Mass spectroscopy
(low pressure reactive / dusty plasmas)

E. Kovacevic

Outline

1. Introduction : method and devices
2. What can mass spectrosopy tell us about:

   a) plasma chemistry

   b) plasma response to the formation of the nanoparticles

3. Some other possibilities – TIMS, MBMS…
4. Conclusions, useful links and hints

Introduction

- An old method: 1st idea 1886, E. Goldstein, 1st experiment 1899 W. Wien, 1st mass spectrometer J. J. Thompson

- charged particle passing through a magnetic field -deflected along a circular path on a radius proportional to the mass to charge ratio, m/e.

- steps: ionization-acceleration-separation-detection

Replica of J.J. Thompson's third mass spectrometer.

Mass spectrometers

1. **Ion Source (electron or chemical ionization)**
2. **Mass Analyzer**

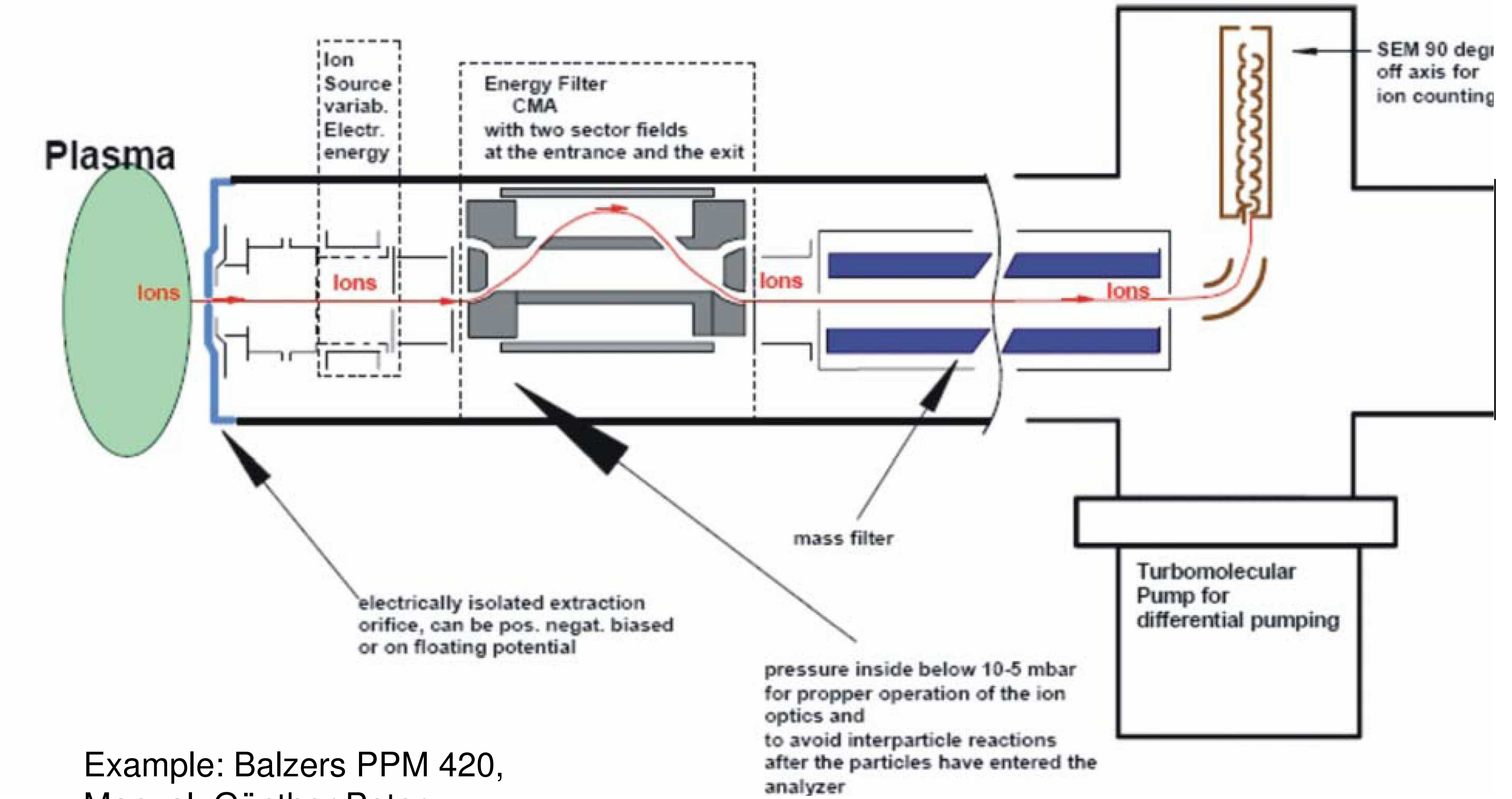
ions are sorted and separated according to their mass to charge ratio.

