Miniature Ion Traps and Arrays for High Pressure Mass Spectrometry

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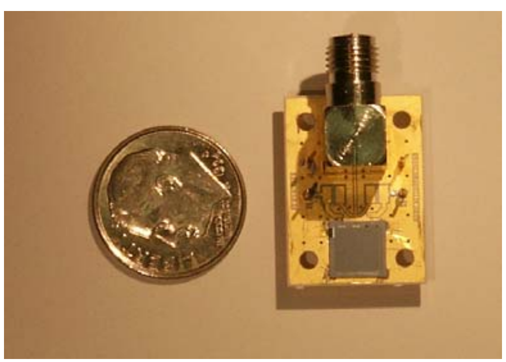
HEMS Workshop 2005

Progress in Miniaturization of Ion Trap Mass Spectrometry

Commercial ITMS, 45 Kg, 1800W

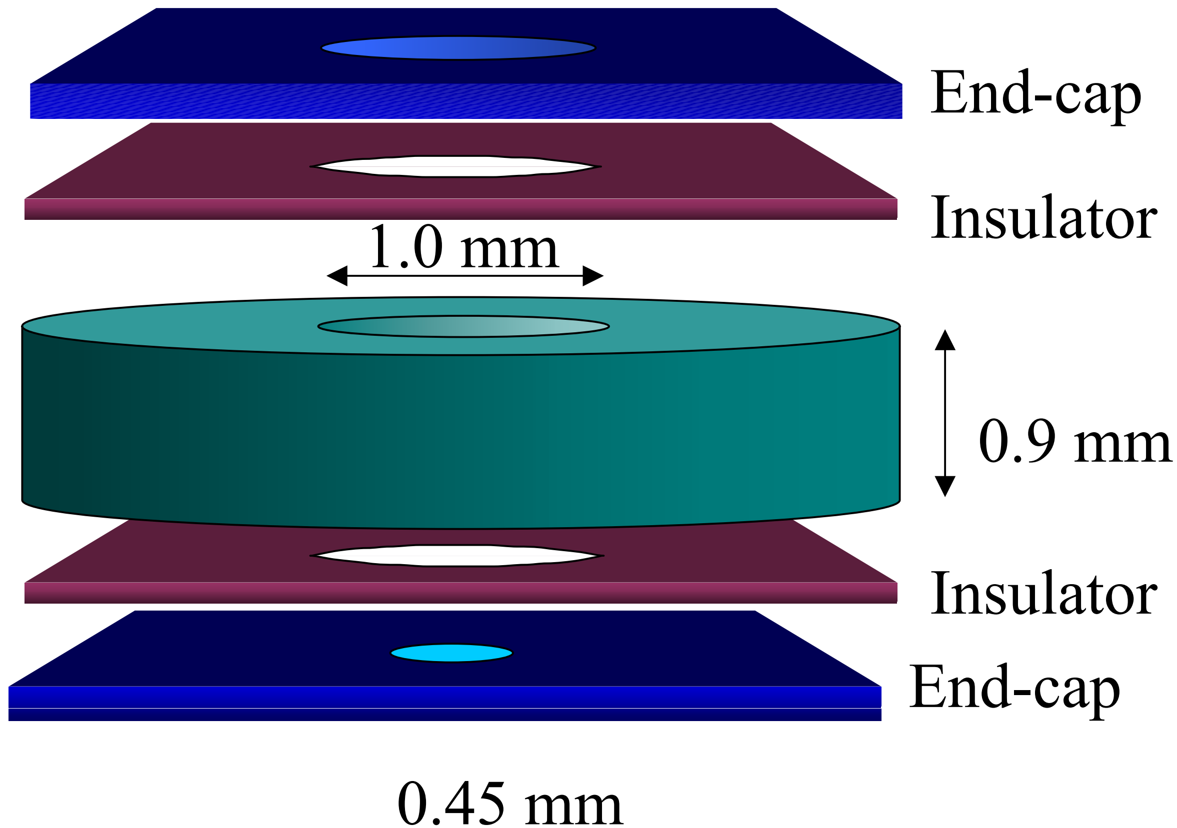


MGA ITMS array, 40-μm traps

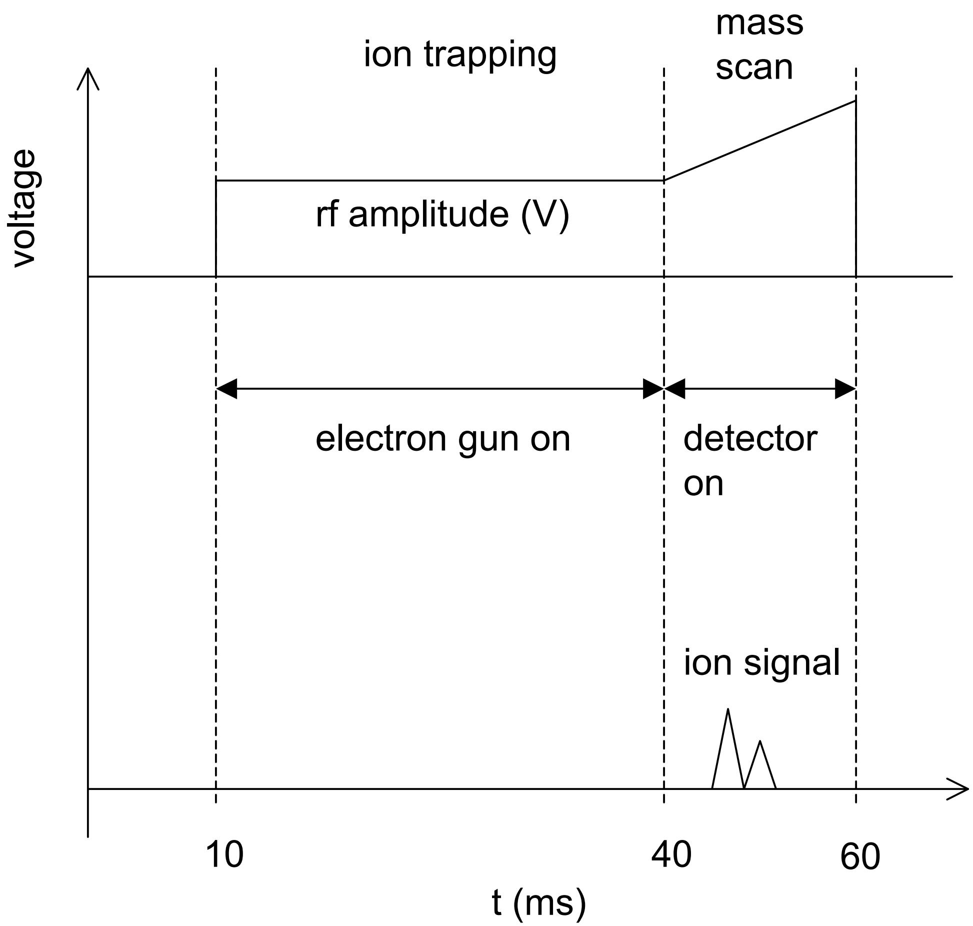
Battery-powered prototype, 10Kg, 60W

Commercial Ion Trap Electrodes

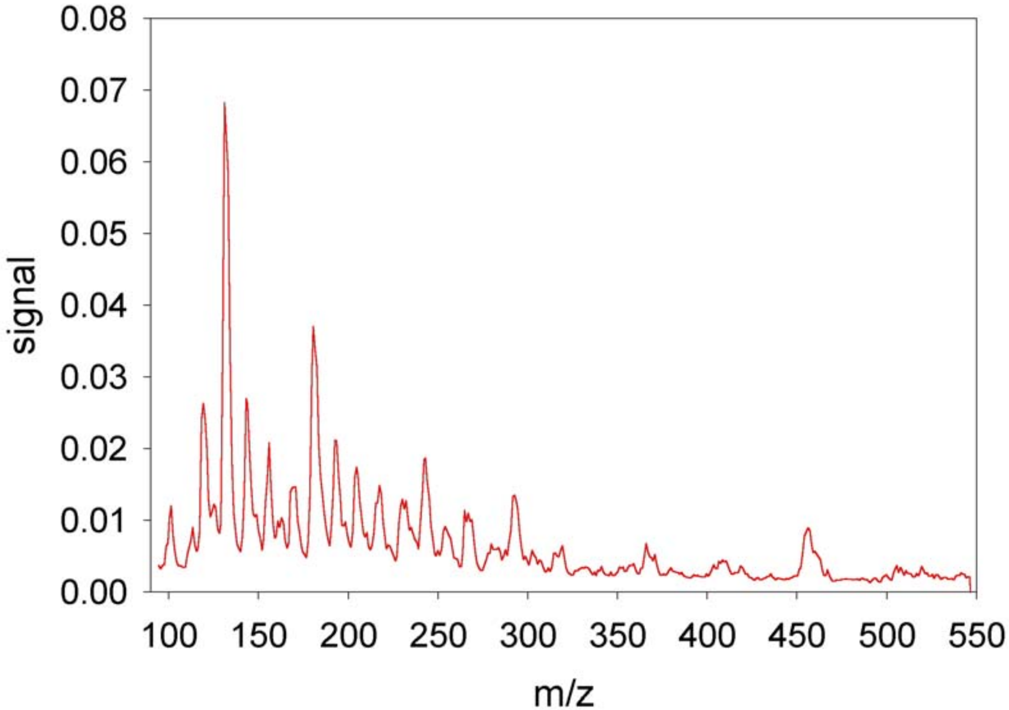
1-mm Cylindrical Ion Trap

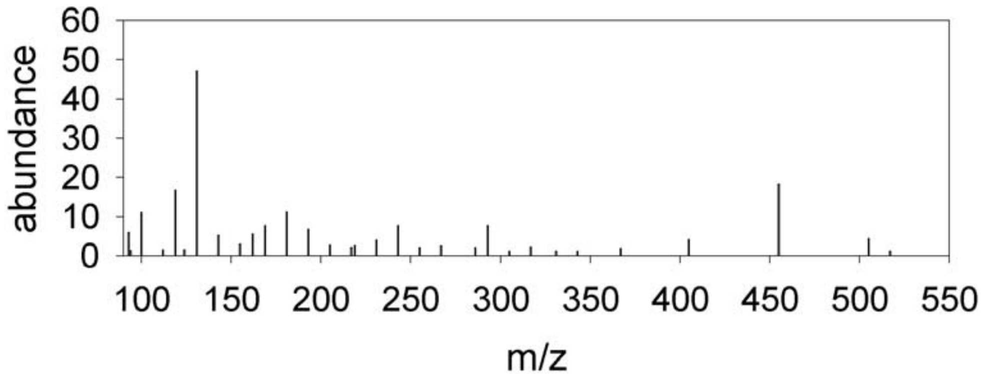


Timing sequence



