ULTRA-HIGH RESOLUTION MASS SPECTROMETRY FOR PLANETARY PROBES

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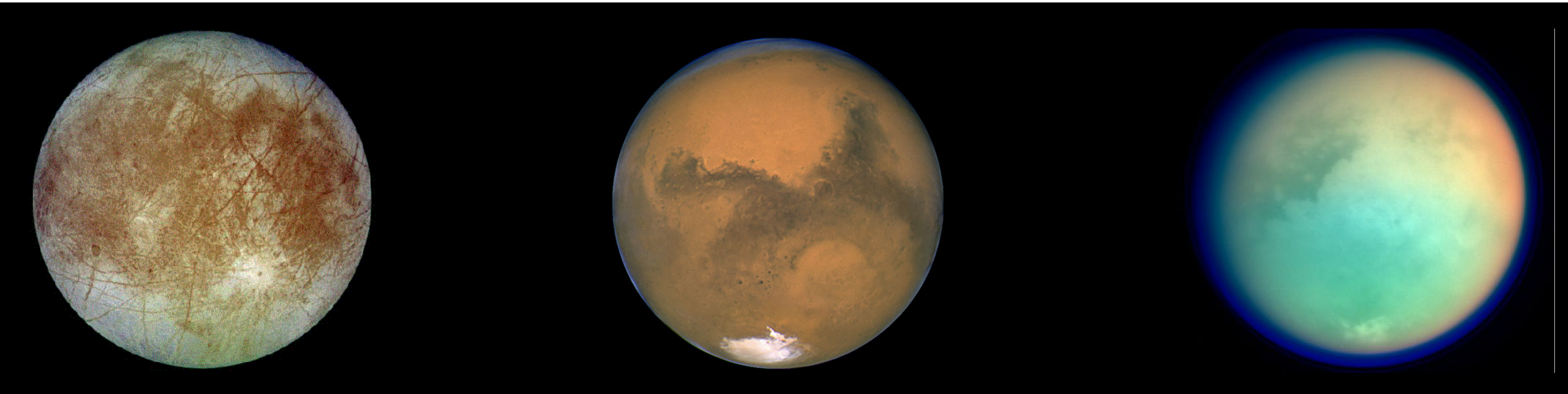


Science Objectives

- Mass Spectrometry is the most general technique for addressing *in situ* geochemical and biological science objectives on planets and satellites of the solar system.
- Objectives are to understand the nature, abundance, and isotopic properties of all important materials above, on and under the surfaces of moons and planets.
- Gases, rocks, soils, ices, liquids
- Important target compounds:
  - Carbonaceous: Biomarkers, non-biogenic organic, inorganic
  - Non-carbon (minerals): Compounds with H, N, O, P, S, Fe, Mg,…
  - Gases: CO_2, N_2, O,…; noble gases

Example 1: Martian Isotope Ratios†

Isotope Ratio	Value vs. Earth	Implications
D/H	5.8	⇒ loss of meters of H_2O
$^{13}C/^{12}C$	1.05-1.07	⇒ loss of ~ bar of CO_2
$^{15}N/^{14}N$	1.6-1.7	⇒ loss of 90% of N_2
$^{18}O/^{16}O$	1.025	⇒ large resevoir (silicates?)
$^{38}Ar/^{36}Ar$	1.3	⇒ loss of 90% of Ar
$^{129}Xe/^{132}Xe$	2.5	⇒ loss of 90% of Xe

† Jakosky, Orig. Life Evol. Biosph., 29, 47, 1999;
Yung and DeMore, ***Photochemstry of Planetary Atmospheres***, Oxford, 1999.

Example 2: Isotopes in Murchison meteorite

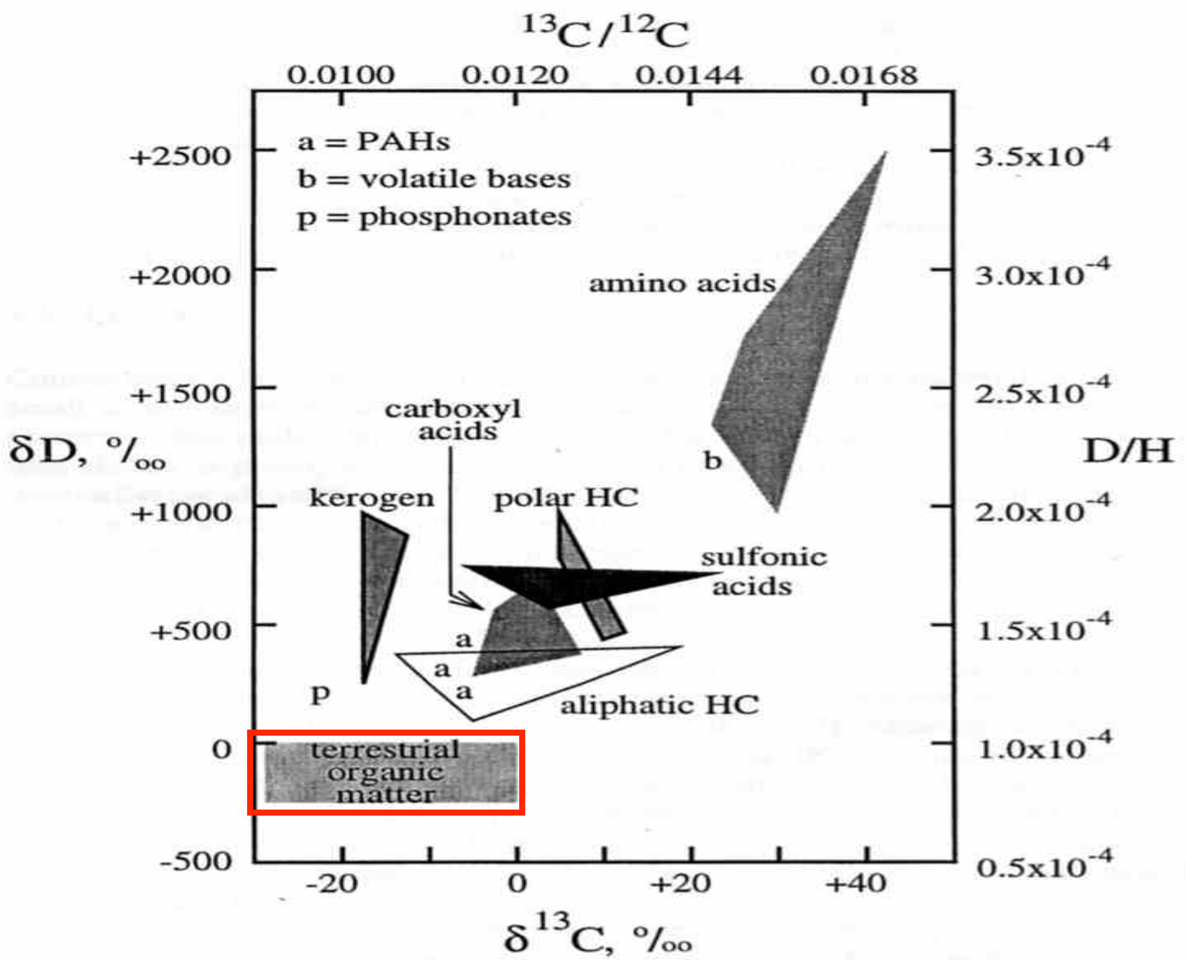
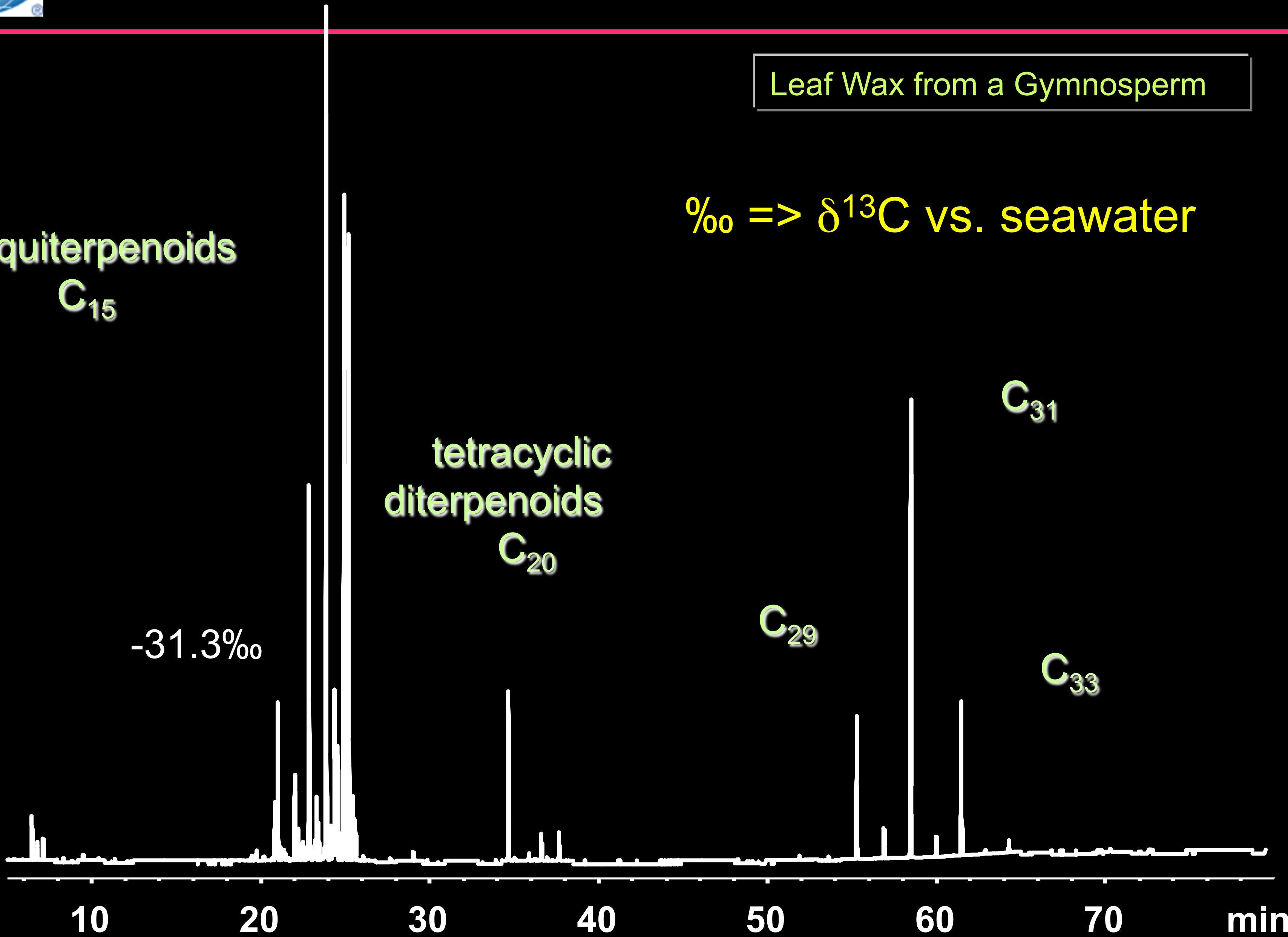


