MEMS/NEMS Based Mass Spectrometry in Harsh Environment and Deep Space Missions

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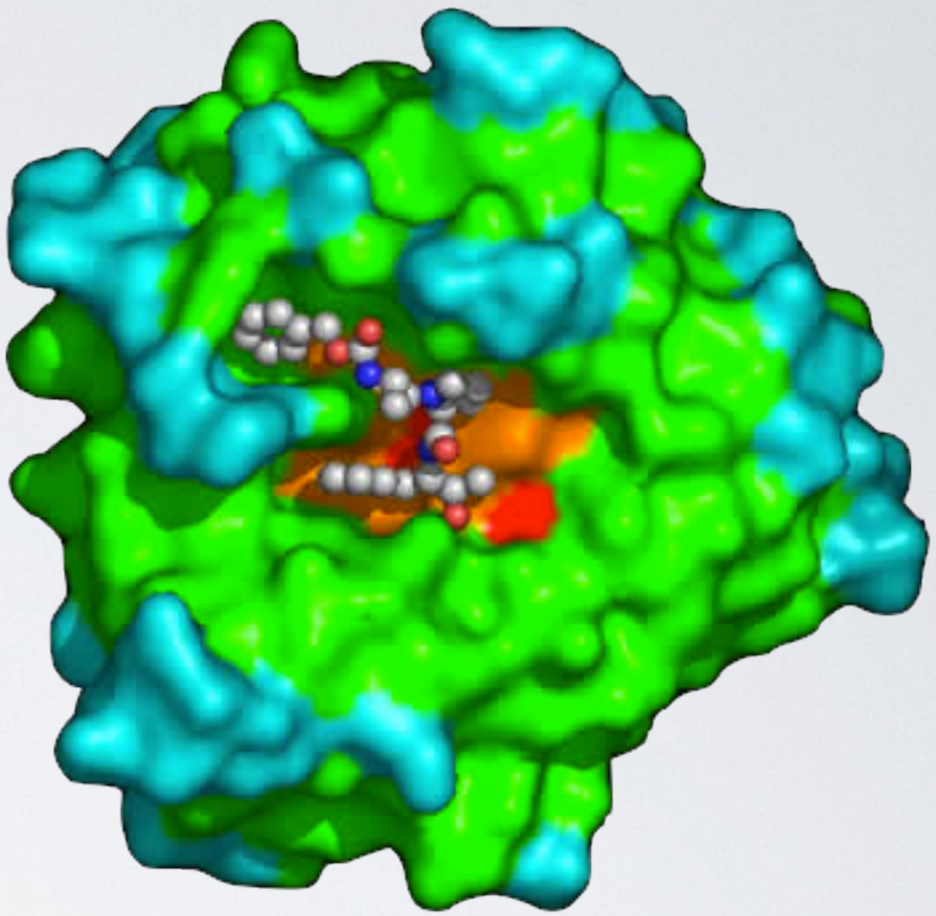
A few note on Mass Spectrometry:

MOTTO:

Structure ⇒ Function

&

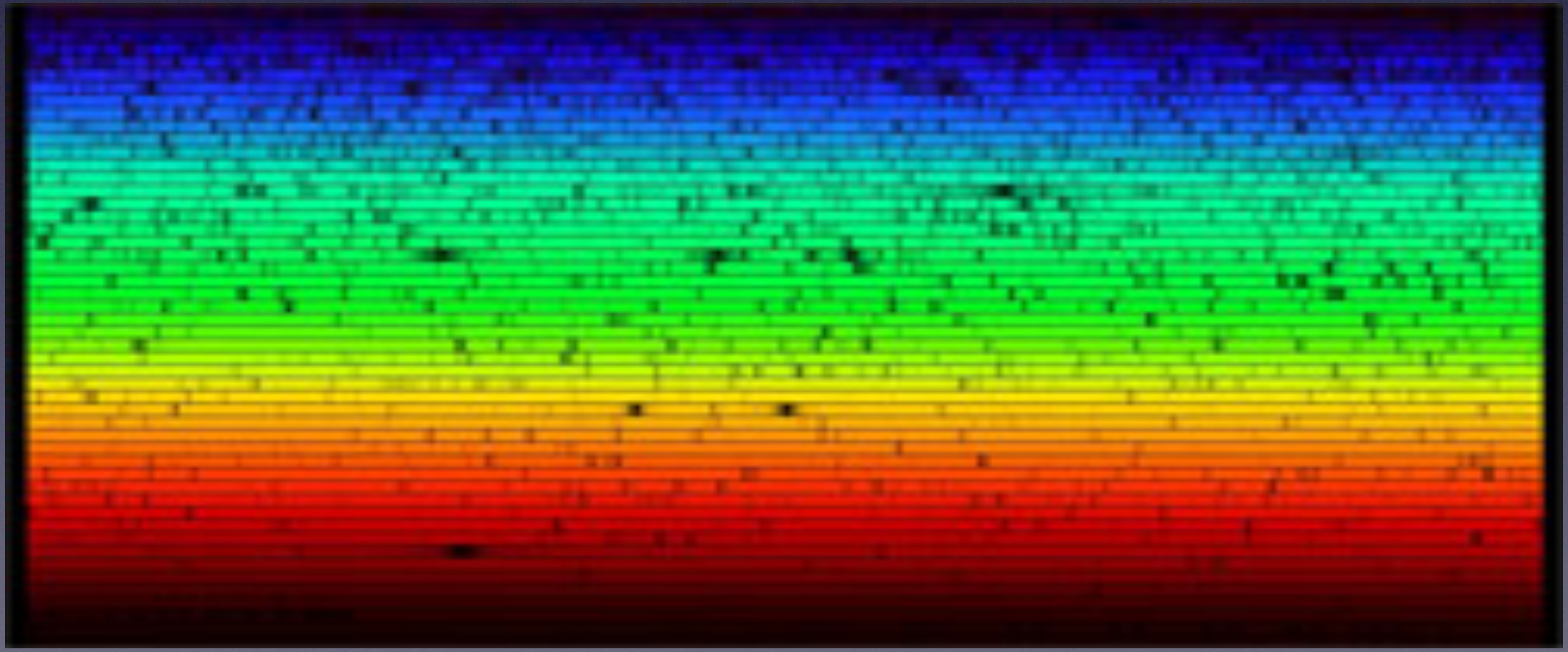
Function ⇒ Structure



Source: http://www.pacificu.edu/as/chemistry/research/index.cfm

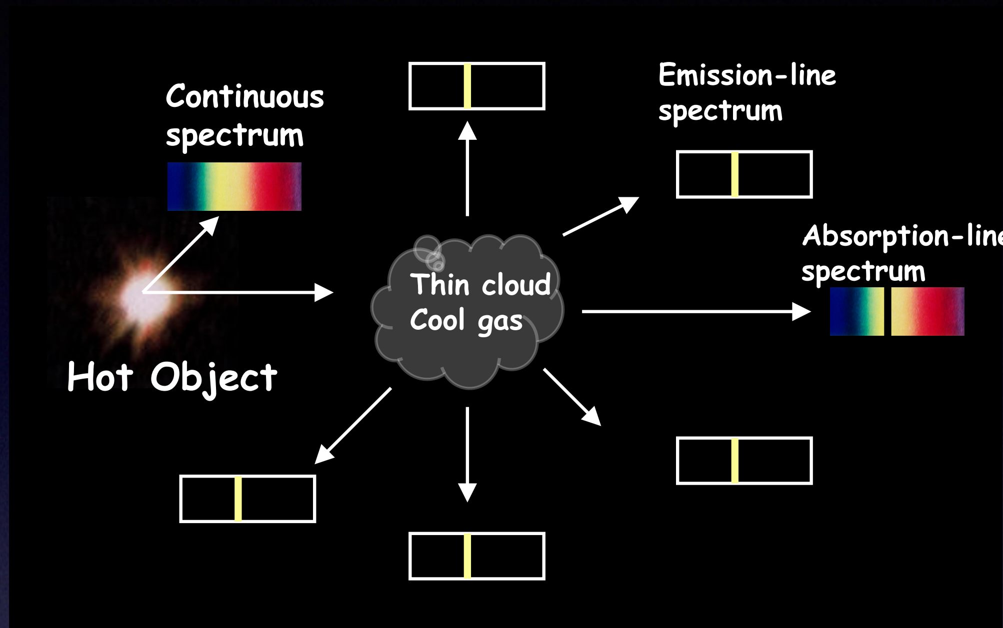
SPECTROSCOPY

Spectroscopy is the study of the interaction between matter and radiated energy.