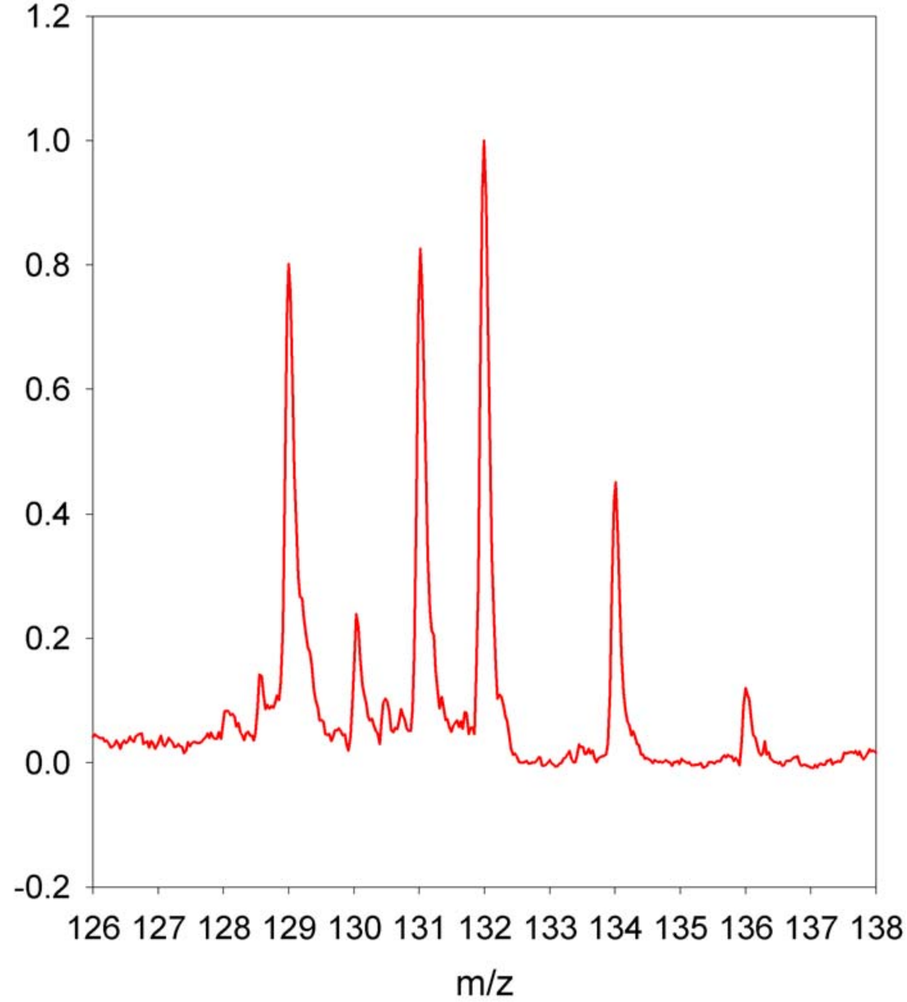
Mass spectrum of perfluorophenanthrene





Mass Spectrum of Xenon isotopes, 1-mm Trap

$\Omega/2\pi$ = 6.8 MHz f_{ax} = 1.7 MHz



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

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

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

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

giving

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

where

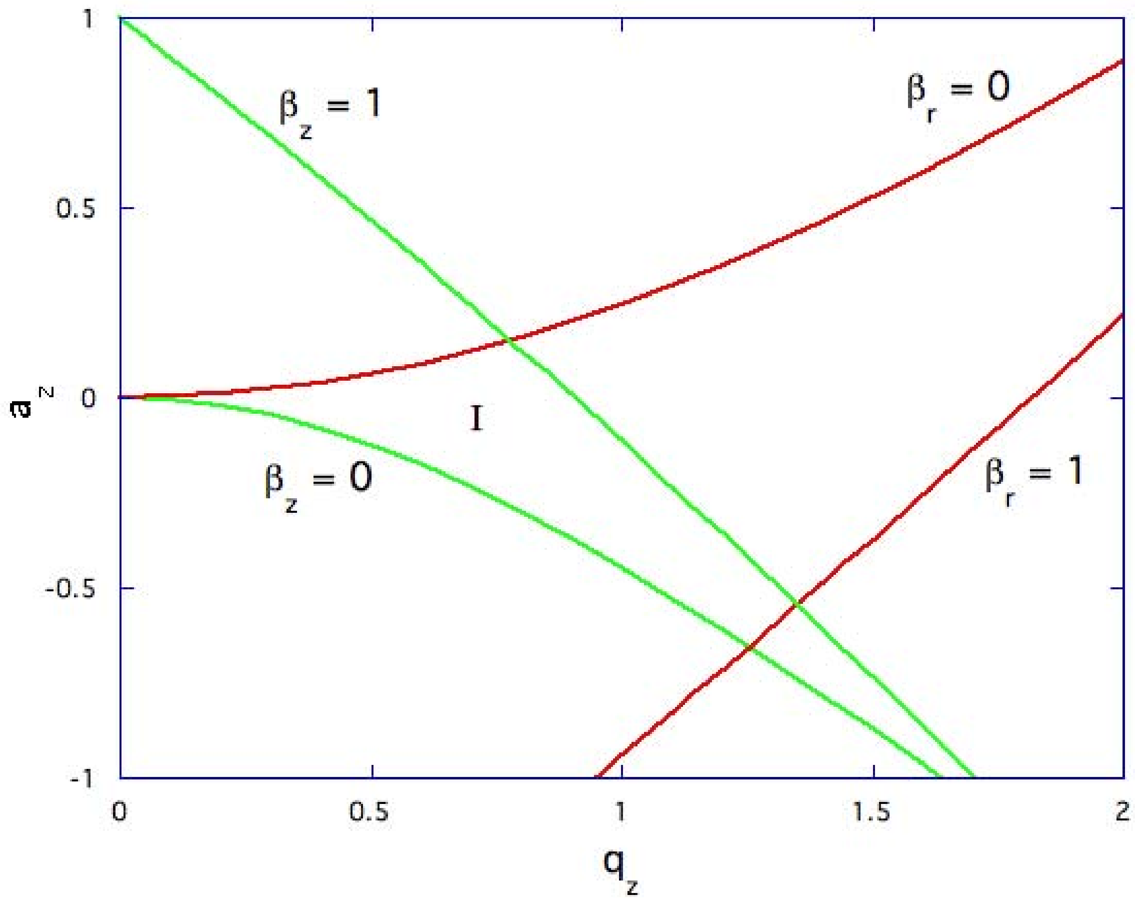
$$a' = \frac{4\alpha e}{m\Omega^2(r_o^2 + 2z_0^2)}V_{DC} - \frac{c^2}{\Omega^2} = a - \frac{c^2}{\Omega^2},$$