3. **Detector**

Types:

1. **By ionization:** MALDI (Matrix Assisted Laser Desorption/Ionisation); ICP-MS, glow discharge,field desorption(FD), fast atom bombardment (FAB), thermospray, atmospherical pressure chemical ionization (APCI), secondary ion mass spectrometry (SIMS),spark ionization, thermal ionization …
2. **By mass** analyzer (either static or dynamic fields, and magnetic or electric fields): sector field , time of flight, **quadrupole**, quadrupol ion trap, Fourier transform ion cyclotron resonance…
3. **By detector:** electron mulitiplier, Faraday cups, ion-to-photon detectors, microchanel plate detectors…

Introduction: common type ms



Example: Balzers PPM 420,
Manual, Günther Peter

Some important parameters

m/z= a.m.u. (in some other fields- Dalthons)

Analysers characteristics:

- **Mass resolving power:** resolution
  ability to distinguish two peaks of slightly different m/z.

$$R = \frac{m}{\Delta m}$$

- **Mass accuracy**

the ratio of the m/z measurement error to the true m/z (ppm or milli mass units)

- **Mass range**

the range of m/z amenable to analysis by a given analyzer

- **Linear dynamic range**

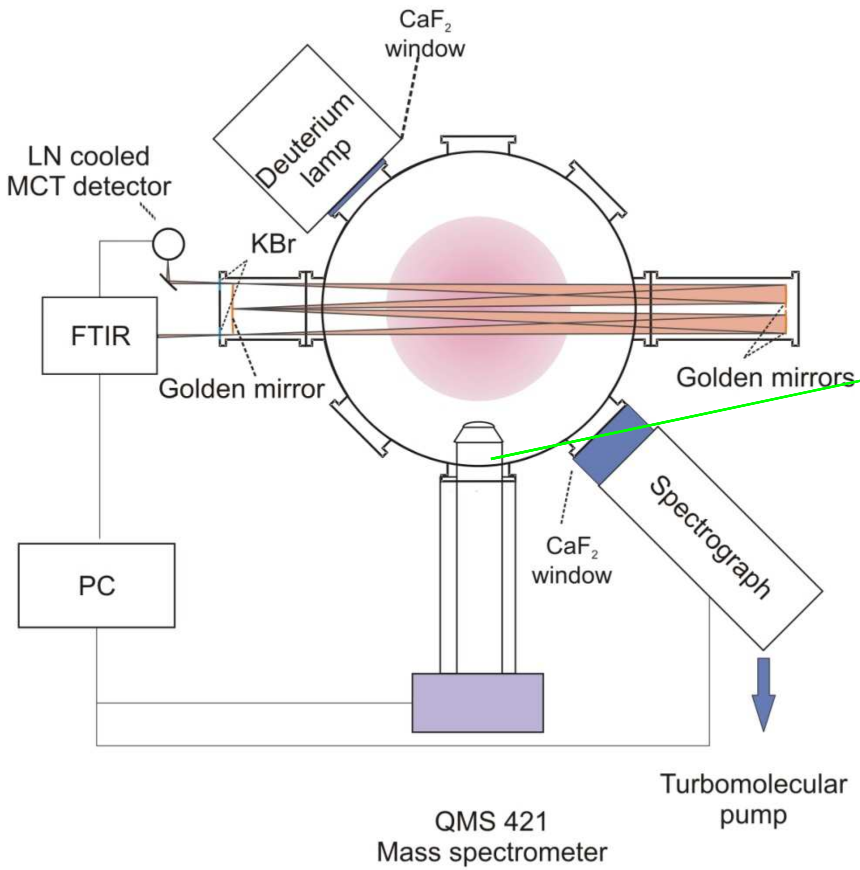
range over which ion signal is linear with analyte concentration.

- **Speed**

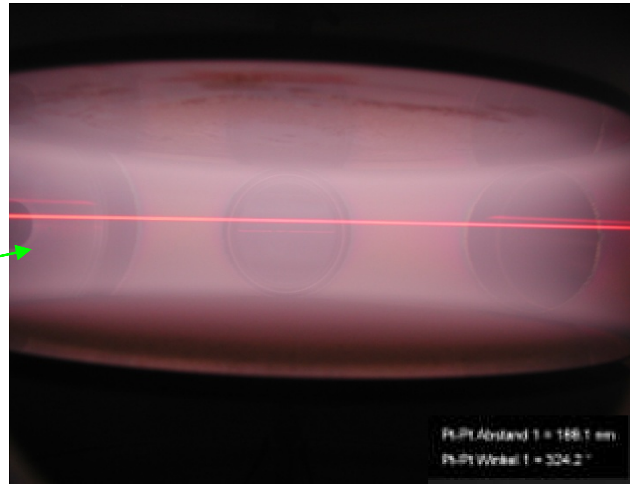
the time frame of the experiment, the number of spectra per unit time

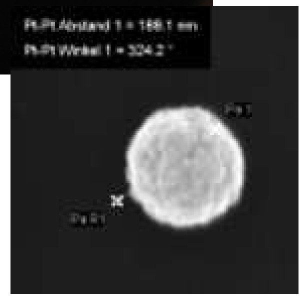
Cracking pattern!!!!!!!