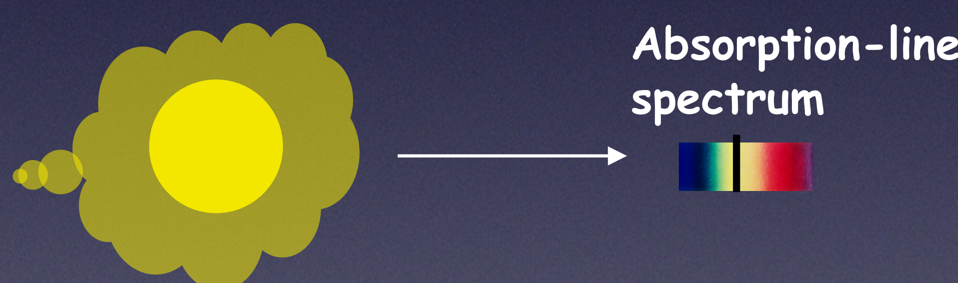


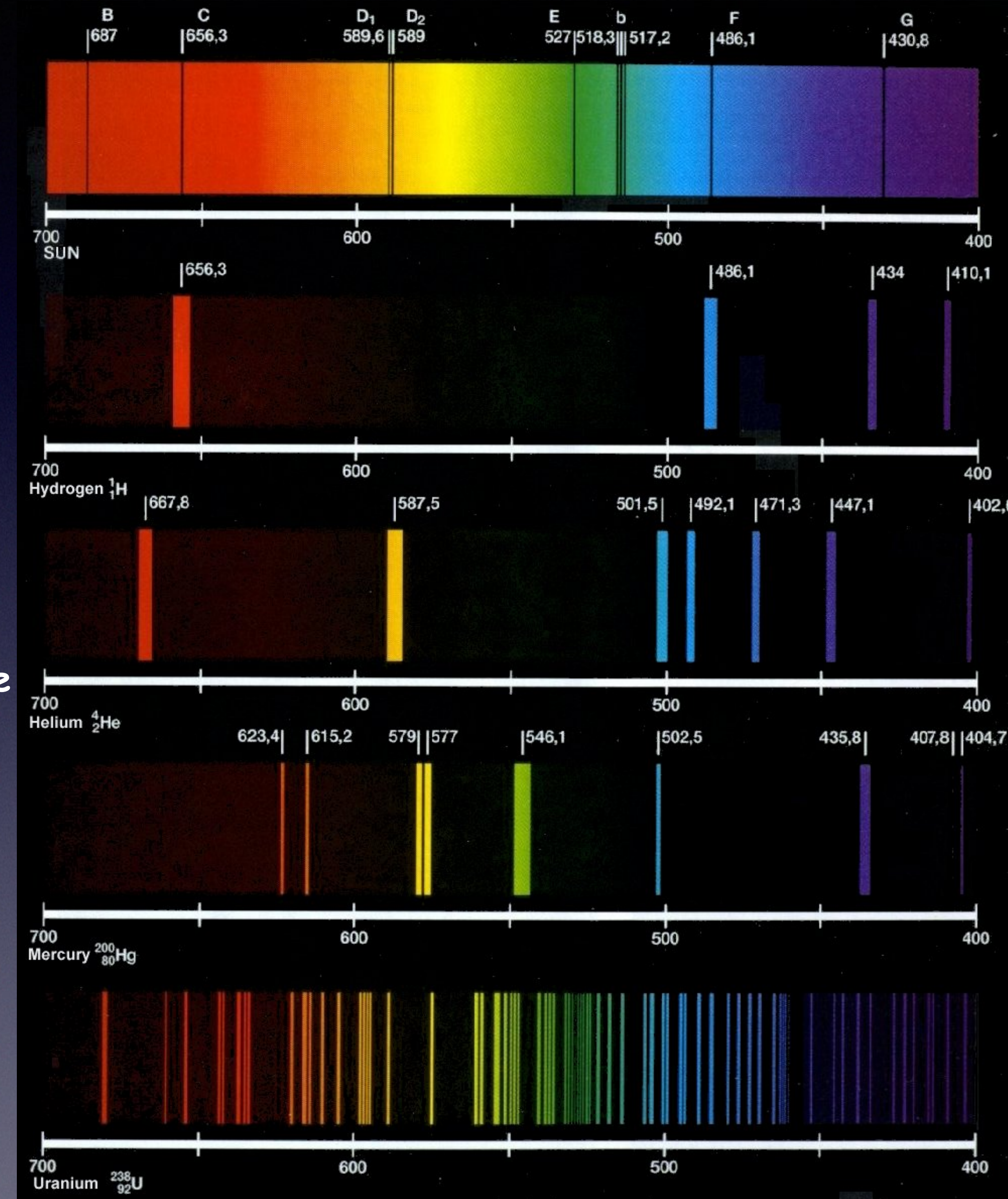
The fingerprint of matter

Putting it Together: Composition of the Stars



Hot Star+cool atmosphere





Two parts to spectrum:
1) the lines 2) continuum
Can have 1,2,2-1, even 2+1

Can read the composition of the stars from absorption spectrum!

Goal number seven of NASA's Astrobiology Roadmap is to "Determine how to recognize the signature of life on other worlds."

Source: http://www.sabinabecker.com/2009/04

Last Image from Titan

No evidence for macroscopic life on Titan's surface except for this one image which is far from certain.

Mass SURFER underwater mass spectrometer system development

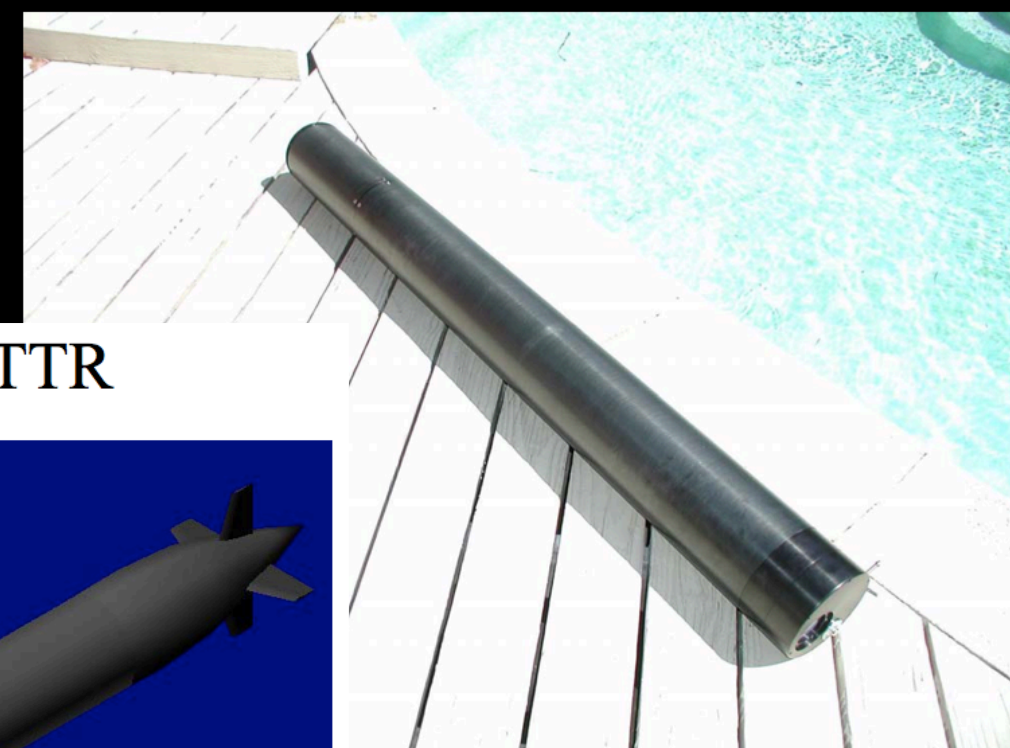
a collaboration project between University of Hawaii and JPL

Project Goals

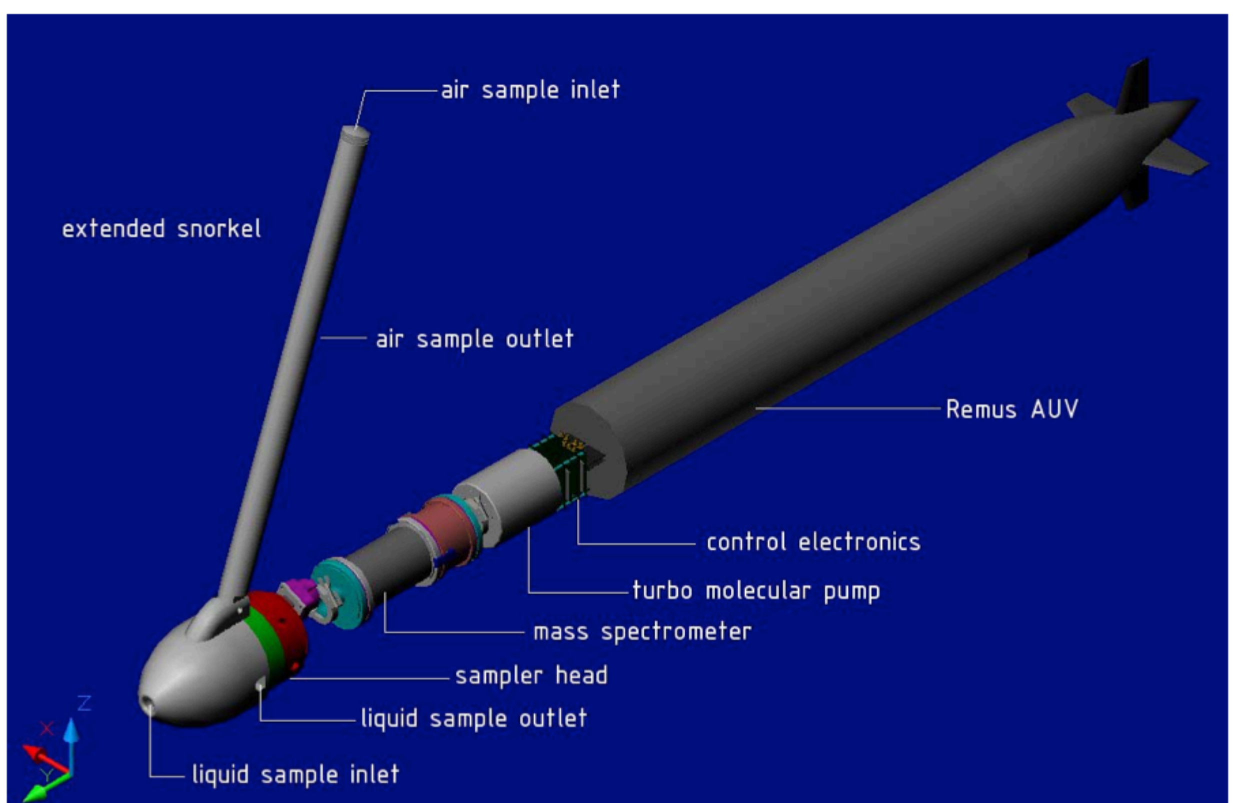
- Develop low-power submarine ms system (<10 watts peak power)
- Attempt direct injection of liquids to include dissolved ions and compounds as well as dissolved gases and volatile compounds (via MEMS)
- Design ms system to go as deep as possible, with full ocean depth as goal
- Explore use of capillary electrophoresis (CE) to separate large organics, etc.

Mass SURFER Prototype

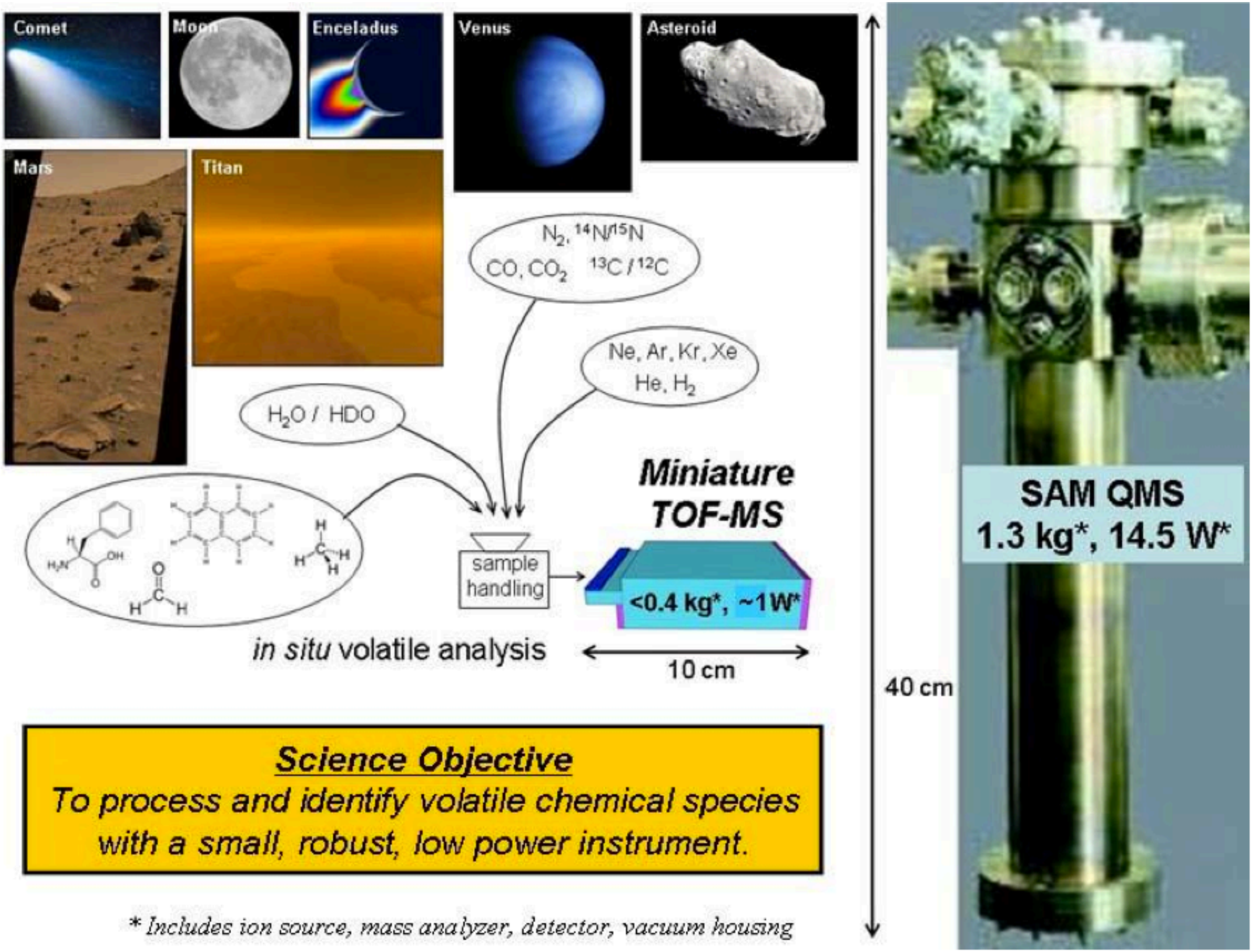
(Mass Spectrometer Using Rotating Fields for Exploratory Ranging)



Schematic of US Navy STTR



Note: All pictures here are from above source.