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

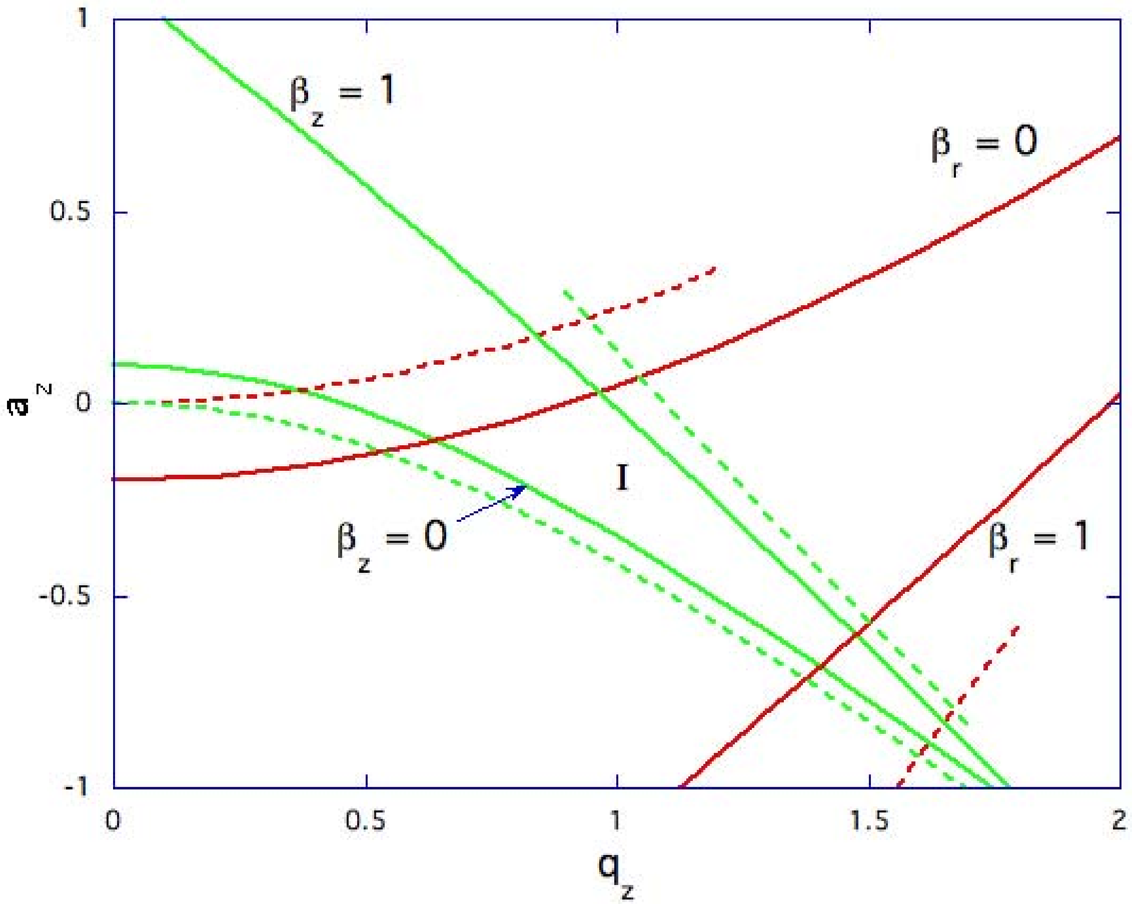
with α = -4 for u = z and α = 2 for u = r.

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 τ = 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.

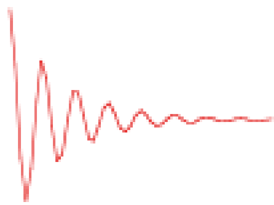
c varies inversely with mass for heavy ions.

We can make Ω 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.

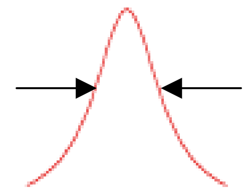
There is an uncertainty relation between collision frequency and linewidth