Figure 3. Isotopic ratios for carbon and hydrogen for various molecular compounds from the Murchison meteorite (Cronin and Chang, 1993; and Chang, 1996, private communication). Terrestrial ocean water has by definition $\delta D = 0$ and the cosmic D/H ratio is $(0.8–2) \times 10^{-5}$ (Irvine and Knacke, 1989).

Example 3: Biomarkers—signatures of life



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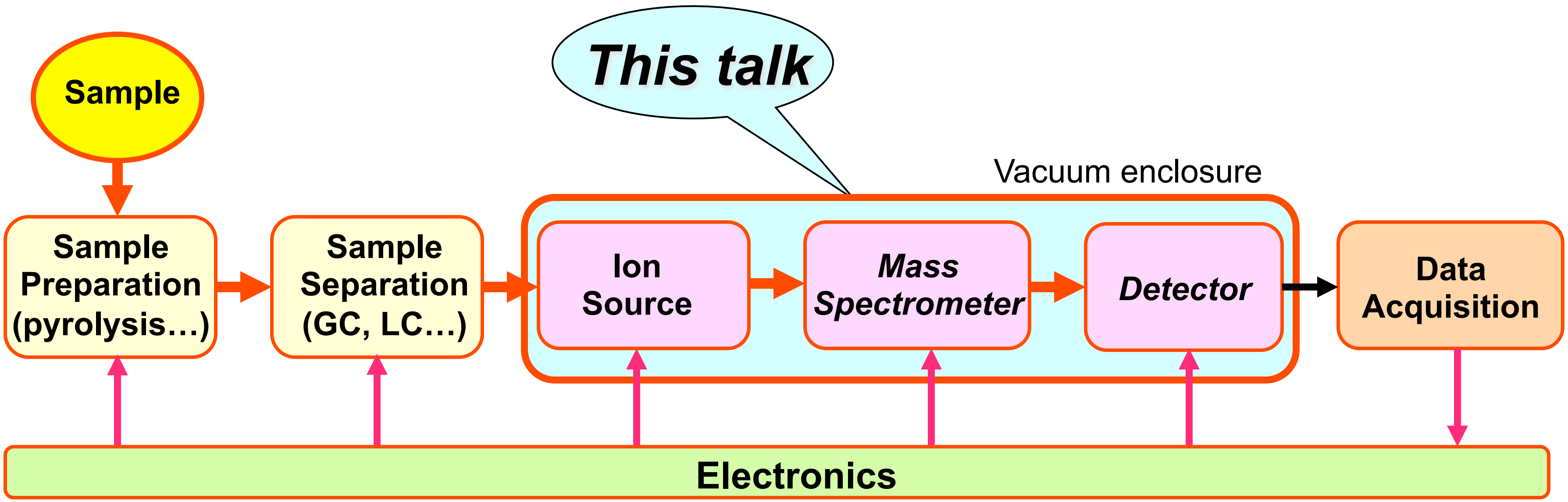
Designing mass spectrometers for space:

- Very complex systems requiring lengthy development
- ALWAYS: Performance vs. resources
- They aren’t cheap

More than meets the eye…

– There’s more to a “mass spectrometer experiment” than just the mass spectrometer…

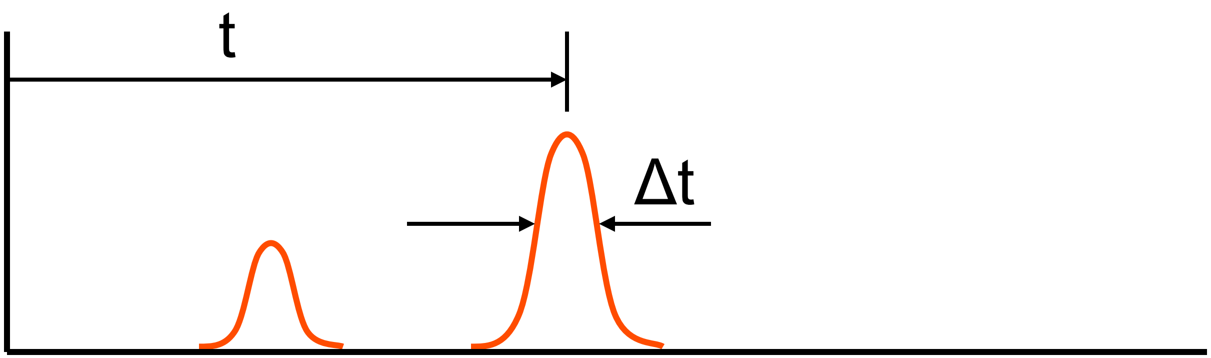
– Preparation and separation techniques are essential: pyrolysis, laser ablation, gas chromatography,…



TOF Principles

- Mass resolution in time-of-flight (TOF):

$$m/\Delta m = t/2\Delta t = L/2v\Delta t$$



- Sensitivity:

  S = current extracted/pressure in source (e.g., Amps/Torr)

  S = minimum detectable mass of sample (e.g., 10^{-12} grams)

  S = minimum fraction of sample (e.g., parts per billion = ppb)

What is “Ultra-High Resolution”?