Comet
Moon
Enceladus
Venus
Asteroid
Mars
Titan
N2, 14N/15N
CO, CO2 13C/12C
Ne, Ar, Kr, Xe
He, H2
H2O / HDO
sample handling
Miniature TOF-MS
<0.4 kg*, ~1W*
in situ volatile analysis
10 cm
40 cm
SAM QMS
1.3 kg*, 14.5 W*
Science Objective
To process and identify volatile chemical species with a small, robust, low power instrument.
* Includes ion source, mass analyzer, detector, vacuum housing

Mars

Goals: Understand Mars' history; figure out how similar Mars was to Earth and how it diverged; locate water, organics, other chemicals, resources; find life (or lack)

Conditions: Atmosphere ~ 7 Torr CO_2 and cold!

- Mars Exploration Rovers (MER) - operating
- Phoenix Mars Scout (2007)
- Mars Science Laboratory (2009)
- ExoMars
- Astrobiology Field Laboratory
- Mars Sample Return

Asteroids

Goals: Relate asteroids to solar and planetary compositions to understand solar system formation; link meteorite and asteroid classes; search for organics, water, metals; determine internal structure

Conditions: Hard space vacuum; thermal gradients

- NEAR (Eros)
- Hayabusa (Itokawa)
- Dawn (Vesta and Ceres)
- Future landers / sample returns

Comets

Goals: Relate comets to asteroids and KBOs; determine if comets supplied water and pre-biotic organics to Earth; inventory cometary chemical and organic composition; determine internal structure, dynamics

Conditions: Hard vacuum; thermal gradients; vents (!)

- Giotto; Vega1, 2; Sakigake; Suisei (Halley)
- DS-1 (Borelly)
- Stardust (Wild 2)
- Deep Impact (Tempel 1)
- Rosetta (Churyumov-Gerasimenko)
- Future landers / rendezvous / CSSR / CNSR

Outer Planetary Satellites

Europa

- Ocean?
- Life?
- Ice chemistry is key goal
- Surface vs subsurface
- Radiation
- Fissure upwellings
- Lander w/drill
- Hard mission!

Titan

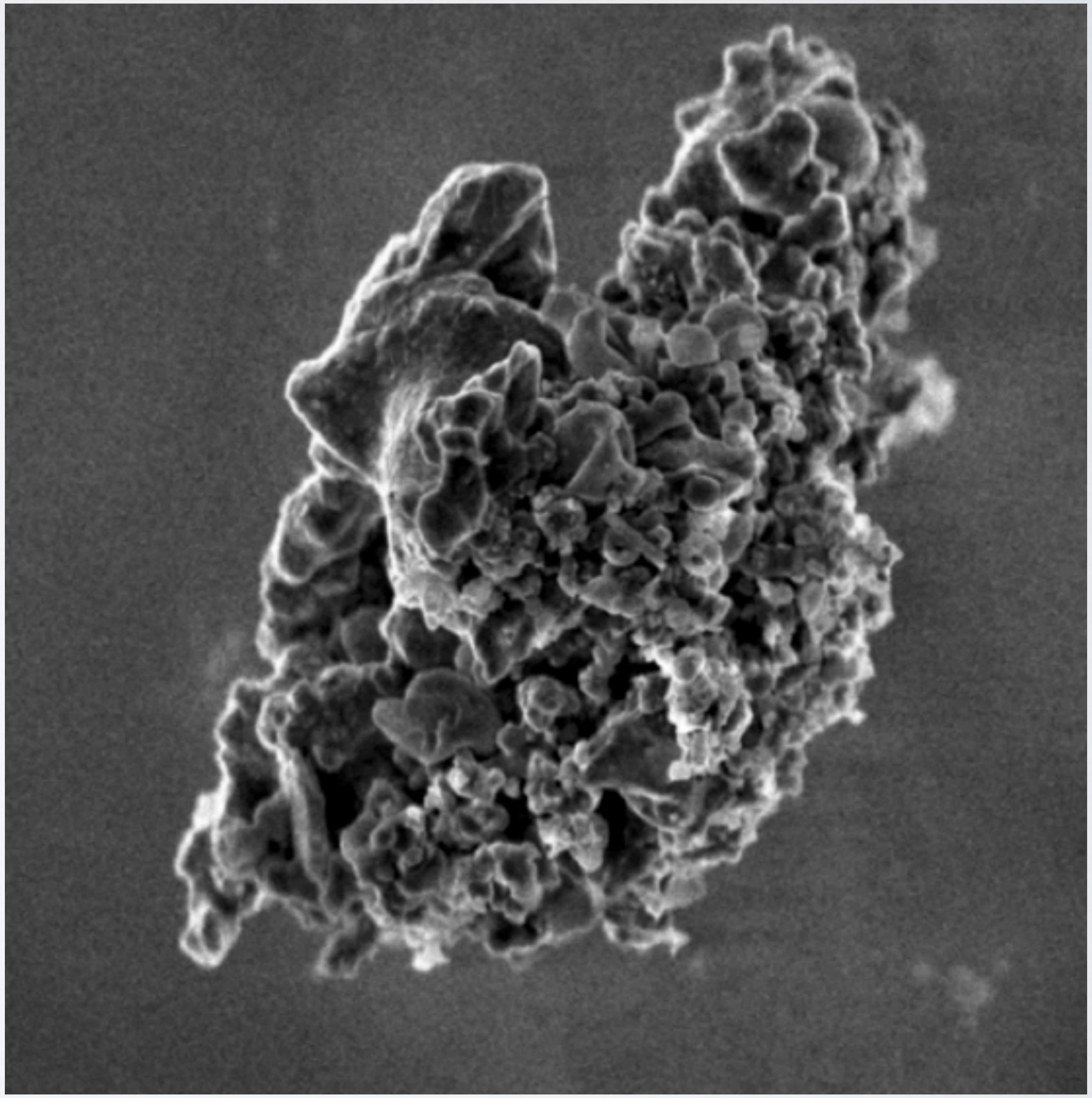
- Seas!
- “Pre-biotic” chemistry
- Atmospheric density is high
- Long-term goal: A mobile lander (or aerobot/lander) equipped with a mass spec!
- Expensive but not so difficult to do.

In Situ Astrobiology at Comets

"Extreme Close-Up" of a comet nucleus?

Cosmic Dust Particle Project at Caltech

Novel Mass Spectrometric Approaches to the *in situ* Chemical Analysis of Galactic and Cometary Dust Particles



Source:http://www.cosmotography.com/images/cosmic_nurseries.html

What is Cosmic Dust?

- Interplanetary dust: microparticle debris from comets, asteroids, etc.
- Interstellar dust: particles originating outside the solar system
- Man-made particulate debris near Earth

http://www.cosmotography.com/images/cosmic_nurseries.html

What can Cosmic Dust tell us?

- Small chemical sample from a distant object
- Elemental and isotopic distribution and fractionation in astronomical processes
- Nucleosynthesis, formation and evolution of planets and stars

Methods for Studying Cosmic Dust

Remote Sensing

- radar, zodiacal light, thermal emissions
- dynamics and distributions

Collection from atmosphere and surface of Earth

- composition and structure
- particles altered by atmosphere

In situ analysis

- study properties of individual dust grains
- limited by weight, power, automation

Sample capture and return

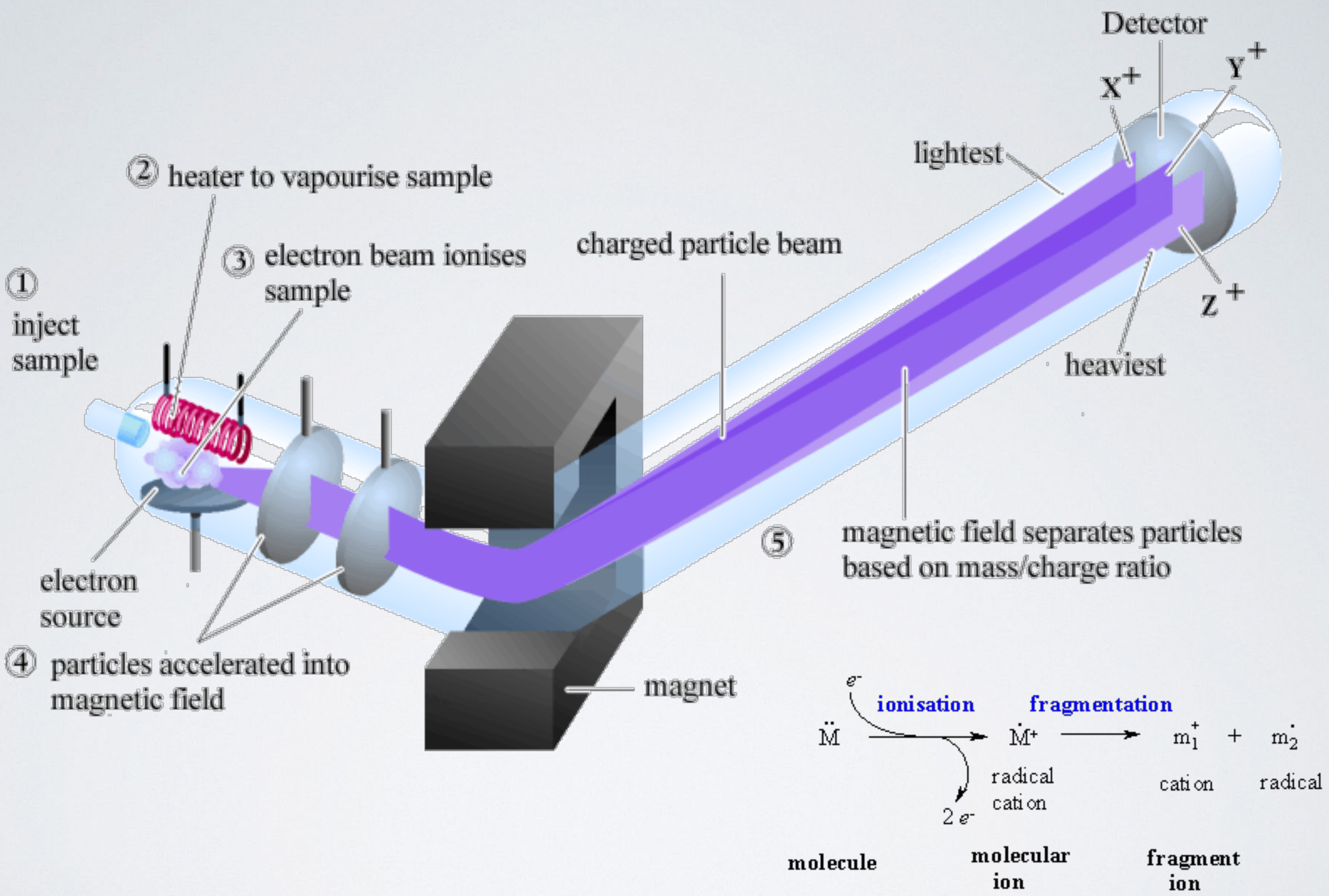
- study properties of individual grains
- capture is difficult, return takes many years