time dependence



$\exp(-t/\tau)\cos(\omega_0 t)$

frequency spectrum



$\Delta\omega = 2(3)^{1/2}//\tau$

$\tau[1+ (\omega-\omega_0)^2\, \tau^2]^{-1/2}$

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,

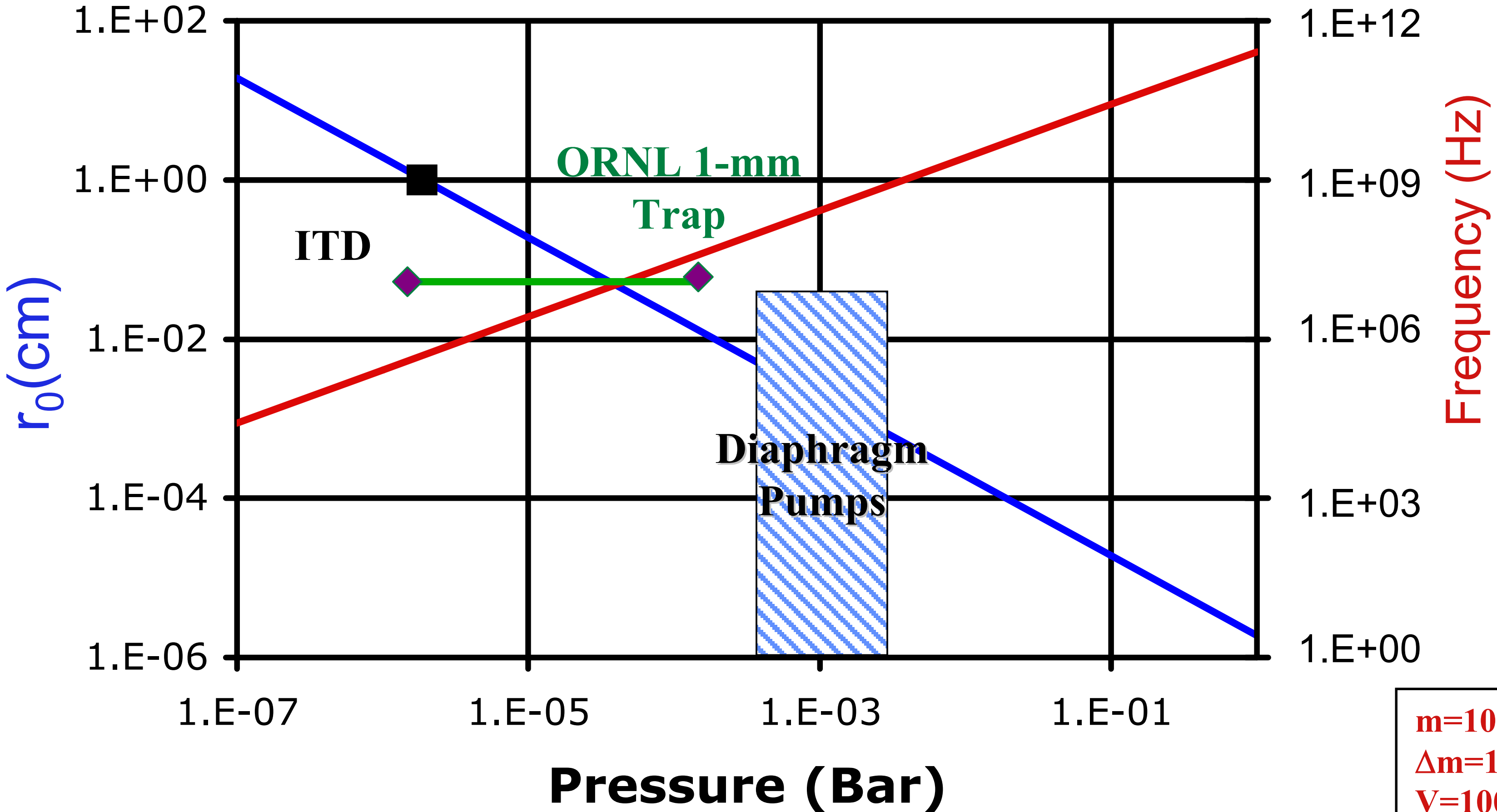
$$m/\Delta m <= \omega_0\tau/2(3)^{1/2} = \omega_0/((3)^{1/2}c)$$

Since c is proportional to the pressure, the frequency ω_0 must also increase with pressure to maintain the same resolution.

Trap Size and Frequency vs Pressure

$$r_0 = 0.3 \times 10^{-7} \sqrt{mVq_z} \frac{\Delta m}{P}$$

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



m=100 amu
Δm=1
V=100V
q_z=0.4

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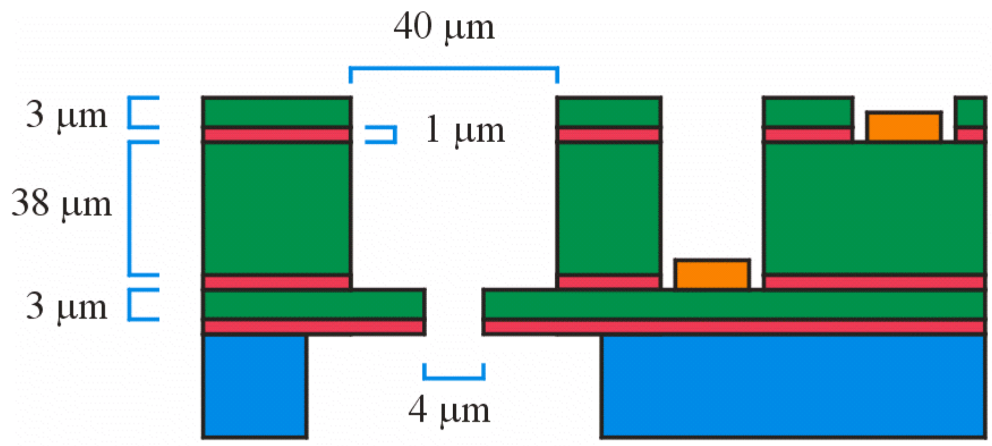
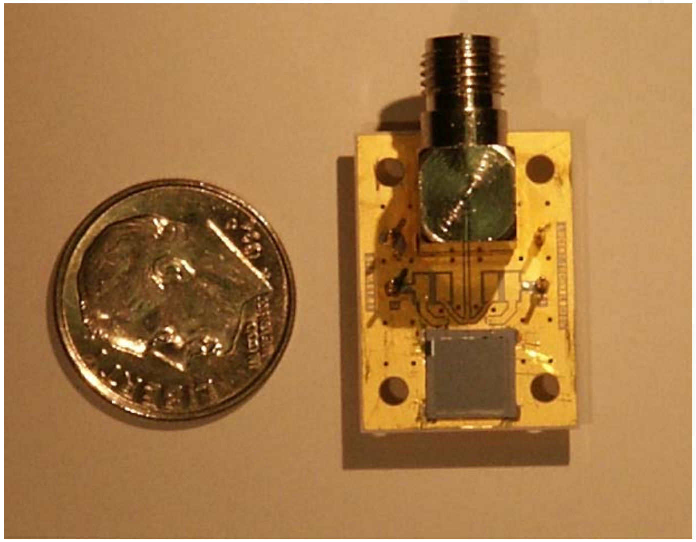
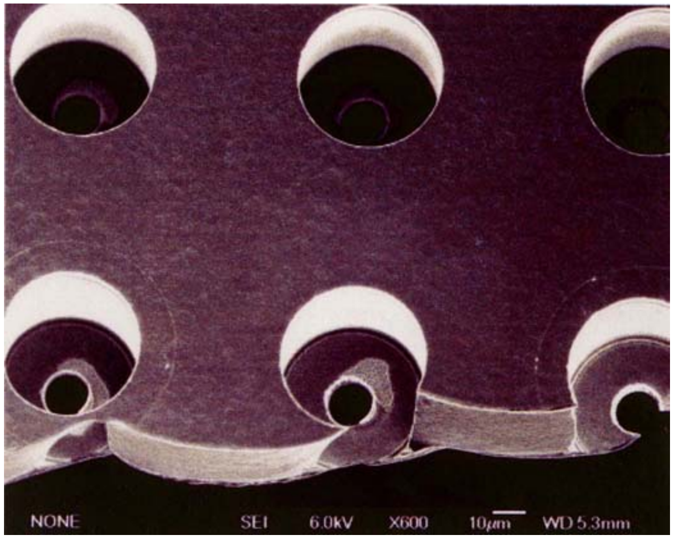
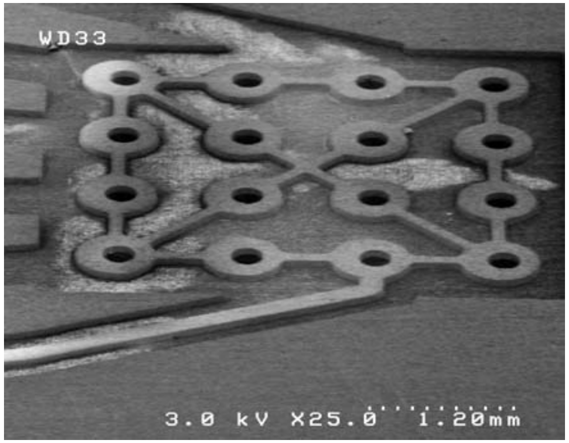
Array of 40-μm poly-Si ion traps fabricated at Bell Labs



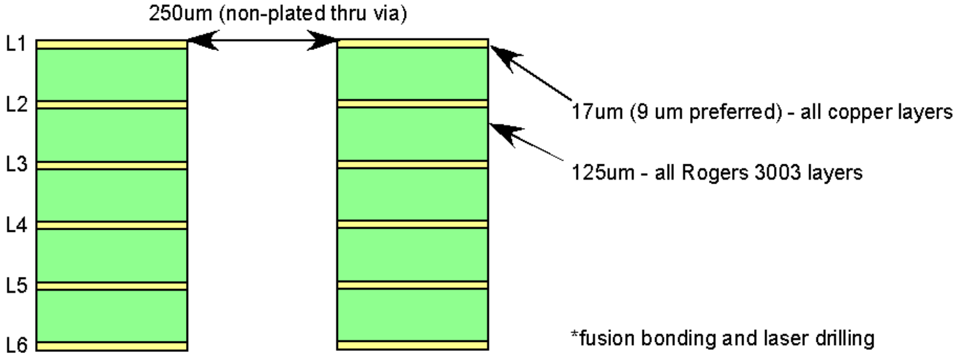




Lucent has also fabricated a series of arrays of 250-mm diameter ion traps from micro circuit-board material. These arrays will be tested in both the ion drift experiment and the electron ionization experiment.