Experimental set-up



Laser light scattering by the dust





Positioning:

sideway,

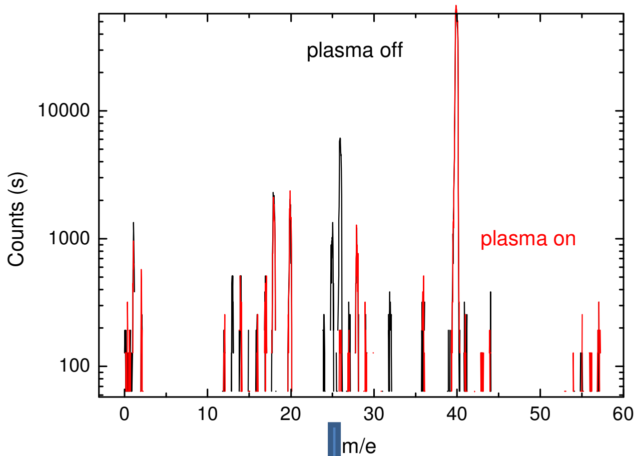
through the electrode,

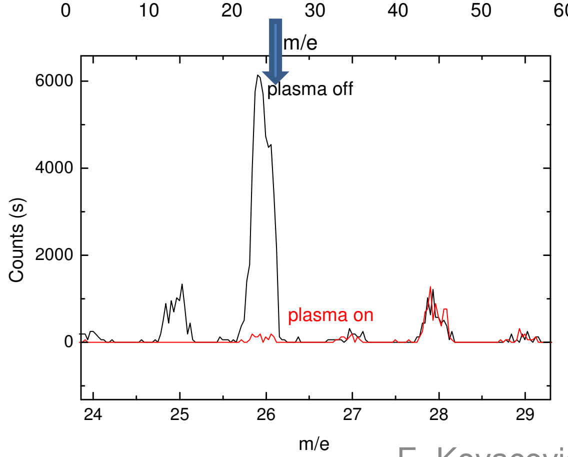
ex-situ(gas extraction)…

Plasma chemistry: neutrals
ions source on

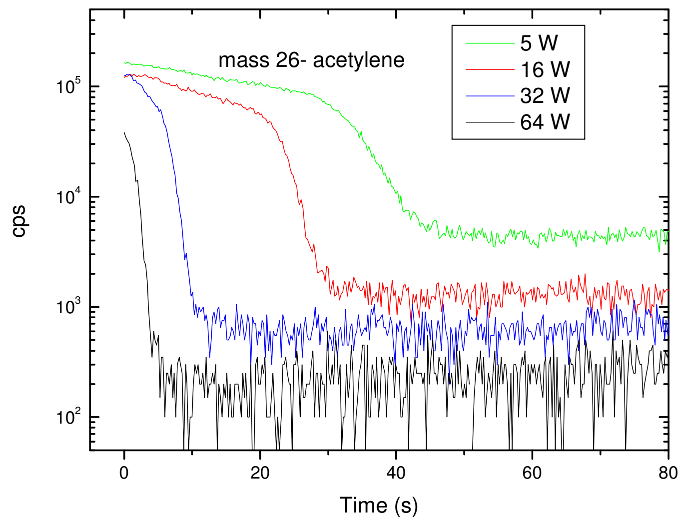
(all examples for: C2H2:Ar= 8:0.5 sccm, p=0.1mbar, P=5-64W, RF CCP)