Previous *in situ* Dust Analyzers

Missions with impact-ionization dust analyzers

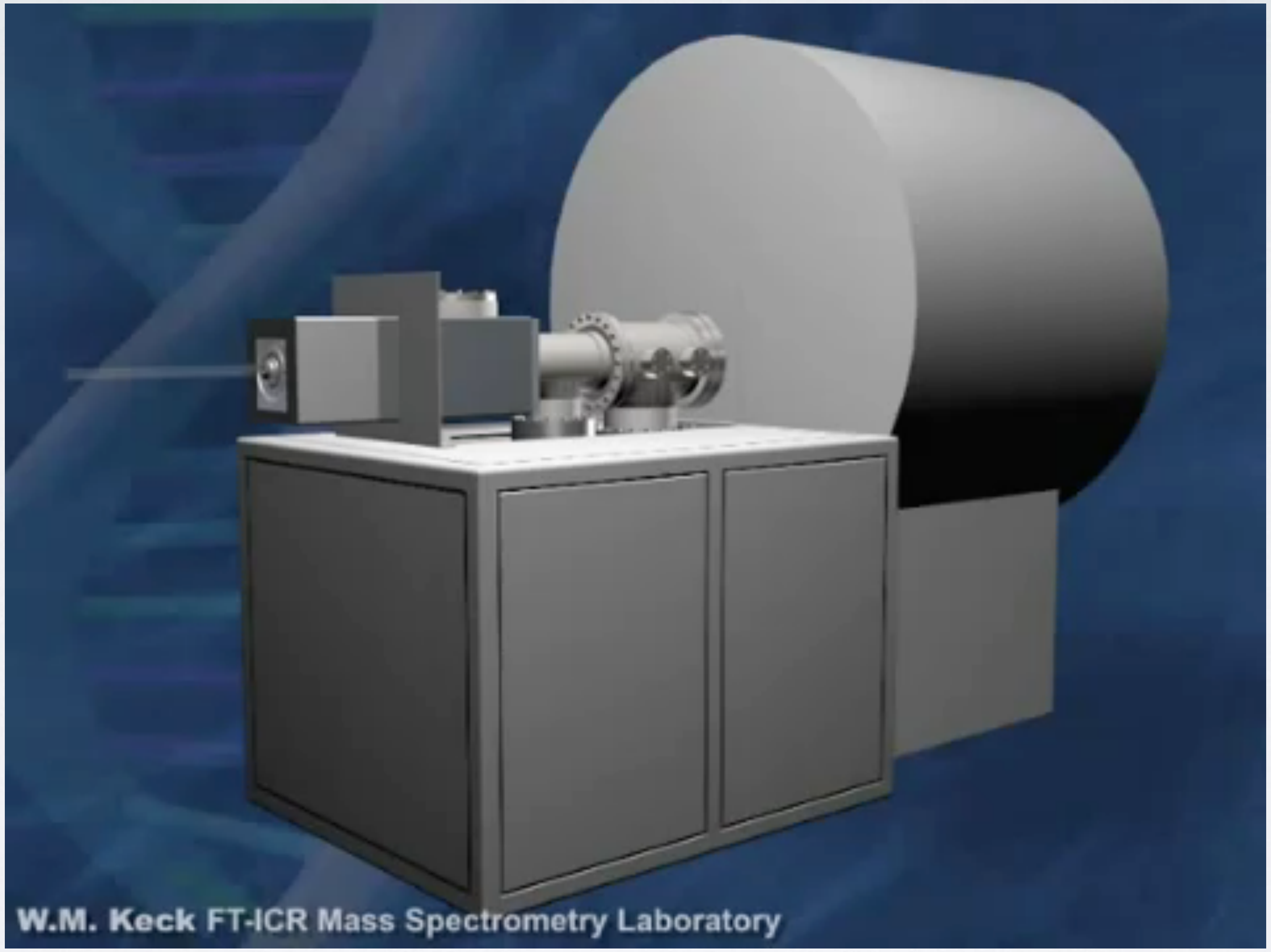
Mission	Launch	Object	Velocity, km/s
Vega 1, 2	1984	Halley	79
Giotto	1985	Halley	69
Galileo	1989	IP/IS dust	2-70
Ulysses	1990	IP/IS dust	2-70
Cassini	1997	IP/IS dust	1-70
		Saturn (2004)	
Stardust	1999	Wild 2 (2004)	6
		IP/IS dust	20-50
Contour	2002	Encke (2003)	28
		SW (2006)	14
		d'Arrest (2008)	12

From Hornung, K.; Malama, Yu. G.; Kestenboim, K.S. *Astrophys. Space Sci.* **2000**, *274*, 355-363.



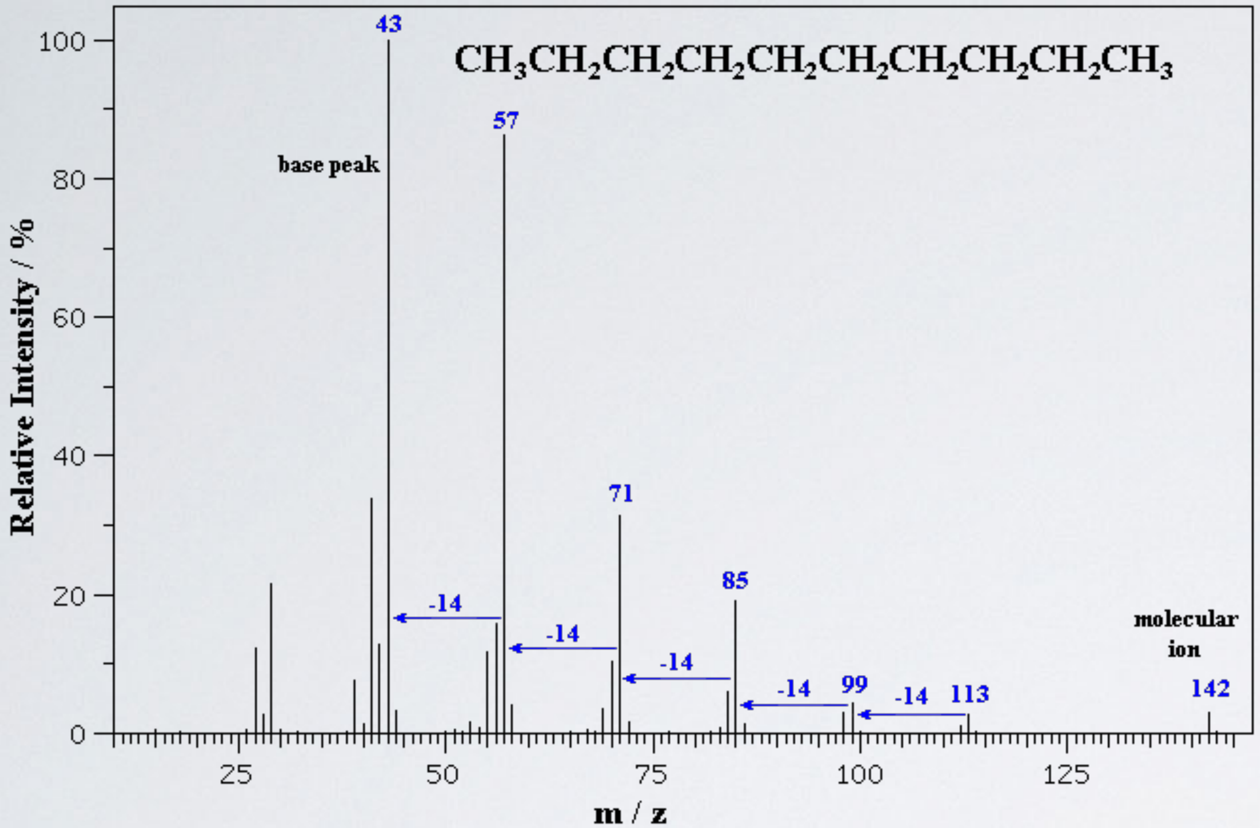
Source: http://www.mhhe.com/physsci/chemistry/carey/student/olc/ch13ms.html

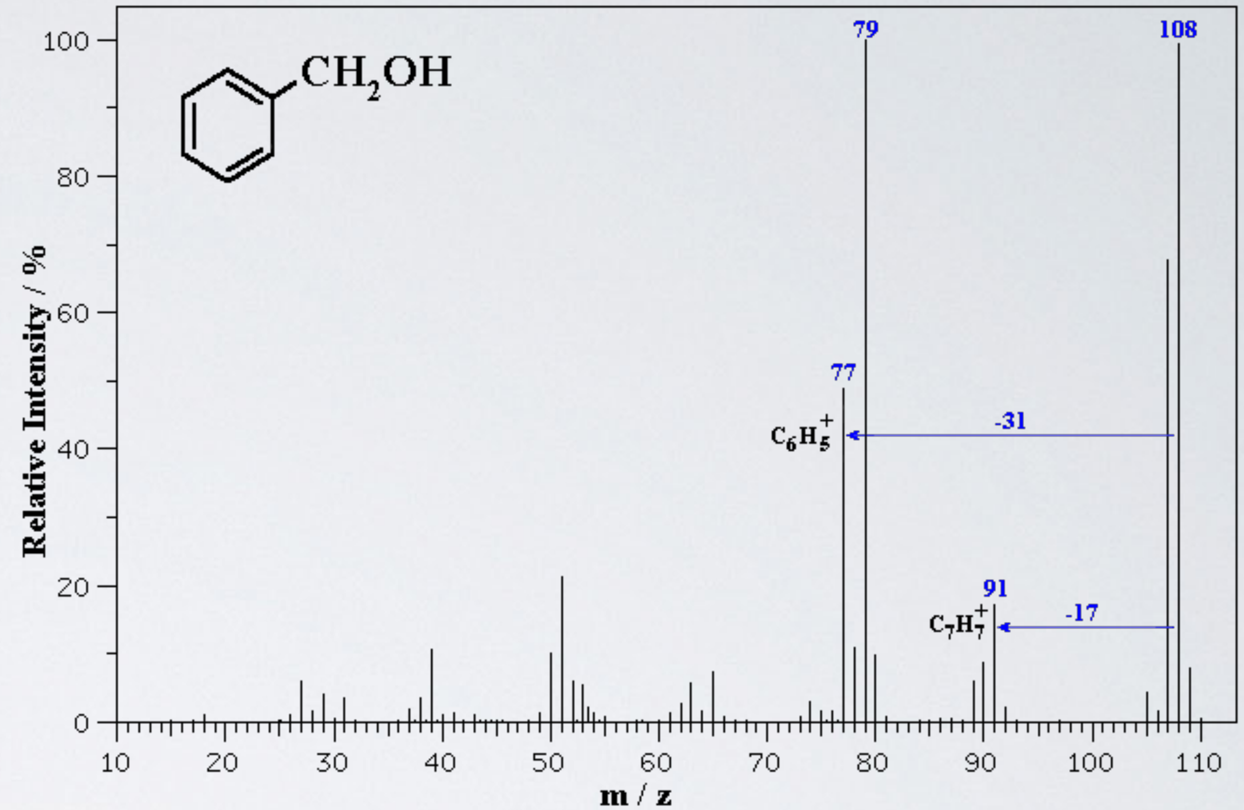
An Animation on How Mass Spectrometry Works!