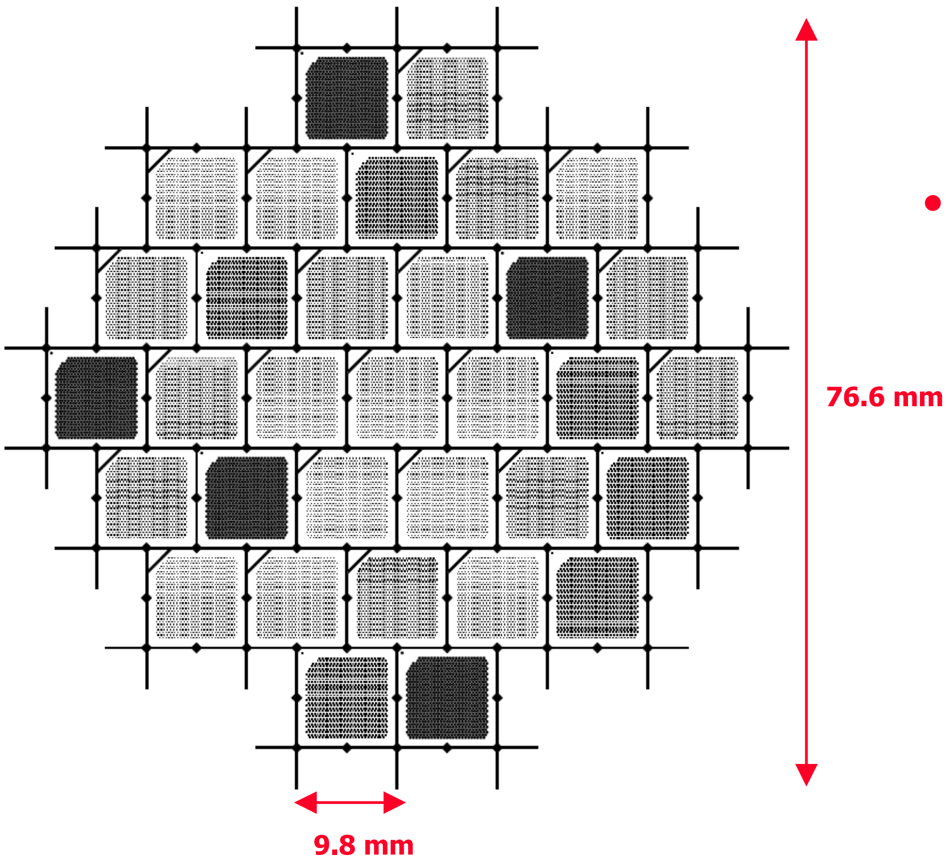


SEM image of circuit-board array



Cross-section view of each non-plated thru-via

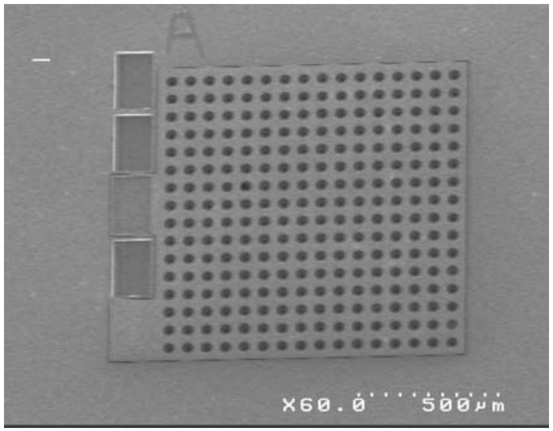
Mask for Fabrication



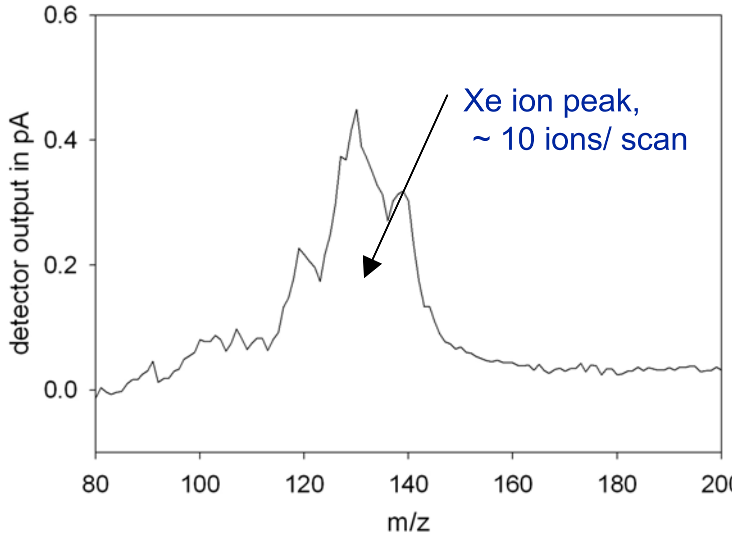
Mask for fabrication of electrode arrays

- Mask contains 33 chips to fit on 4-in Silicon wafer
- Each chip has 808 holes of the same diameter
  - 5 chips have 200-μm holes
  - 6 chips have 100-μm holes
  - 10 chips have 60-μm holes
  - 12 chips have 30-μm holes

A second generation array of 40-micrometer traps has fewer traps, lower capacitance. We can now detect trapped xenon ions at low pressure.