- “High” resolution: $m/\Delta m$ ~ few 100
  - Viking, Venus, Galileo Probe, Huygens
- “Very high” resolution $m/\Delta m$ ~ few 1000
  - Rosetta RTOF, DFMS, COSAC
- “Ultra high” resolution: $m/\Delta m$ >~ few 10,000
  - SwRI prototype (this paper)

Three types of mass spectrometers

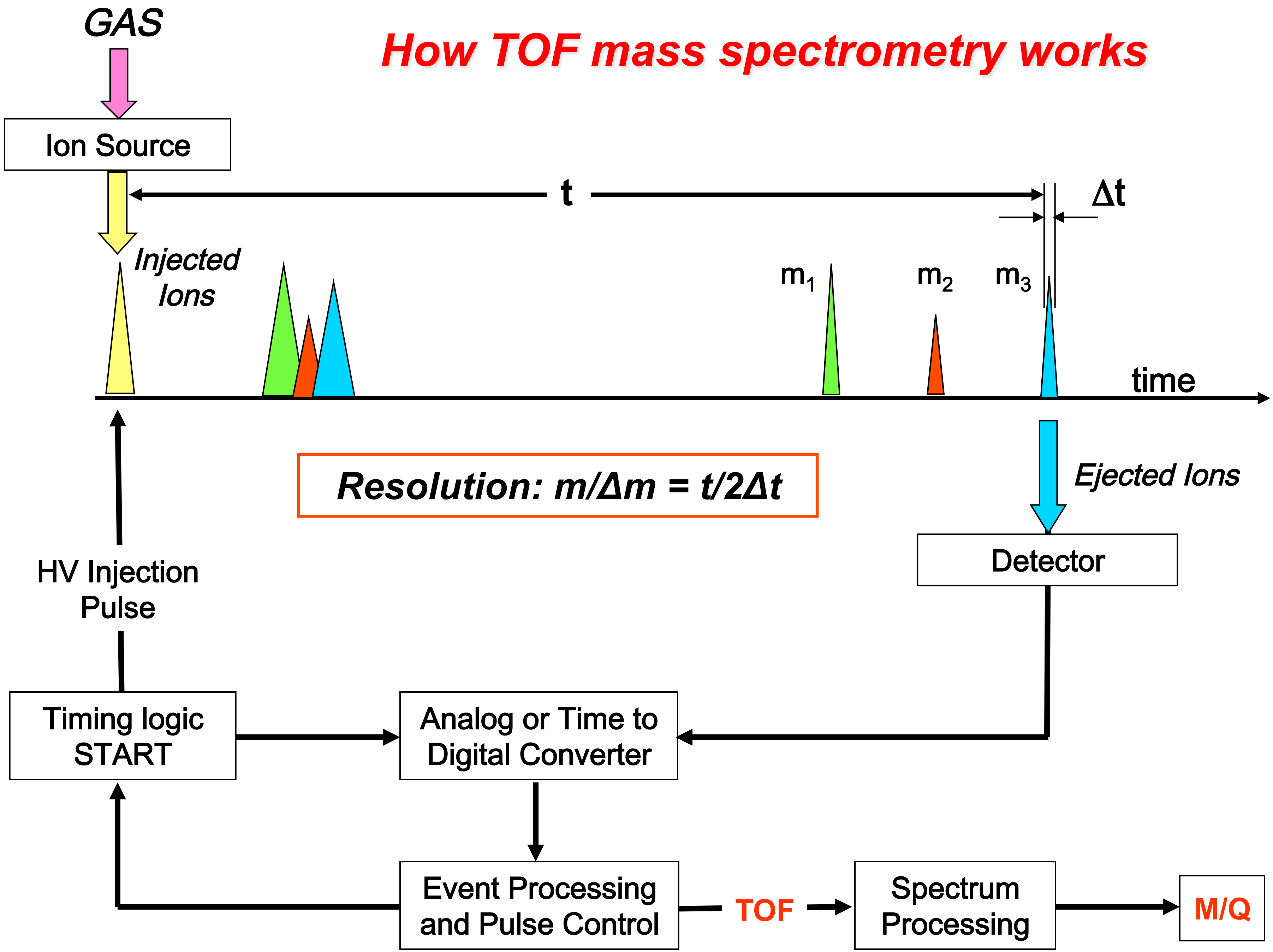
- **Magnetic**
  - First miniaturized by Nier (Viking); Hoffman (Pioneer Venus); Krankowsky and Eberhardt (Giotto)
  - High resolution DFMS on Rosetta (Balsiger et al.)
- **Quadrupole**
  - Used extensively by Niemann (Galileo Probe, Huygens, Cassini INMS); also Rushneck (Viking)
- **Time-of-Flight *(TOF)***
  - First high resolution instruments are on Rosetta
    - RTOF/ROSINA (Balsiger et al.)
    - COSAC (Casares et al.)

- *Is one type better than the others?*

The answer is ***YES***

- In many (not all) cases TOF has advantages:
  - Resolution depends primarily on length of the flight path
    - Longer flight path = higher resolution
    - Flight path can be folded using the multi-bounce technique
  - Resolution and sensitivity are decoupled
    - Unlike magnetic and quadrupole spectrometers, resolution does not depend on slits
    - Transmission from source to detector ~50% (losses <1%/bounce)
  - High spectral sampling speed
    - 1000 to 10,000 spectra/s
    - Ideal for GC x GC and laser ablation techniques
  - High duty cycle ~50%
    - Scanning is not required to get spectra