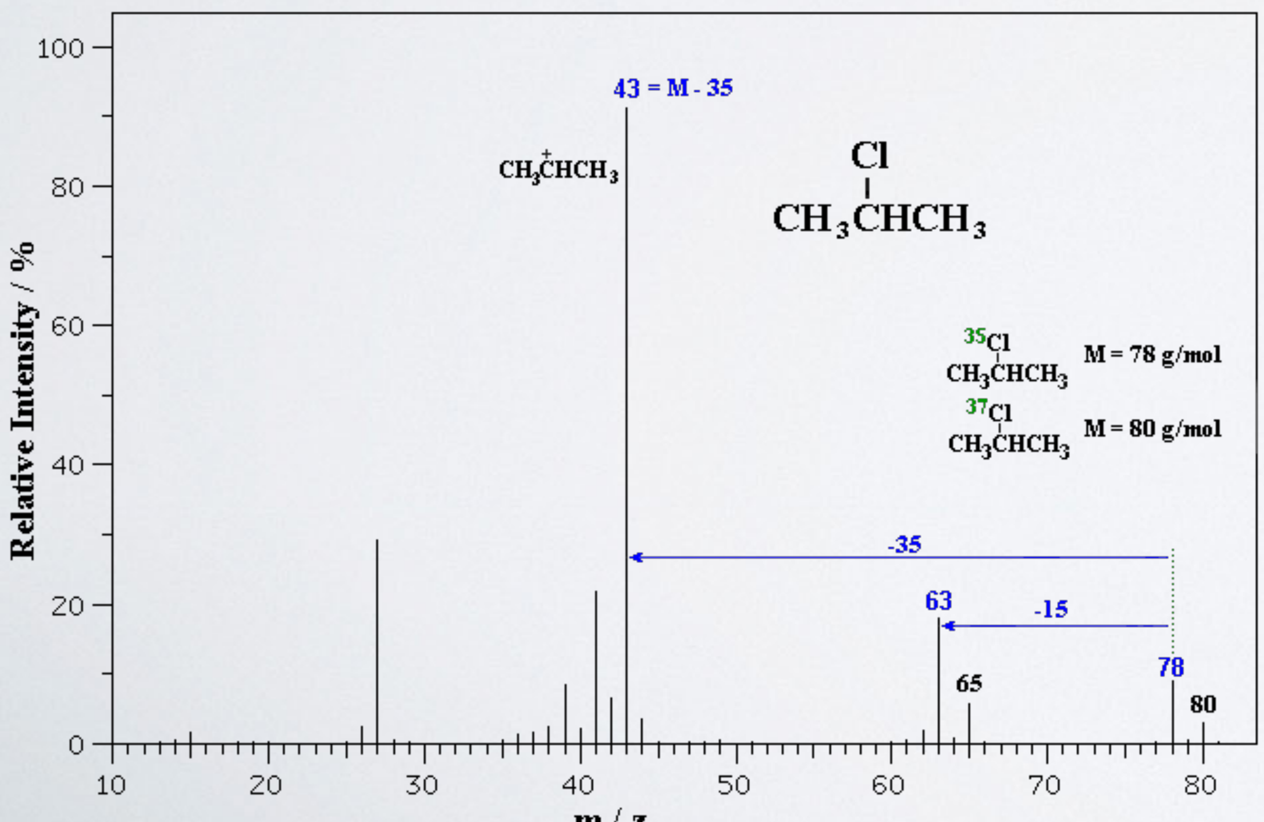


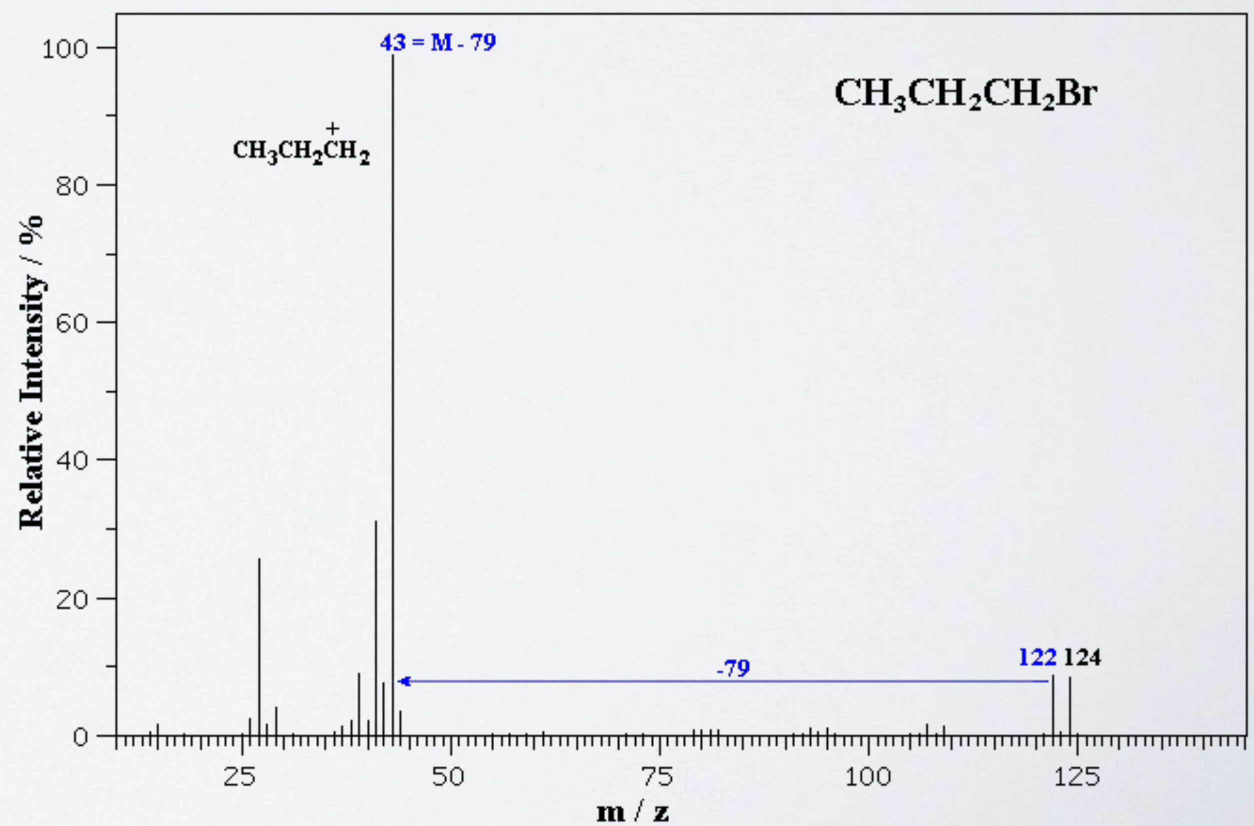
Source: http://www.youtube.com/watch?v=a5aLlm9q-Xc&feature=player_detailpage

Some Examples:









Source: http://www.mhhe.com/physsci/chemistry/carey/student/olc/ch13ms.html

Some of Reviewed Papers:

[1] E.R. Badman, R.G. Cooks, J. Mass Spectrom. 35 (2000) 659.
[2] M.J. Madsen, W.K. Hensinger, D. Stick, J.A. Rabchuk, C. Monroe, Appl. Phys. B (2004).
[3] H. Peddanenikalava, K. Potluri, S. Bhansali, R.T. Short, D. Fries, A micro-fabrication strategy for cylindrical ion trap mass spectrometer arrays, in:Proceedings of IEEE Sensors, Orlando, FL, IEEE, 2002.
[4] J. Maxam, P.T.A. Reilly, W.B. Whitten, J.M. Ramsey, Rapid Commun. Mass Spectrom. 18 (2004) 721.
[5] S. Pau, C.S. Pai, Y.L. Low, J. Moxom, P.T.A. Reilly, W.B. Whitten, J.M. Ramsey, Phys. Rev. Lett. 96 (2006) 120801.
[6] M.G. Blain, L.S. Riter, D. Cruz, D.E. Austin, G. Wu, W.R. Plass, R.G. Cooks, Int. J. Mass Spectrom. 236 (2004) 91.
[7] S. Boumsellek, R.J. Ferran, Am. Soc. Mass Spectrom. 12 (2001) 633.
[8] S. Taylor, R.F. Tindall, R.R.A. Syms, J. Vacuum Sci. Technol. B 19 (2) (2001) 557.
[9] M. Geear, R.R.A. Syms, S. Wright, A.S. Holmes, J. Microelectromech. Syst. 14 (5) (2005) 1156.
[10] H.J. Yoon, J.H. Kim, E.S. Choi, S.S. Yang, K.W. Jung, Sens. Actuators A 97–98 (2002) 441.
[11] N. Sillon, R. Baptist, Sens. Actuators B 83 (2002) 129.