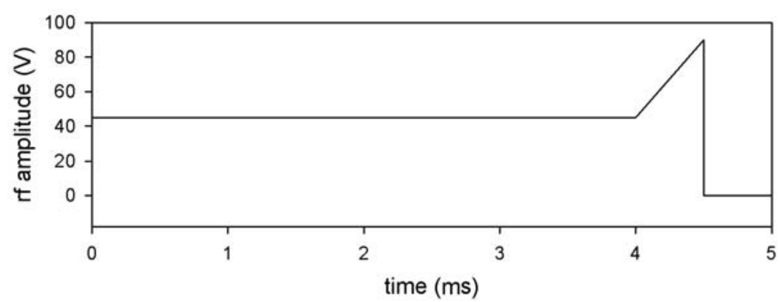


SEM image of low-capacitance array fabricated by Bell Labs



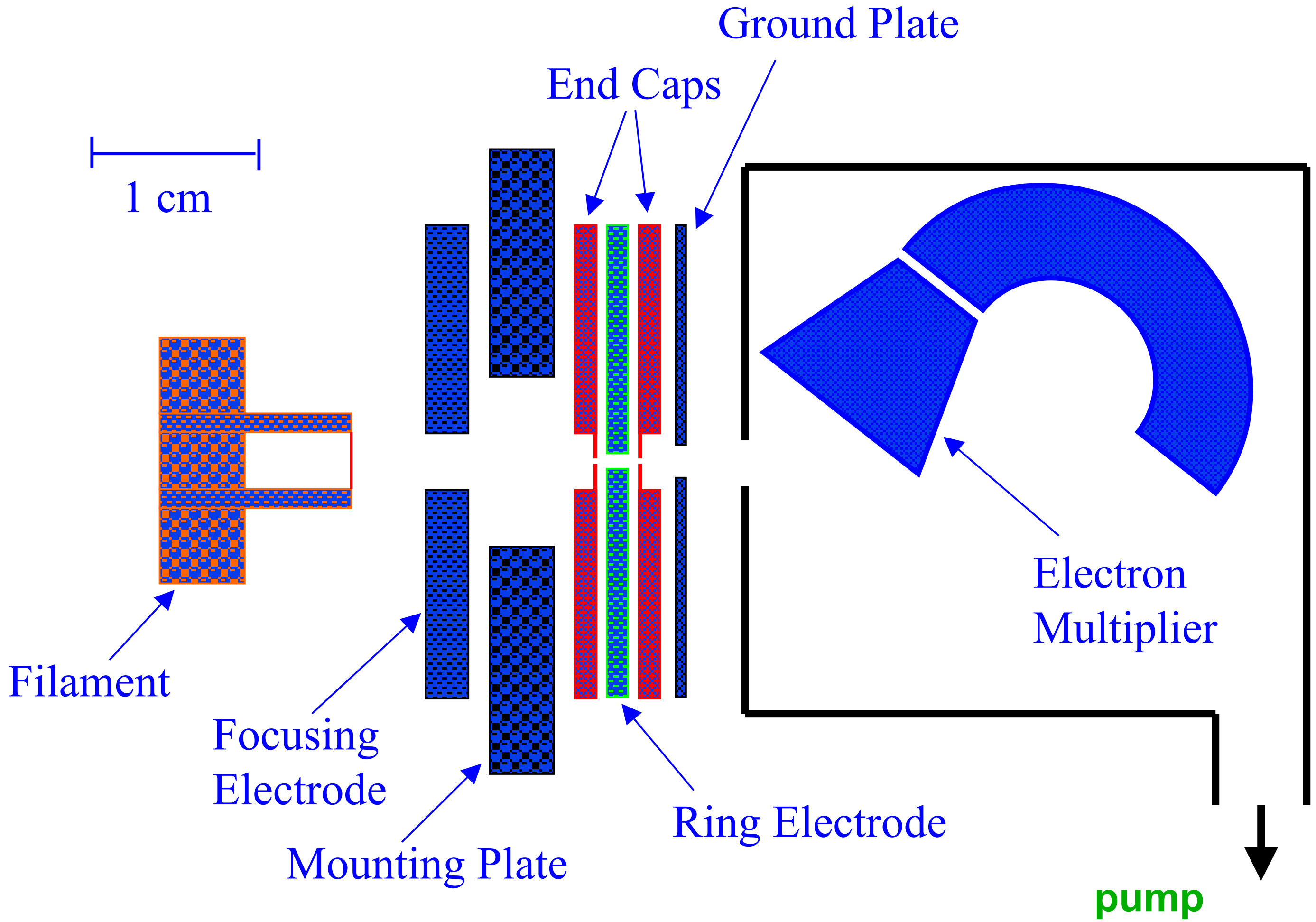
Ion signal (xenon) obtained with the array at left at low helium pressure (10^{-4} Torr) Origin at 4.090 ms.

RF frequency - 100 MHz
RF amplitude vs time at right
Mass scan rate - 1 amu/μs
Multiplier gain ~10^6 e/ion