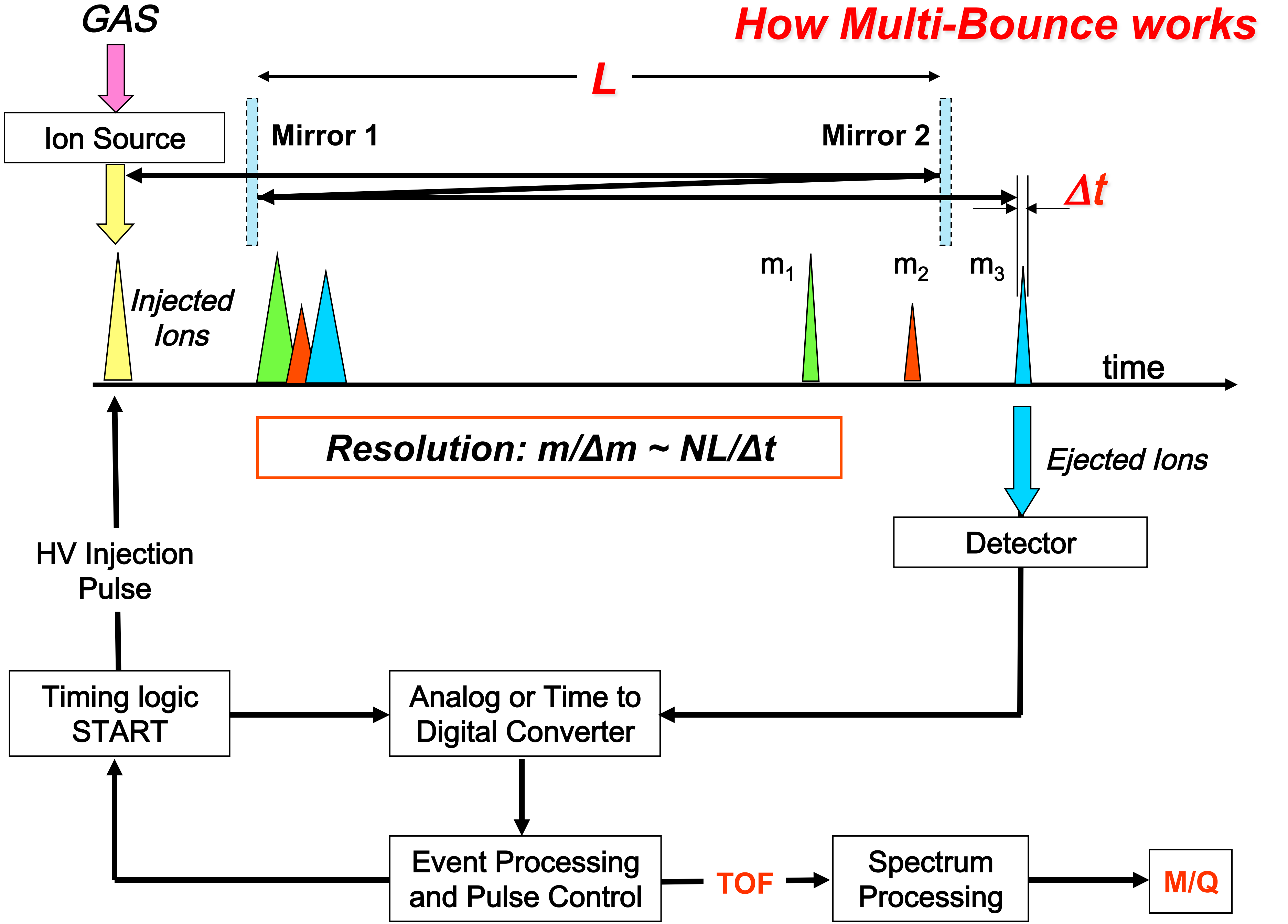
How TOF mass spectrometry works



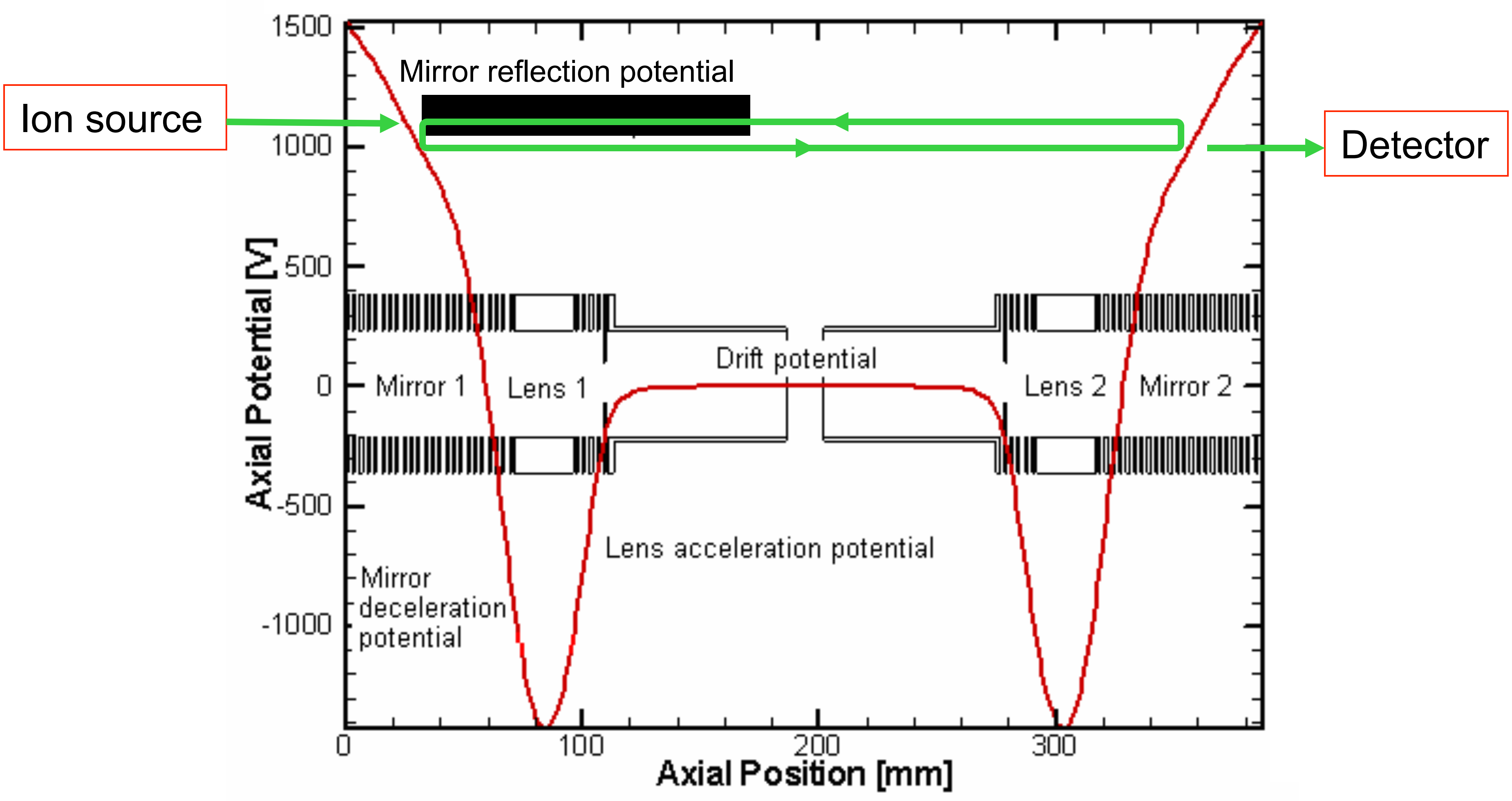
What's better than TOF MS?

- Multi-bounce time-of-flight (MBTOF) mass spectrometry
- MBTOF offers a much longer flight path and therefore higher mass resolution for the same volume of length *L*:
  - $m/\Delta m = t/2\Delta t$
  - $t = D/v$
  - multiple bounces: $D = NL/v$
  - $m/\Delta m = NL/2v\Delta t$
- For resolution to increase with the number of bounces the ions *must* stay time-focused: Δt cannot increase as N increases!