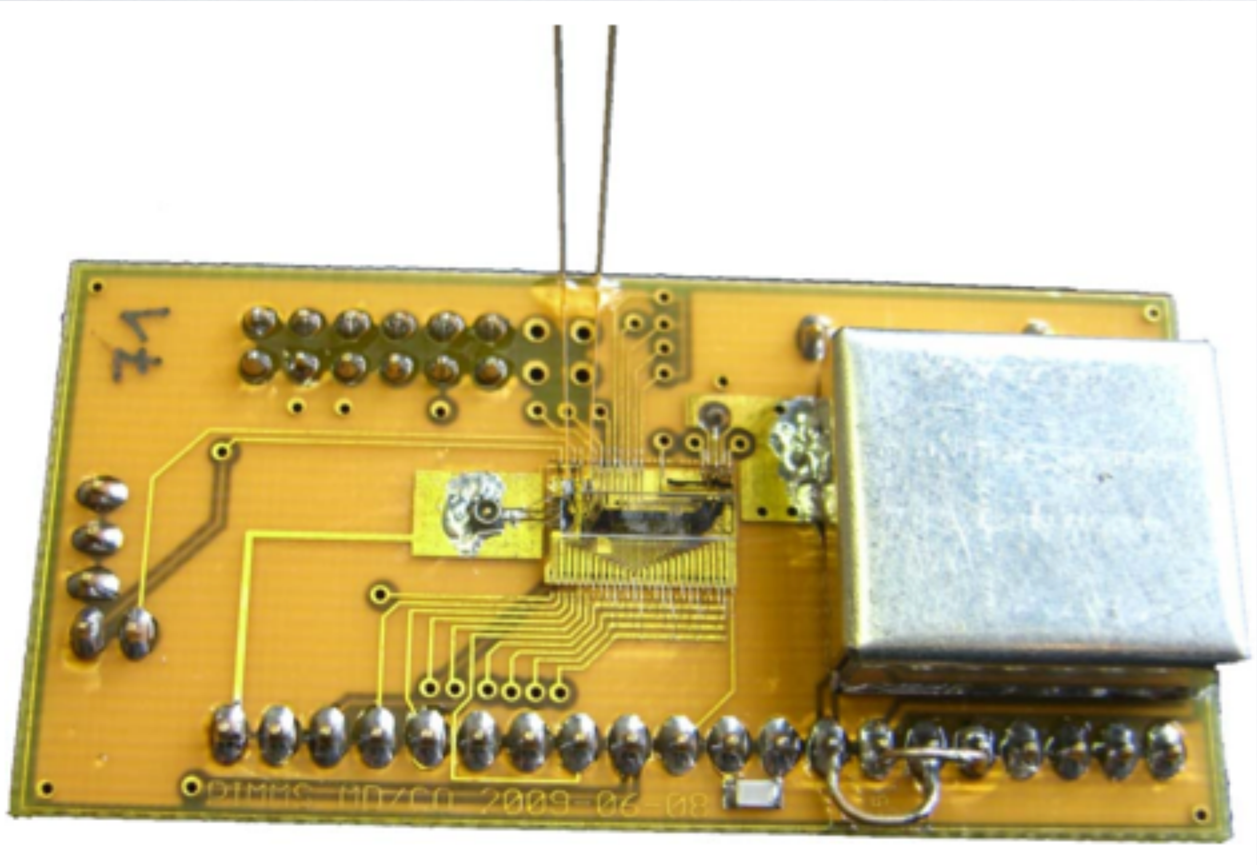
[1] The miniaturization of different types of mass separators in micro-electro-mechanical systems (MEMS) technology is reported.
[2] An approach to match the field requirements of an ion trap with the restrictions in MEMS technology is reported.
[3-6] Cylindrical ion traps (CIT) have been fabricated in arrays to use the advantages of miniaturization (e.g., reduced cost, low operating voltage), while keeping the sensitivity at a moderate level.
[7] Arrays of quadrupole mass separators have been investigated for increased performance.
[8,9] The difficulty of fabricating a perfectly aligned linear quadrupole in MEMS technology has been solved.
[10] A time-of-flight (TOF) mass spectrometer fabricated by electroplated nickel structures on silicon is presented.
[11] A Wien filter in MEMS is proposed which addresses the application of low cost helium leak detection. Preliminary results are shown for a microfabricated mass separator using external magnets.

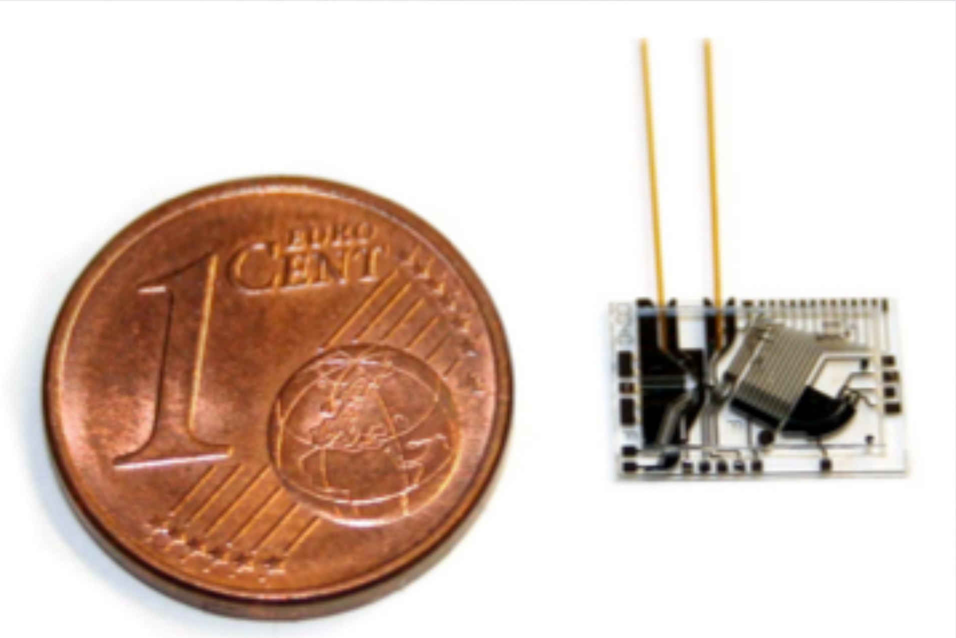
All above publications have in common that only components of a mass spectrometer have been miniaturized and tested as separate units.

Planar-Integrated Micro Mass Spectrometer (PIMMS)

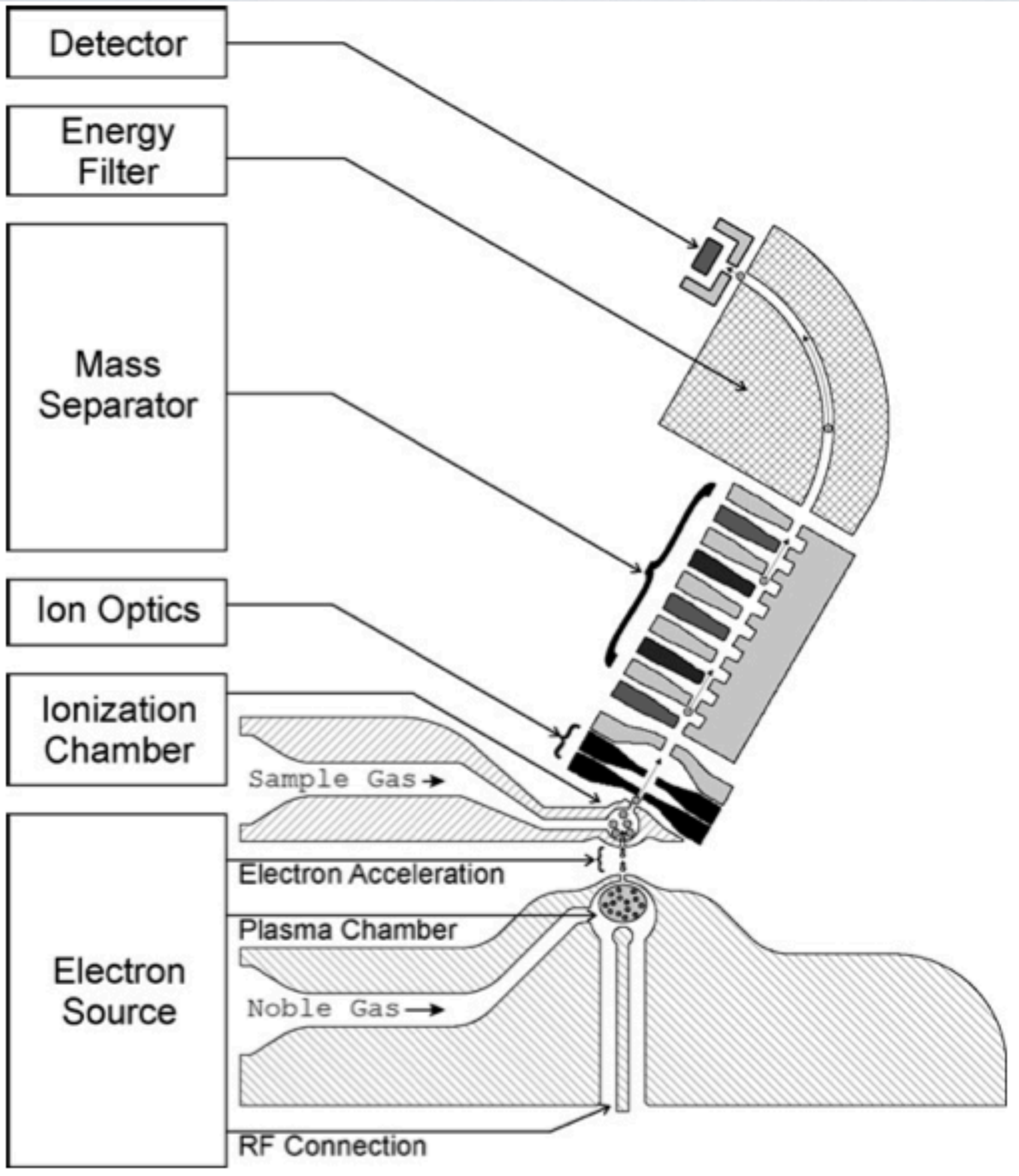
Dimensions 7x10mm^2

Fabrication using only MEMS technologies





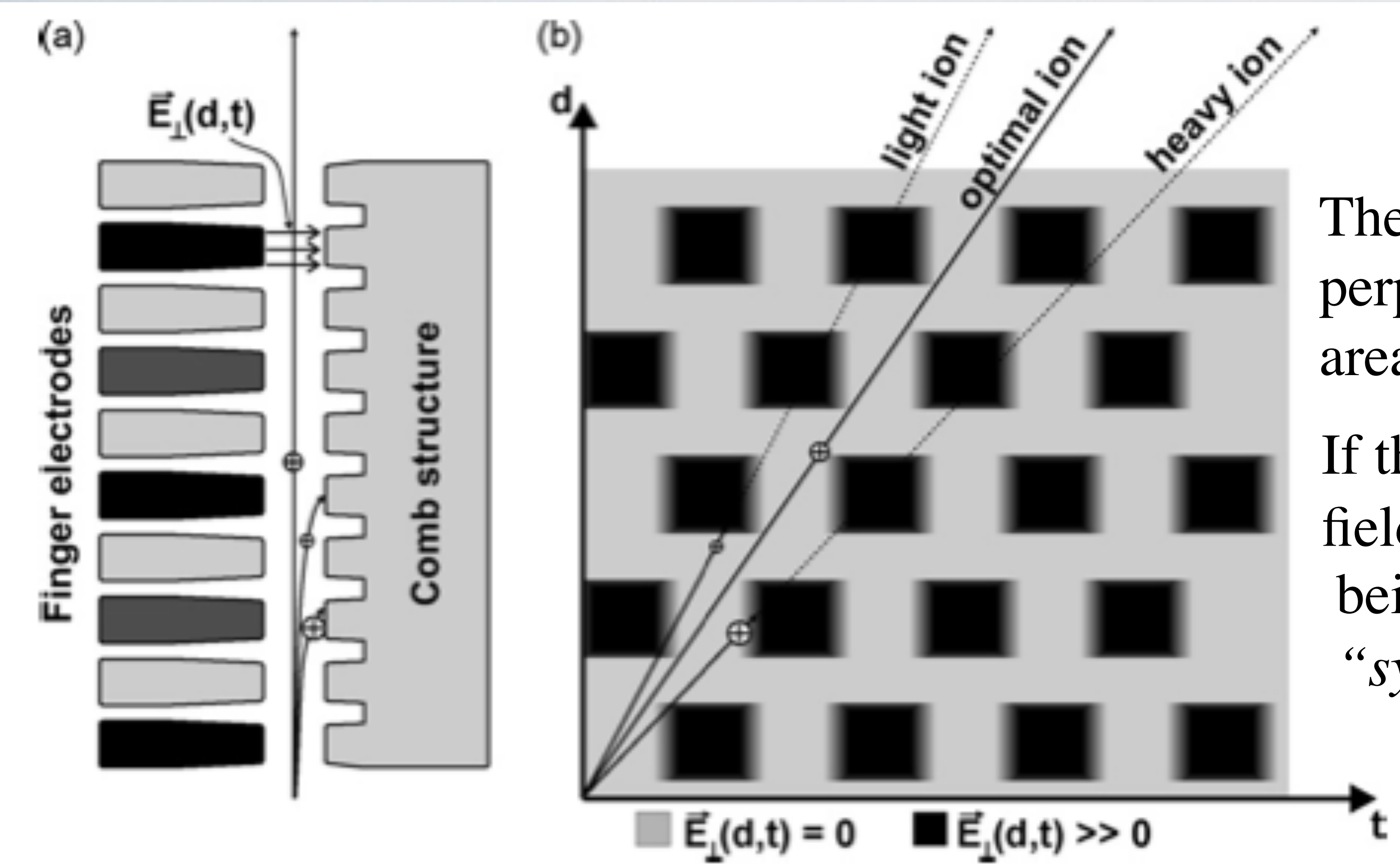
Source: Mass Spectra measured by a fully integrated MEMS mass spectrometer by J. P. Hauschild et al. *International Journal of Mass Spectrometry 2007*



