Xe isotopes.
- Mass peaks could be observed with chamber pressure as large as 1.7 Torr. Pressure within trap is somewhat lower.
Mass Spectrum of CW Surrogate, DMMP, in a single 1-mm Ion Trap with Chamber at 1.7 Torr

The stick spectrum shows the parent ion and fragment ions resulting from electron-impact ionization of DMMP, furnished by NIST. RF voltage from 80-130 V 0-p.
0.8 and 0.3-µm microfabricated devices from Lucent are being tested at low pressure. We have observed ions being formed when a voltage is applied between the two electrodes.

Soft ionization array, before cavity etch

Ion generation from 0.3 µm membrane
Summary

- Mass spectrometry with ion traps of submillimeter dimension is feasible
- Mass resolution is comparable to or better than from conventional ion traps
- They operate at lower voltages, higher frequency, and higher pressure
- Arrays of traps can store greater number of ions for higher sensitivity
- All components are amenable to microfabrication

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