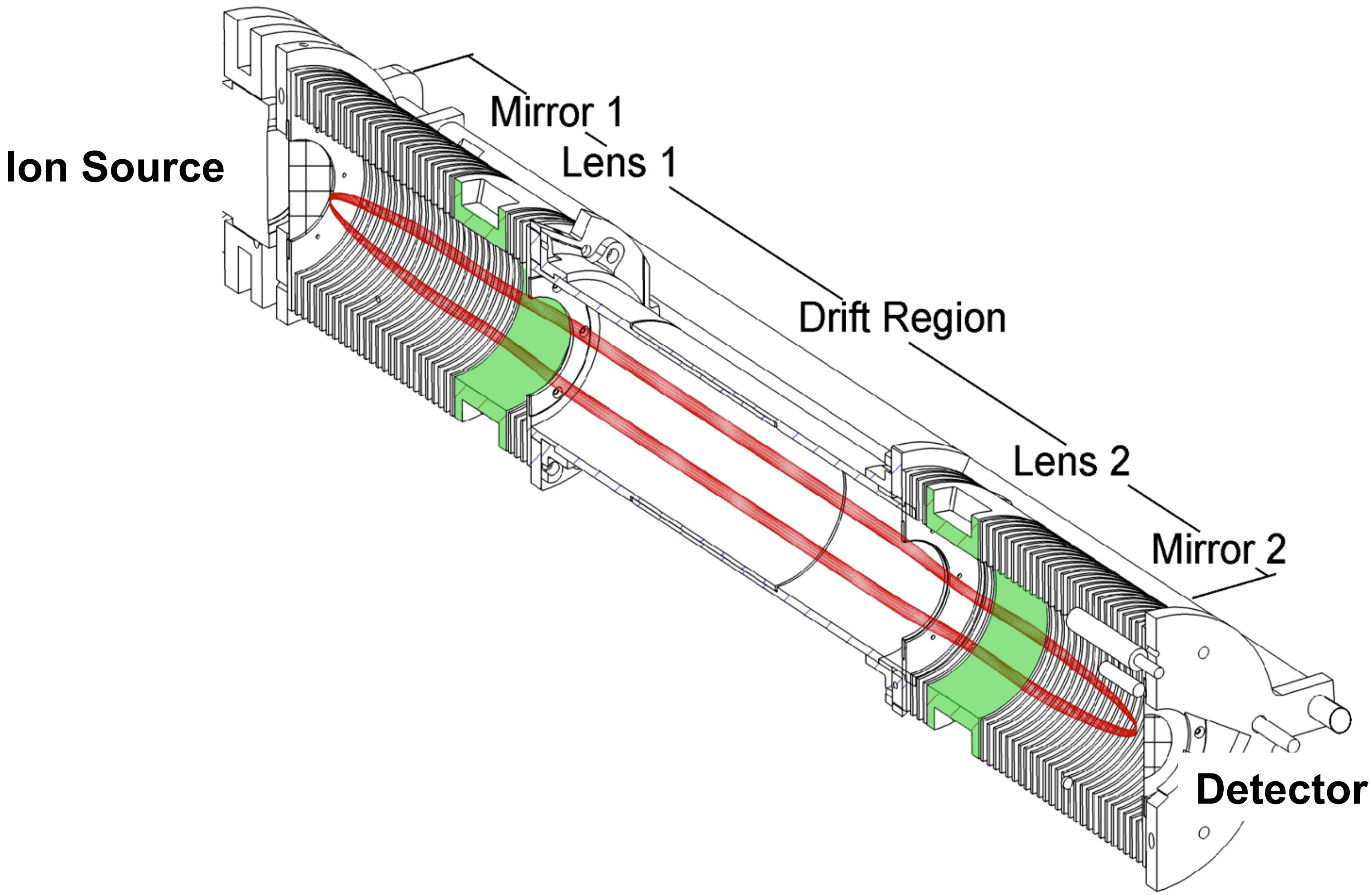
How Multi-Bounce works



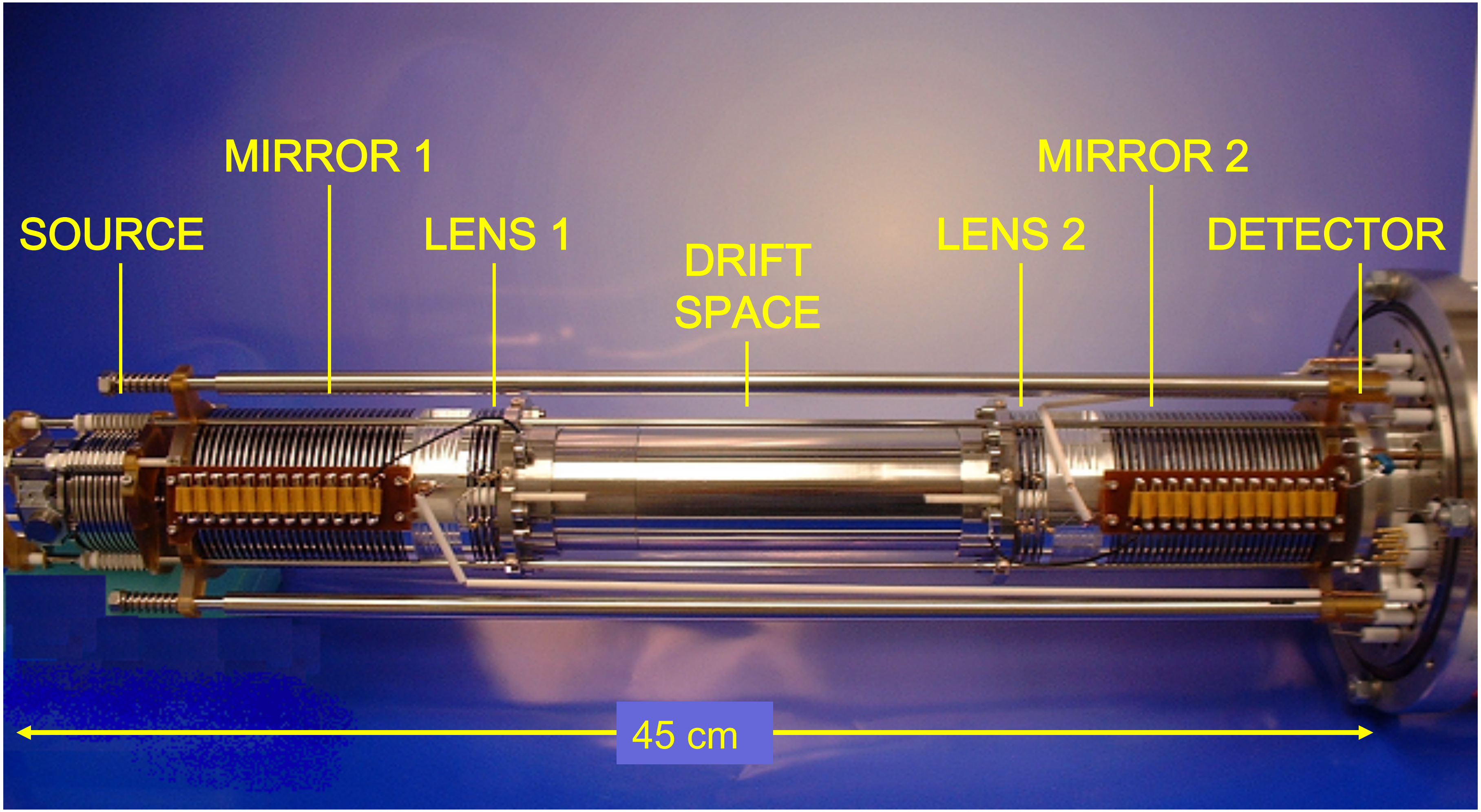
Electric fields *trap and time-focus* ions