Schematic view of PIMMS structures

Source: Mass Spectra measured by a fully integrated MEMS mass spectrometer by J. P. Hauschild et al. *International Journal of Mass Spectrometry 2007*

Synchronous Ion Shield Mass Separator



The dark areas denote a strong electric field perpendicular to the ion path, while the bright areas denote a field free region.

If the ion speed is synchronous to the traveling field, the ion moves along the channel without being deflected. This is referred to as *"synchronous ion shield mass separator"*

The vacuum requirements of a mass spectrometer can be described by the mean free path length ($\bar{l}_{ion}$) of the ions with the radius r_{ion} in air (r_{gas}).

$$\bar{l}_{ion} = \frac{1}{n\pi(r_{gas} + r_{ion})^2},$$

with

$$n = \frac{p}{kT}.$$

At a pressure p of 1 Pa and at room temperature (T = 300 K) the mean free path length of Ar (r_{ion} =98pm) in air (r_{gas} =370pm) is l_{ion} = 6.02 mm.

The calculations show, that the pressure required to run the PIMMS should be 1 Pa or lower to separate even larger molecules.

Source: Mass Spectra measured by a fully integrated MEMS mass spectrometer by J. P. Hauschild et al. *International Journal of Mass Spectrometry 2007*

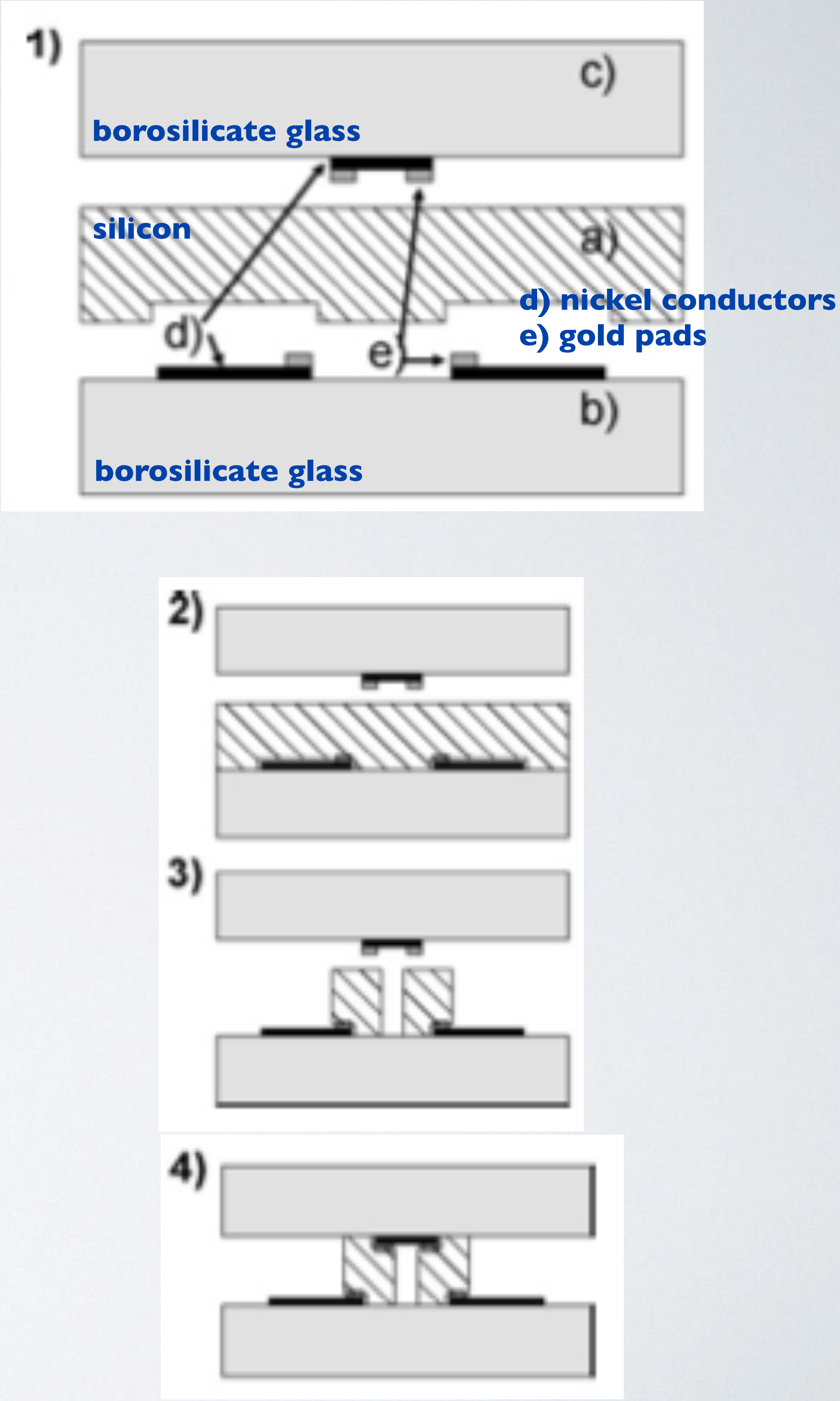
Fabrication:

Features:

> all units of the mass spectrometer are integrated planar on one chip

> the critical structures are fabricated in a one mask anisotropic deep reactive ion etch (DRIE) process.

> in order to achieve free standing silicon structures, the DRIE process is applied to a sandwich of a borosilicate glass (500μm thick) and a highly conductive silicon (300μm thick) substrate.



Steps:

1- the nickel conductors with gold pads at the contact areas on top of both glass substrates are patterned, and the cavities are etched into the silicon substrate.

2- the silicon wafer is bonded to the bottom glass wafer.

3- the silicon is etched by a DRIE process followed by bonding the second glass substrate on top of the silicon structures

4- the processed substrate is diced to finalize the fabrication of about 100 micro-mass spectrometers.

What is the need for nano in MS?

- Mass spectrometers actually measure mass-to-charge ratios, which means that the molecules have to be ionized in the first instance and, moreover, that the charge on the ionized molecules needs to be known before their mass can be extracted. These factors can cause problems because not all molecules are easy to ionize, and uncertainty about the charge of the molecules leads to uncertainty in the mass values reported.
- Using NEMS the true mass of the molecules can, in principle, be determined without any need to ionize the molecules.
- It offers unrivaled mass sensitivity, allowing real-time detection of individual molecular species.

NEMS-based MS Principles:

Mass spectrometry based on single biological molecule detection with a NEMS system
In this NEMS–MS system, nanoparticles and protein species are introduced by electrospray injection from the fluid phase in ambient conditions into vacuum, and are subsequently delivered to the NEMS system detector by hexapole ion optics.
Precipitous frequency shifts, proportional to the mass, are recorded in real time as analytes adsorb, one by one, onto a phase-locked,
ultrahigh-frequency NEMS resonator.

Features:

➡NEMS sensor is used as both mass analyzer and mass detector

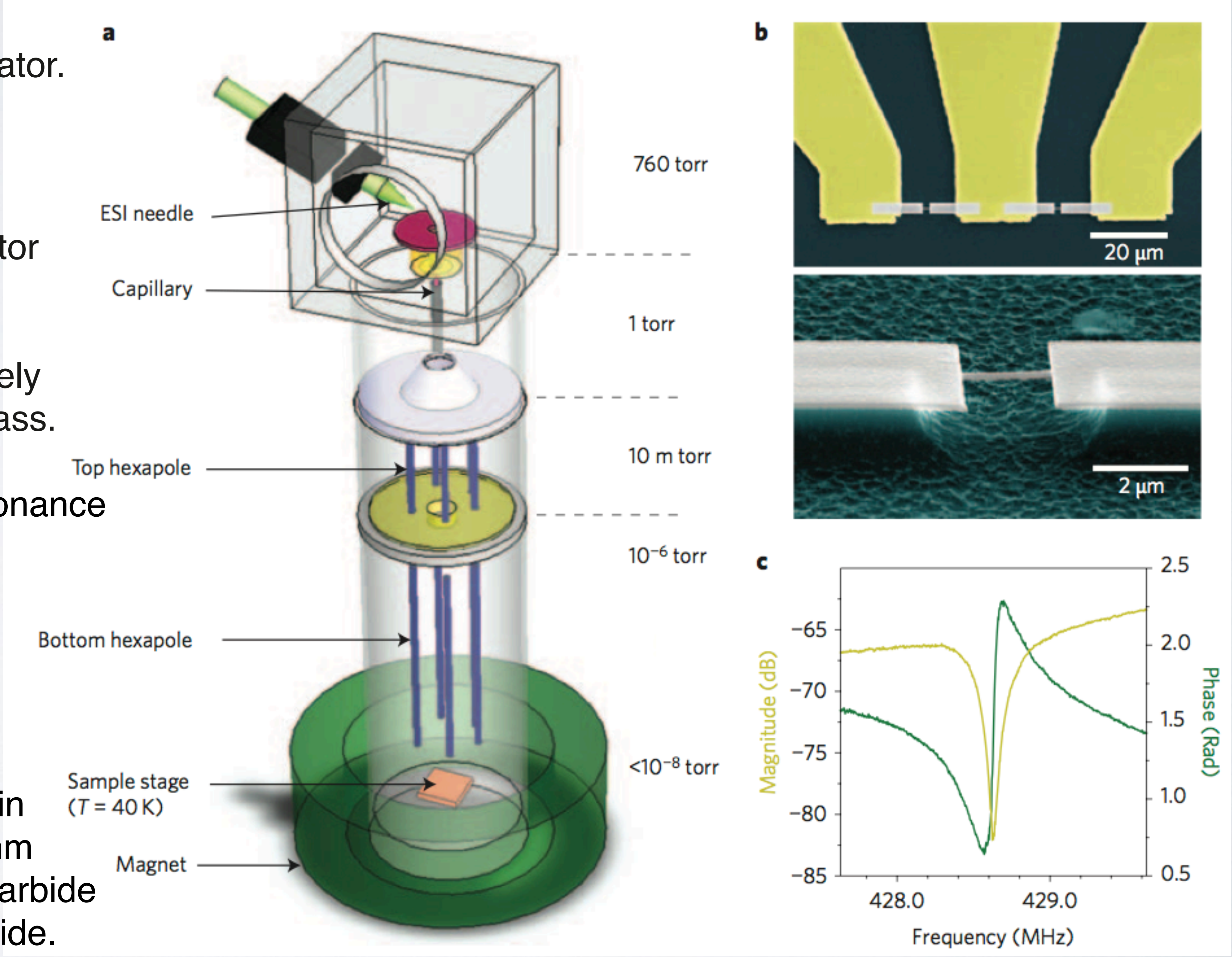
➡The vibrational frequency of a NEMS resonator is an exquisitely sensitive function of its total mass.