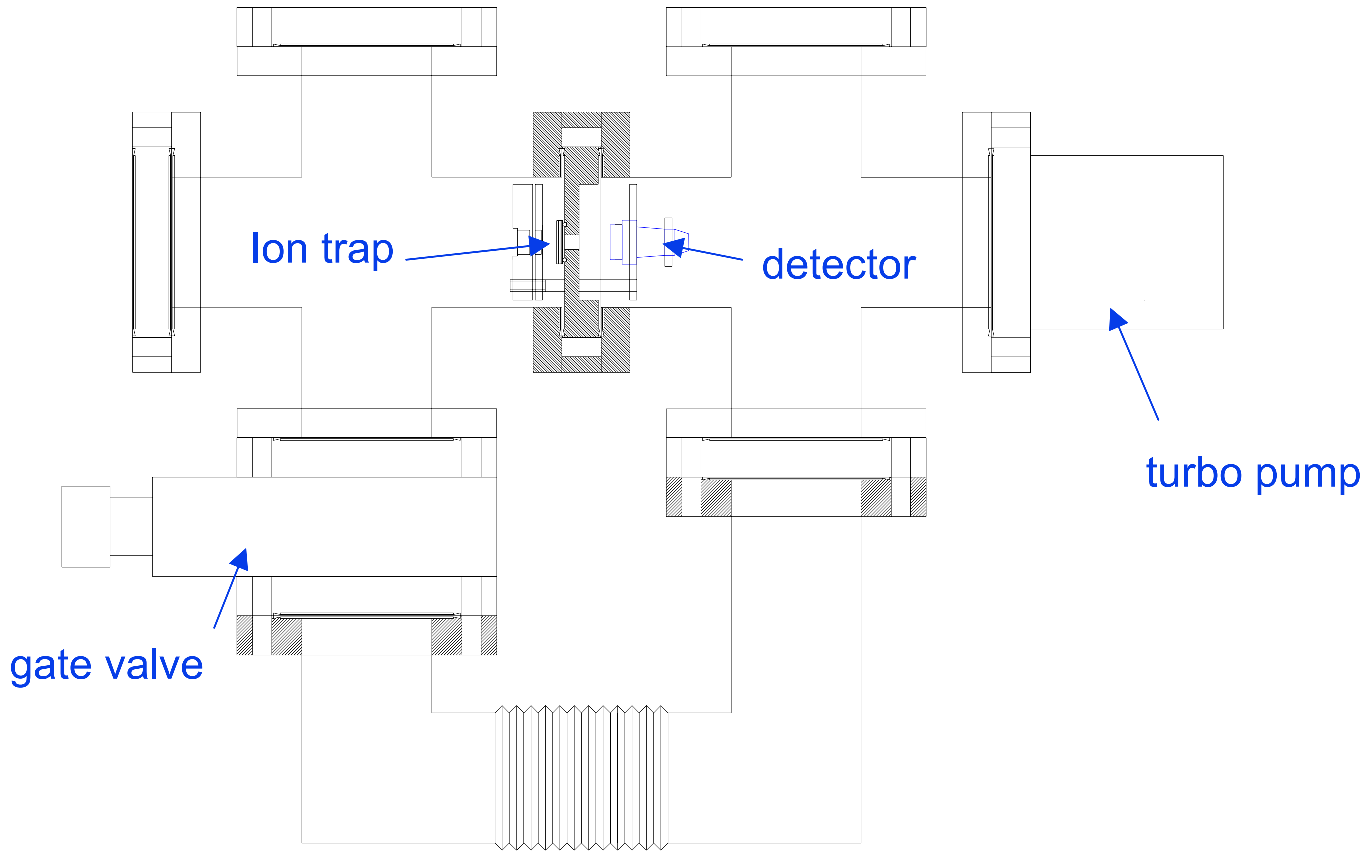


Scan function - electron gun on, 0-4 ms
Detector on 4-5 ms

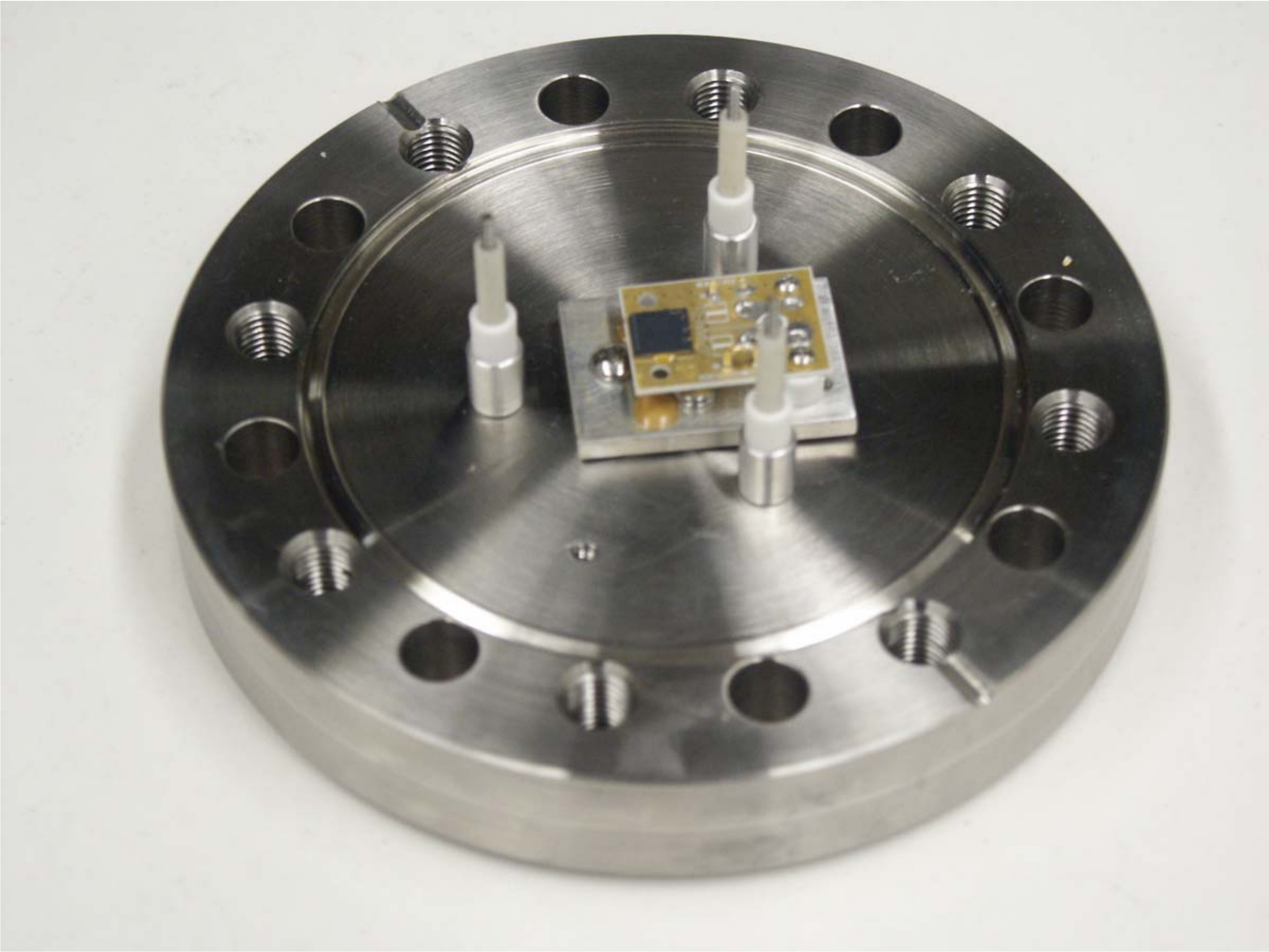
Micro Ion Trap, Ionization Source And Detector



Dual-chamber system for high-pressure MS

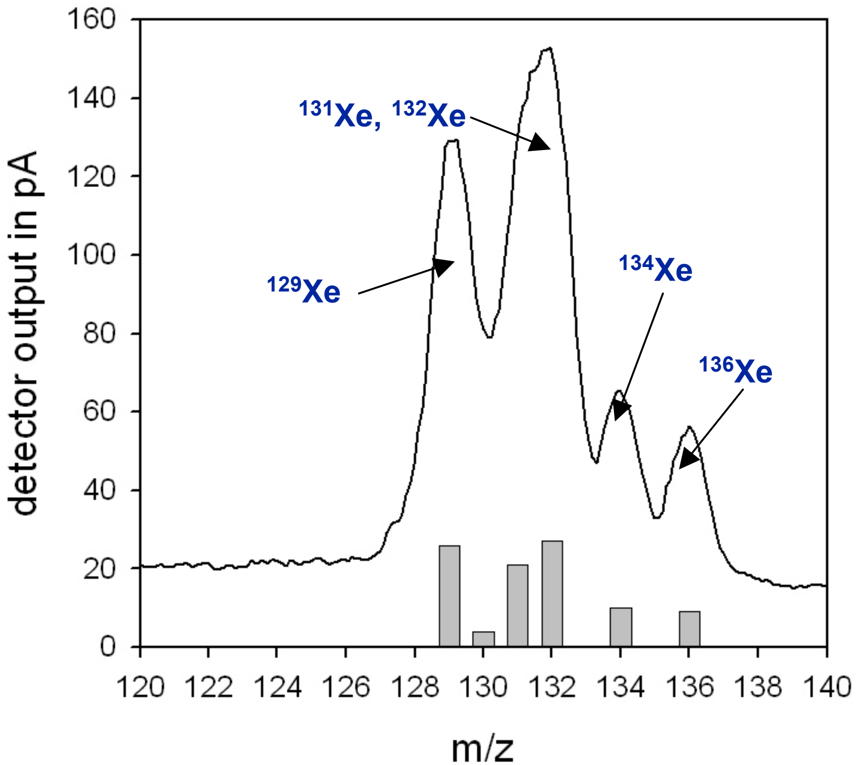


View of mounting flange, ion trap array

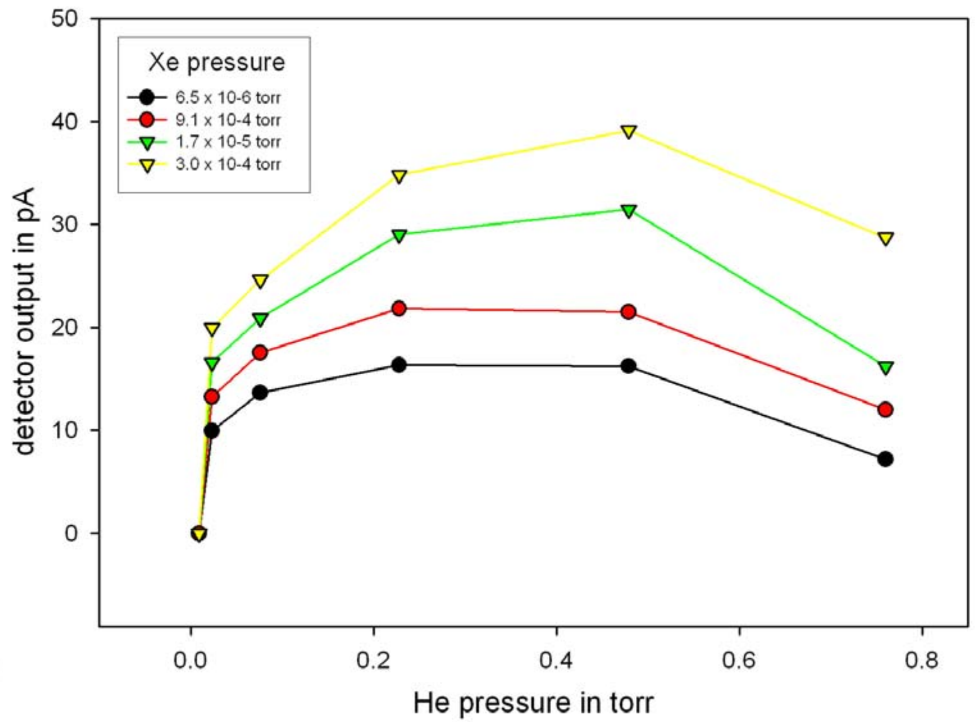


View of detector assembly

Experiments with a single 1-mm ion trap at high pressure, using a detector in vacuum