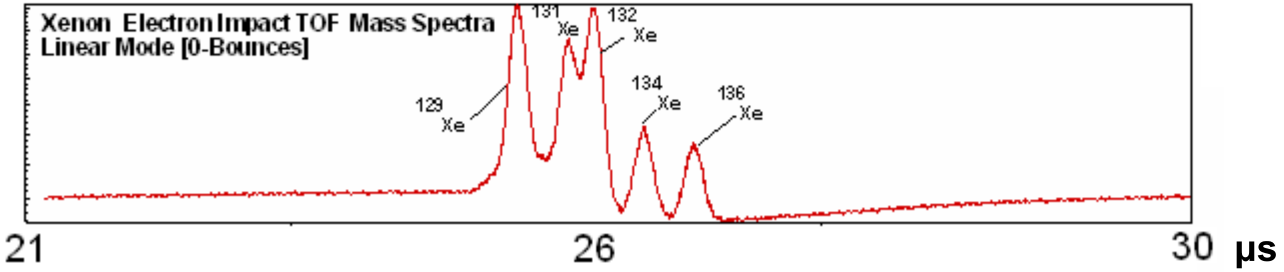
SwRI MBTOF: Ray-tracing



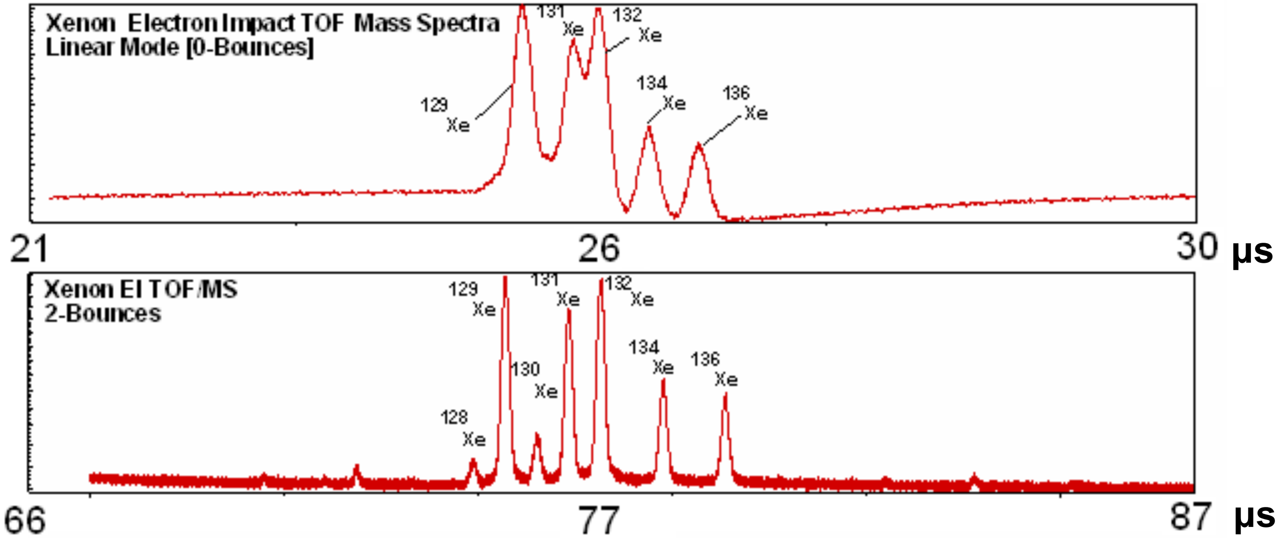
SwRI MBTOF prototype



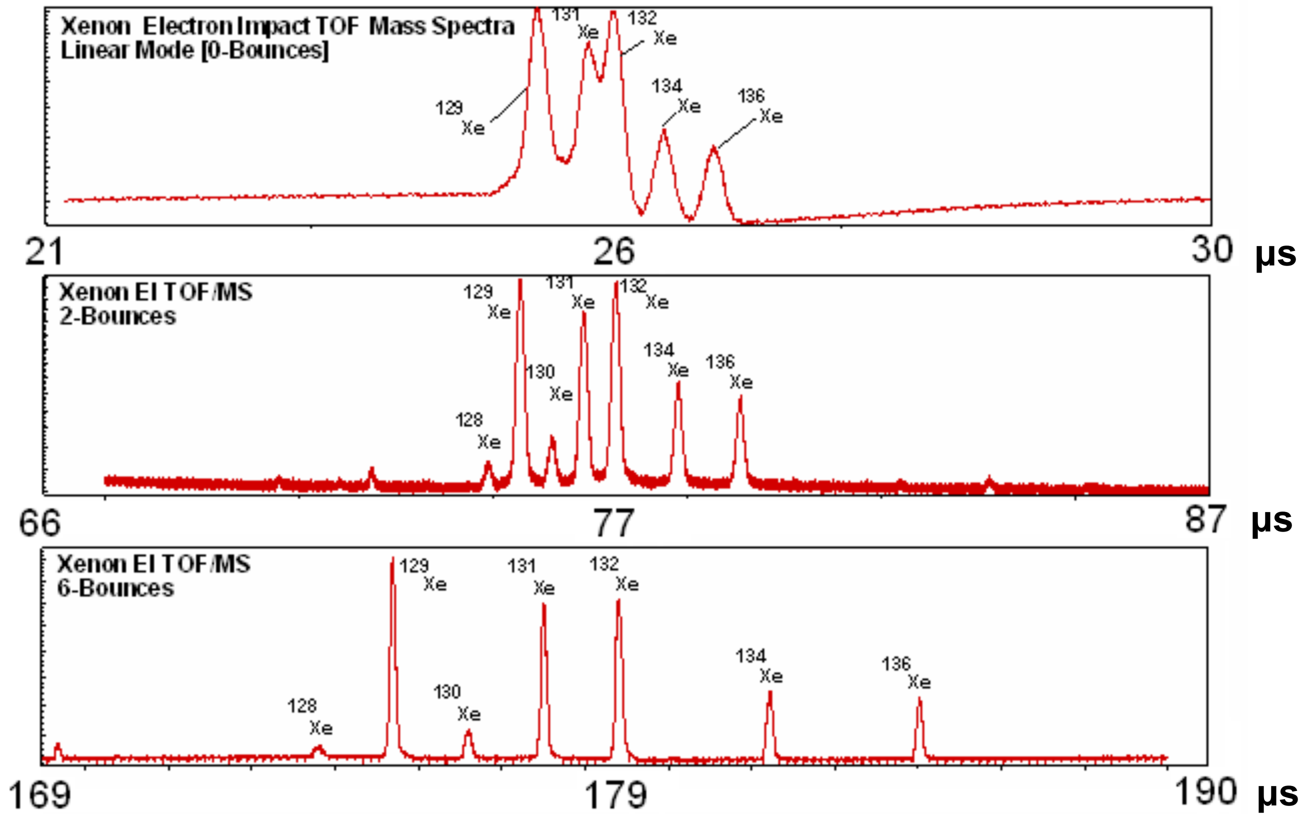
Xe isotopes with 0 bounces



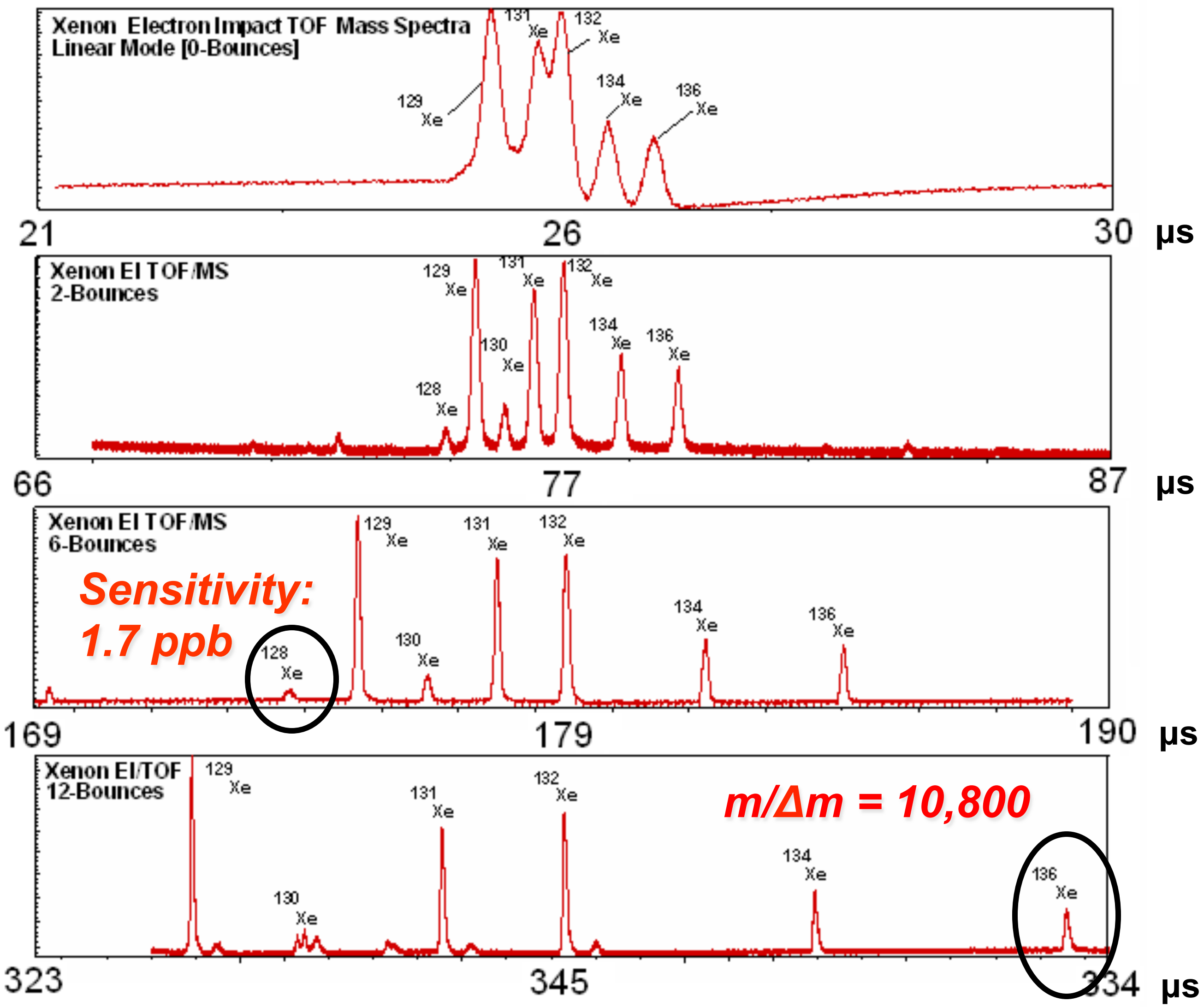
Xe isotopes with 2 bounces



Xe isotopes with 6 bounces

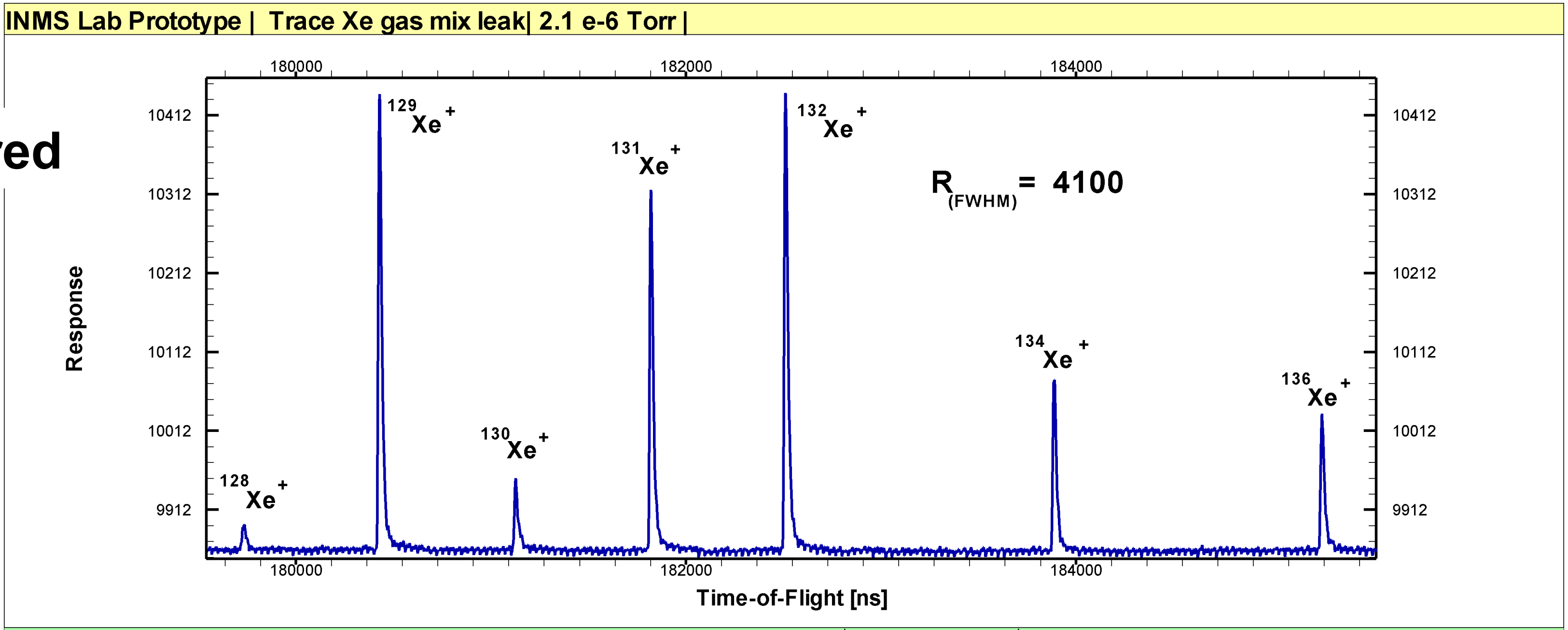


Xe isotopes with 12 bounces

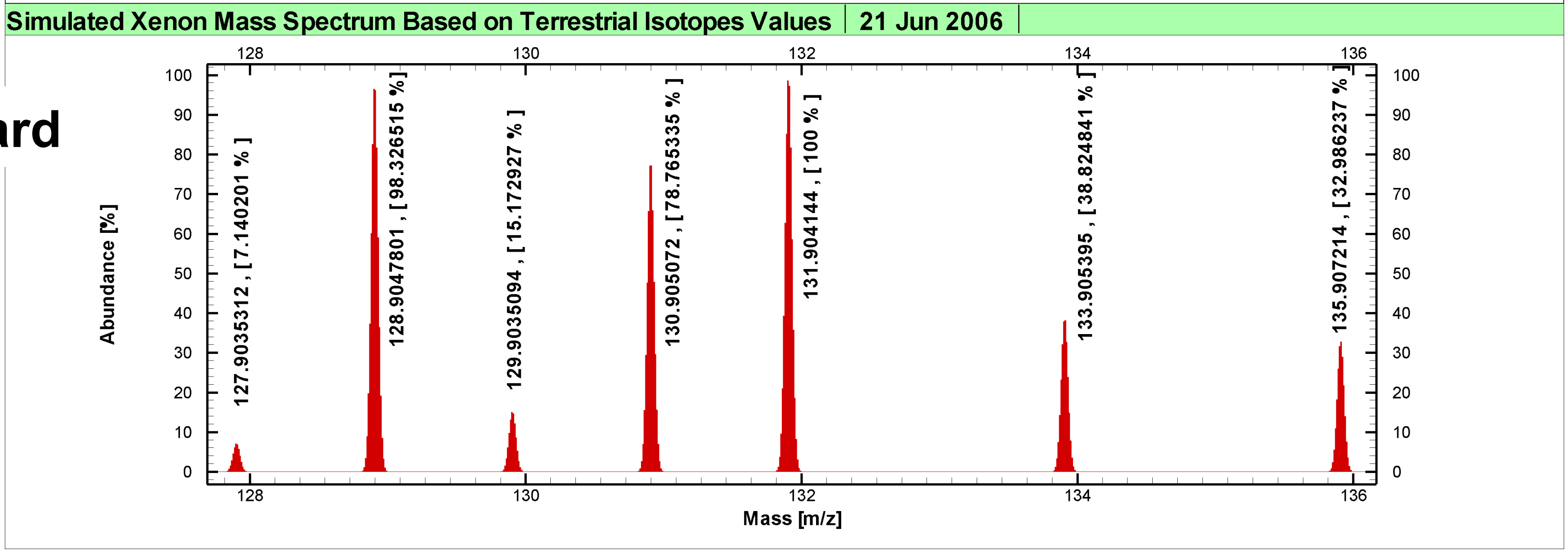


Accuracy: Xe spectrum vs. NIST standard

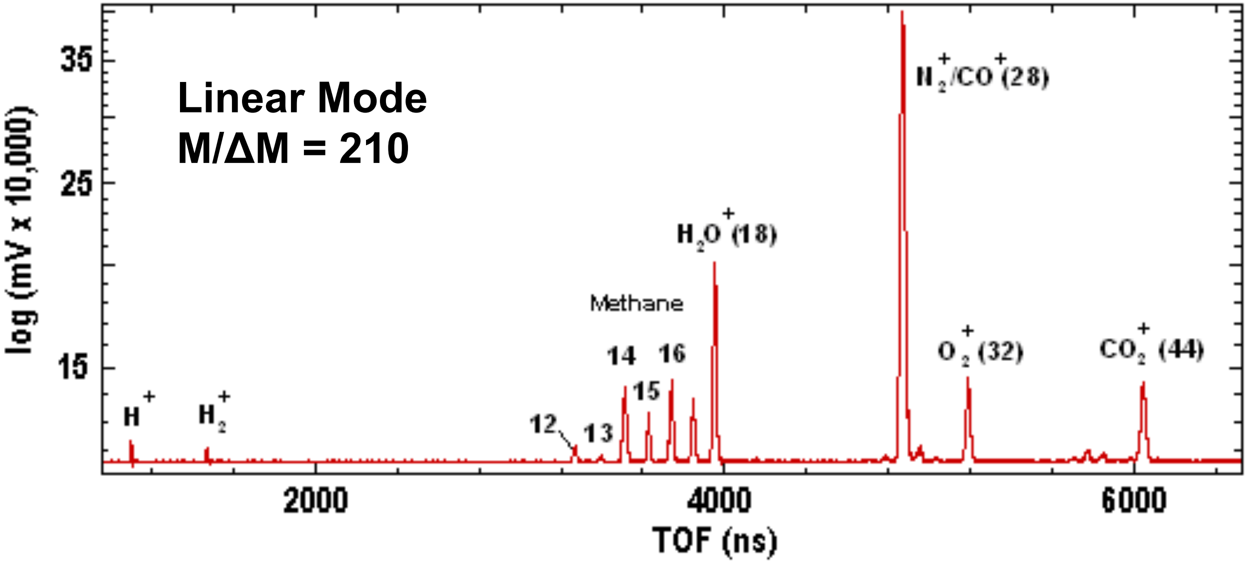
Measured

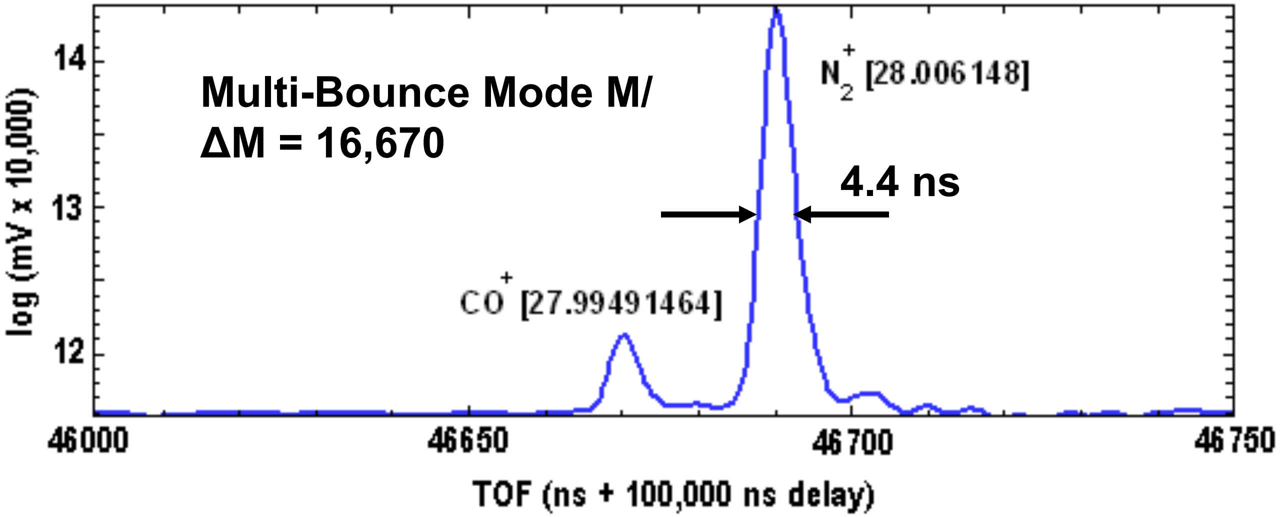


Standard



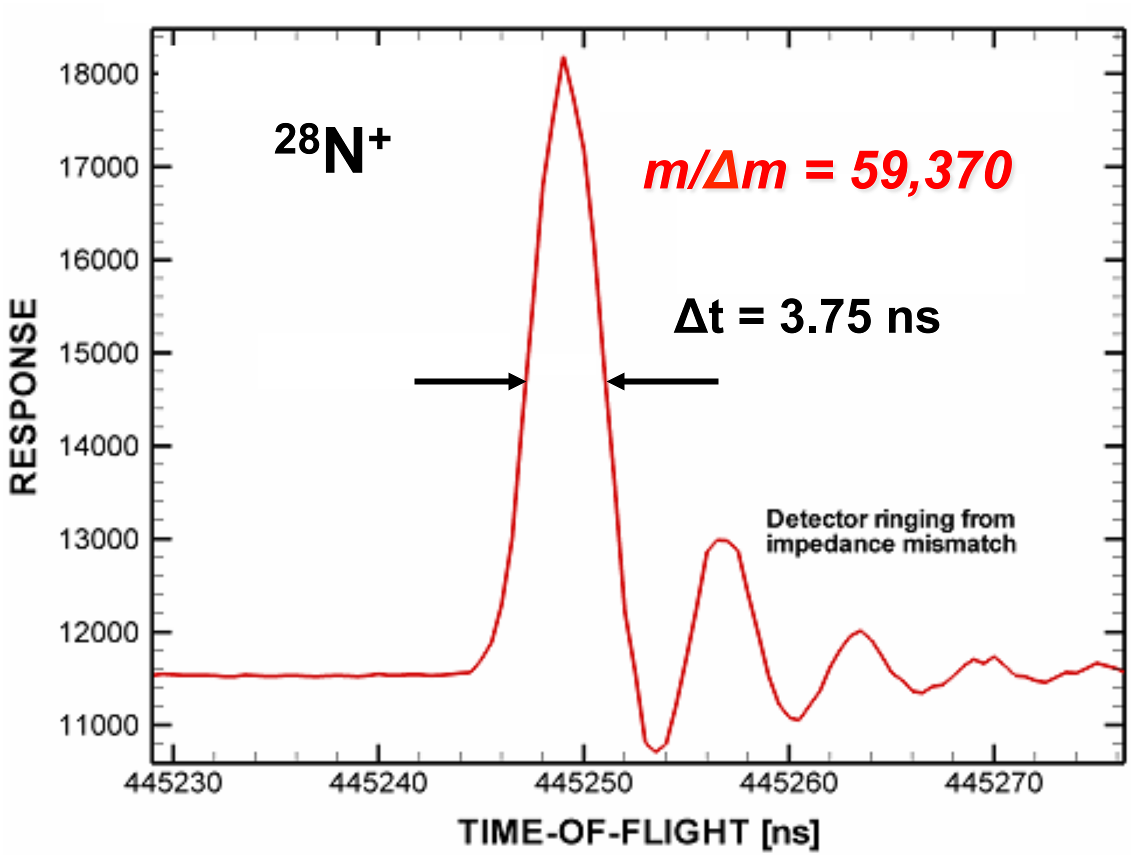