➡Typical fundamental mode resonance at ~450MHz

➡Quality factor of ~2000.

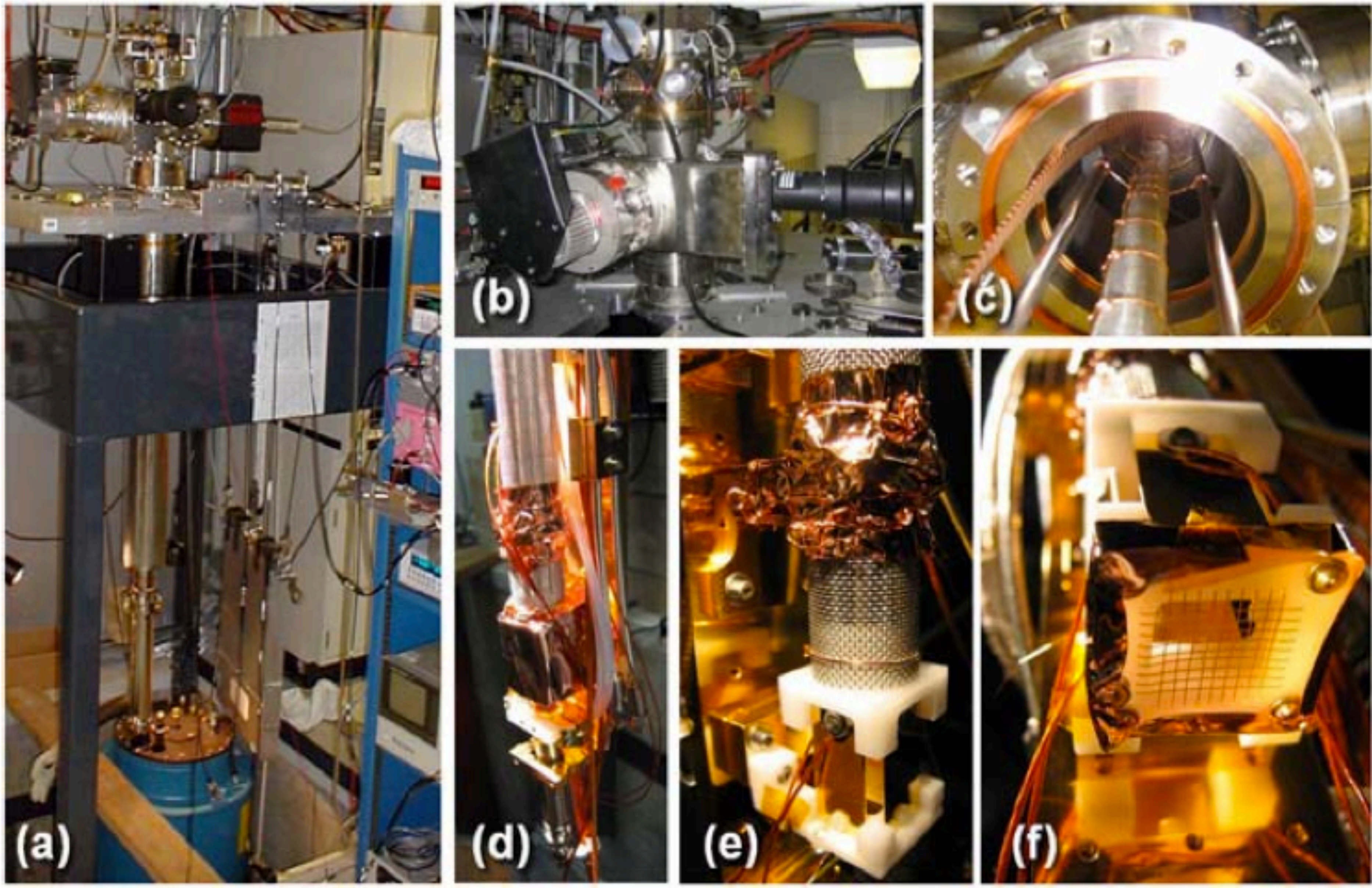
➡Resolution sensitivity of ~1Da

➡The NEMS mass sensor used in these measurements is a 100nm thick, doubly-clamped silicon carbide beam ~1.7µm long, ~120nm wide.

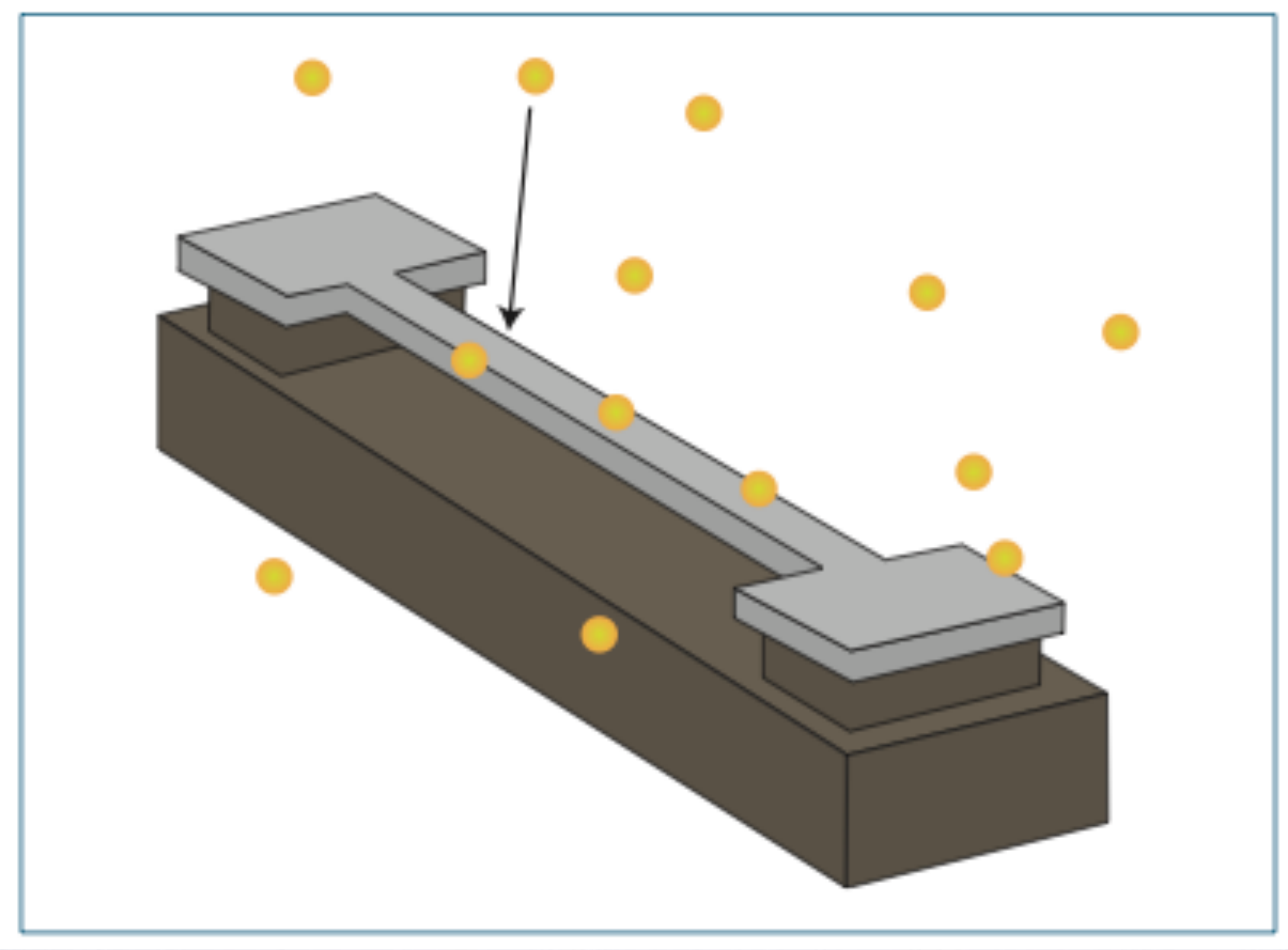


Source: Toward single-molecule nanomechanical mass spectrometry, Naik et al. *Nature Nanotechnology 2009*

Figure S1. First Generation NEMS-MS System. *(a) The cryostat, its vibration isolation & support system, and (in pit) the super-conducting magnet, and its dewar. (b) Electrospray ioniza-tion unit at top of system. (c) Hexapole ion guide from bottom. (d)(e) Sample stage region; progres-sive magnifications. (f) Hexapole ion guide; outlet detail.*



Source: Toward single-molecule nanomechanical mass spectrometry, Naik et al. *Nature Nanotechnology 2009*



The resonant frequency of a nanoscale bridge (grey) is reduced when molecules (orange) land on it, with the frequency change depending on the mass of the molecule and where it lands on the bridge. A mass sensor of this kind has been combined with an electrospray injection system to develop a mass spectrometer that does not require the molecules to be ionized first.

Source: Toward single-molecule nanomechanical mass spectrometry, Naik et al. *Nature Nanotechnology 2009*

Ideas for improvement:

✦ Decoupling mass and position! (the position of the added mass on the bridge influences the resulting frequency change, with the change being largest for particles landing at the centre of the bridge where the amplitude of the oscillations is the largest and zero at the ends.

✦ One challenge is to ensure that the molecules are captured on the surface of the sensor and not lost to the sidewalls of the chamber or elsewhere. Using two-dimensional arrays containing thousands of nanoscale bridges that can capture the individual binding events in a highly parallel approach would be an elegant solution to this problem.

✦ Using piezoresistive rather than magnetomotive readout would remove the need for large magnetic fields, allowing the devices to be made much smaller and more portable.

✦ Miniaturizing the sample injection system, the sample volume could be made as small as a single cell.

The End