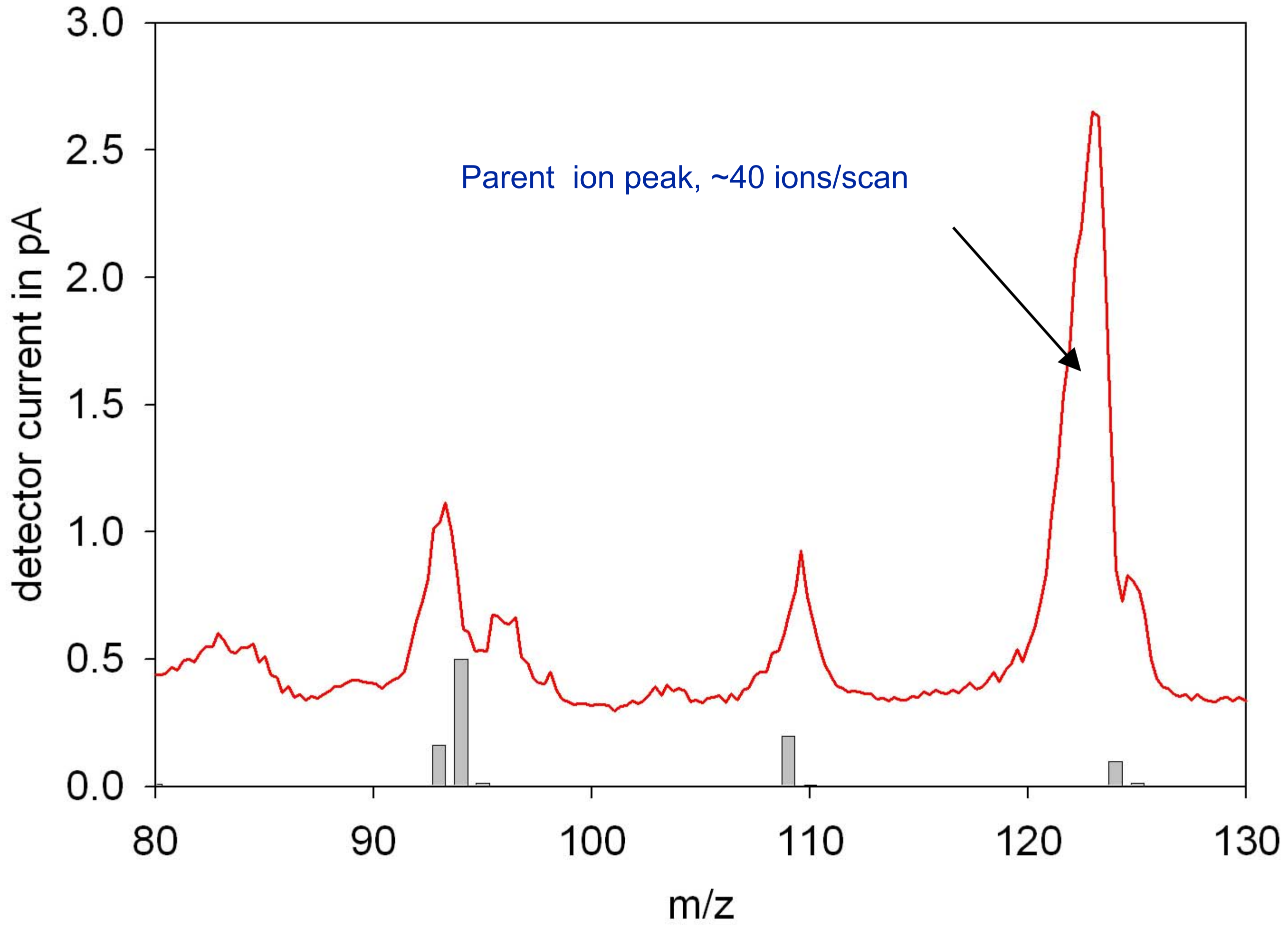


Mass spectrum of xenon isotopes
with helium pressure of 0.46 Torr in
chamber. Sticks show major Xe isotopes.
RF frequency - 6.5 MHz
RF voltage - ~120-140 V 0-p
Scan rate - ~5 amu/ms ~600 Xe ions detected/scan



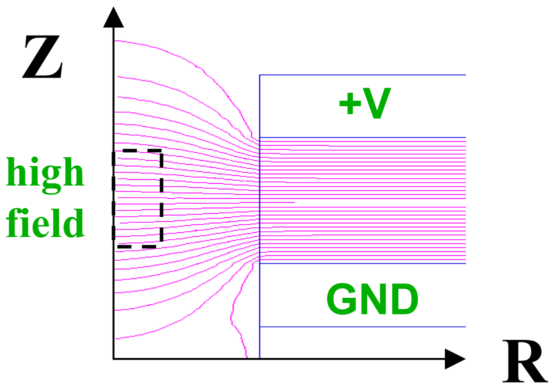
Mass peaks could be observed with chamber pressure as large as 1.7 Torr. Pressure within trap is somewhat lower

Mass Spectrum of CW Surrogate, DMMP, in a single 1-mm Ion Trap with Chamber at 1.7 Torr

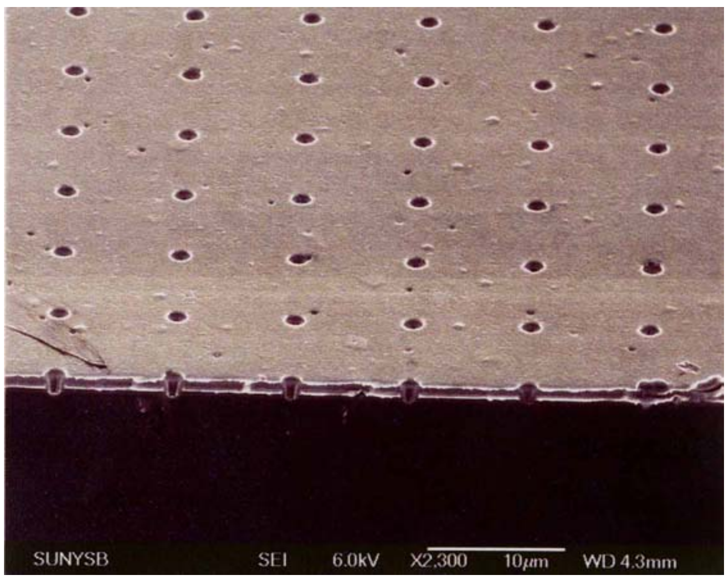


The stick spectrum shows the parent ion and fragment ions resulting from electron-impact ionization of DMMP , furnished by NIST. RF voltage from 80-130 V 0-p.

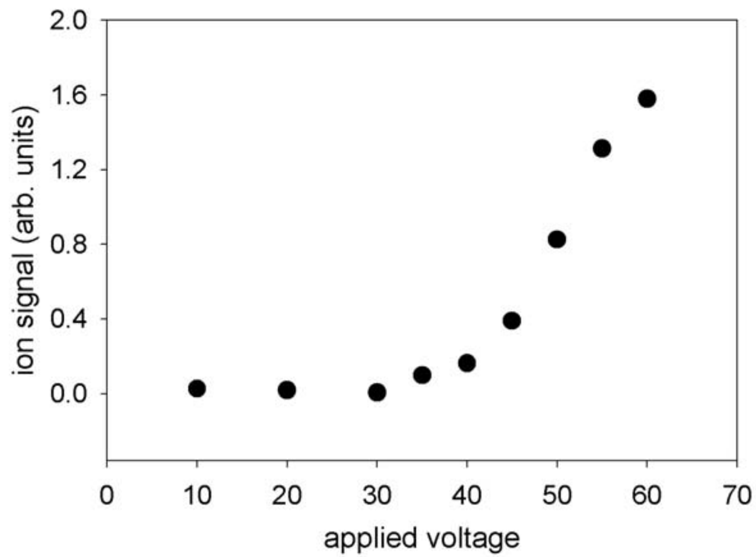
Soft Ionization Membrane



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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