Mars: Separation of CO and N_2





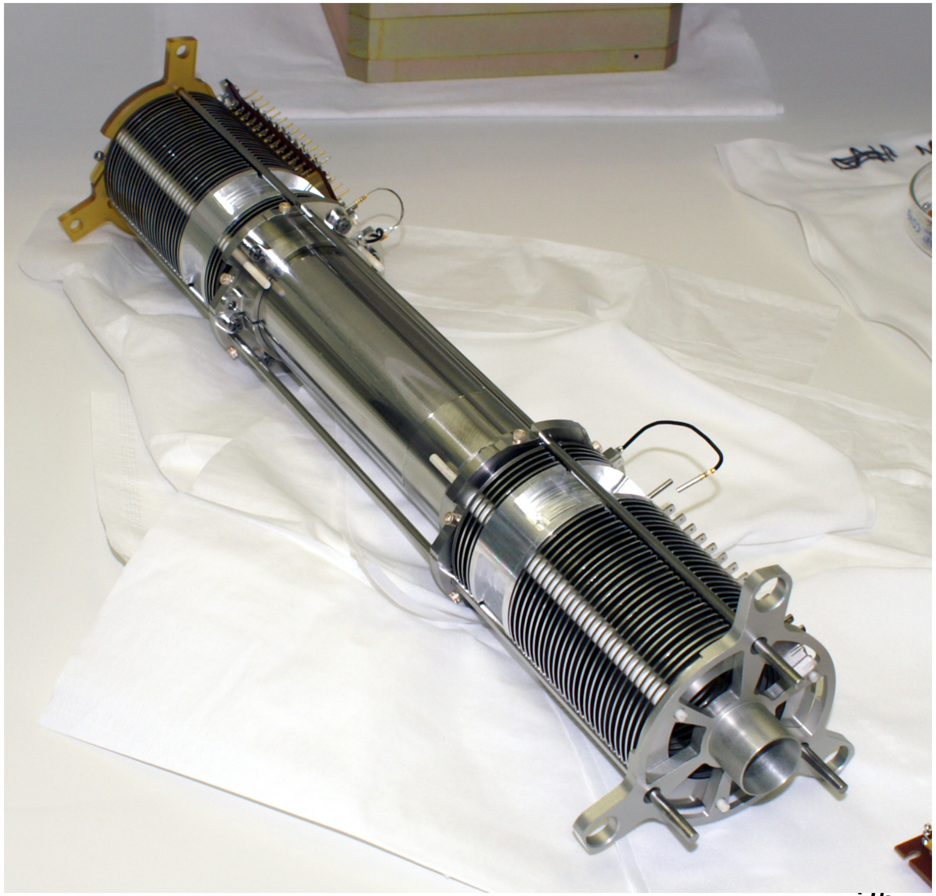
$m/\Delta m$ = 59,370: Phased ejection

- Mirror-2 potential is dropped while ions are still in mirror
  - Ions are refocused in time just before they reach the detector
  - Time resolution is actually higher than HV pulse rise times of ~20 ns



Generation-2 MBTOF Prototype

- MBTOF has been re-built to higher mechanical tolerances
  - Optical planes parallel to 30 μm over 40 cm (1 part in 13,000)
  - Axial alignment to 100 μm over 40 cm
- Tests begin in late July
- Goal is $m/\Delta m = 100{,}000$



Conclusions

- MBTOF-2 is next generation high performance MS
  - Demonstrated *m/Δm ≈ 60,000* => *might resolve* ^{87}*Rb*/^{87}*Sr*
  - Sensitivity *~1 parts per billion* => *martian methane*
  - GC x GC *(=> biomarkers)* and laser ablation *(=> dating)*
- Estimated resources for a full-up MBTOF flight unit
  - Including gas inlet, getters, ion source, high voltages, signal acquisition and processing electronics:
  - *~12 kg & ~35 W*, comparable to Rosetta spectrometers
  - *High performance isn't cheap*
- Methods for lowering resources:
  - Power: fast ADCs; nanotube emitters rather than filaments
  - Mass: monolithic optics; nanotube emitters