Overview mass spectra



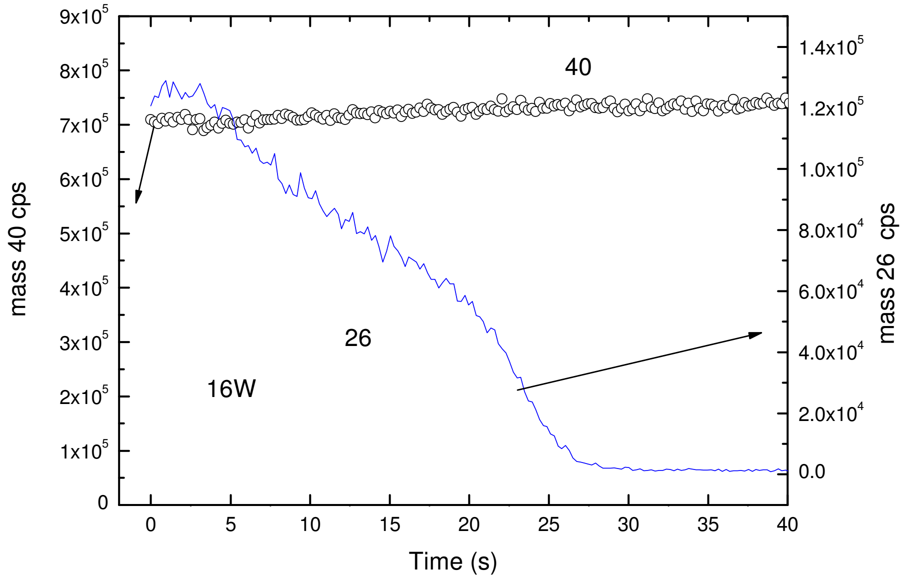


Time resolved behavior of acetylen <u>precursor</u> (acetylen depletion)

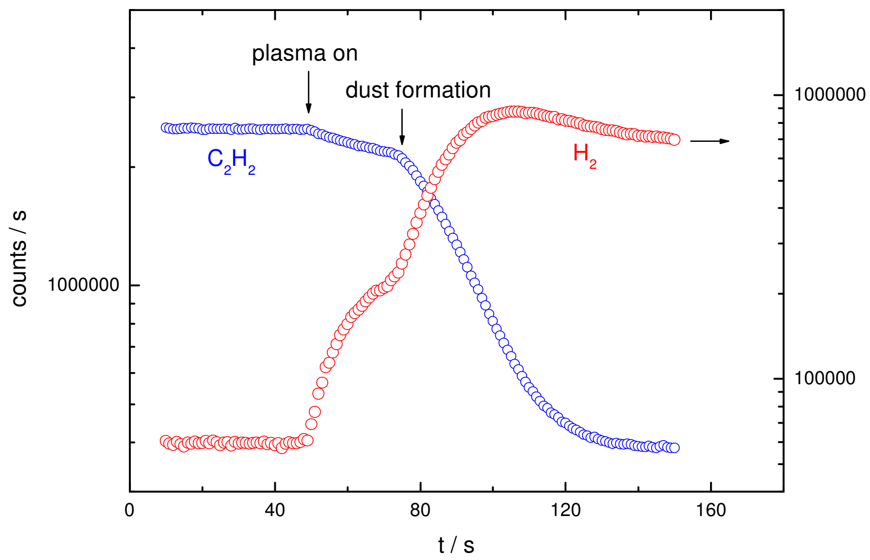


Plasma chemistry: neutrals

(ion source on)



Temporal behavior for:
precursor (26) and carrier gas (40)

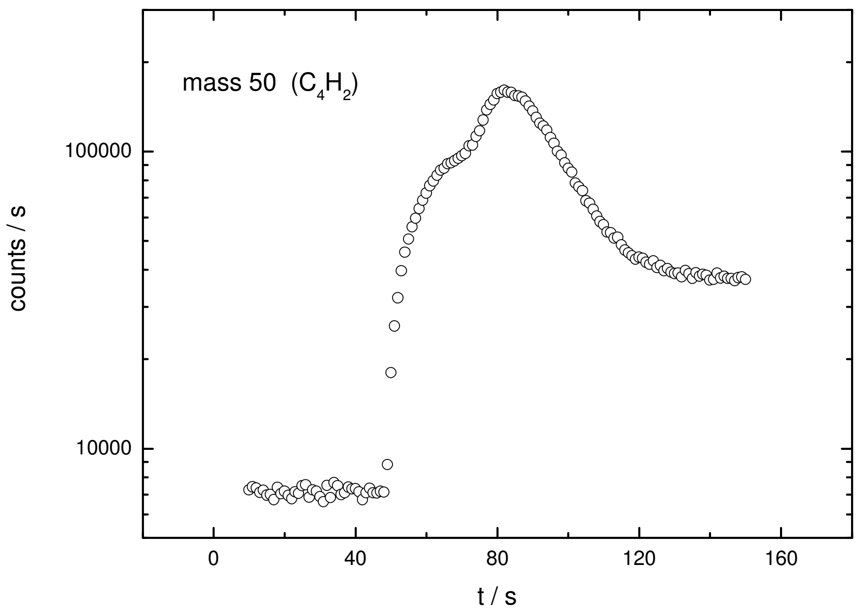


Temporal behavior for:
precursor (26) vs product (H_2; 2)

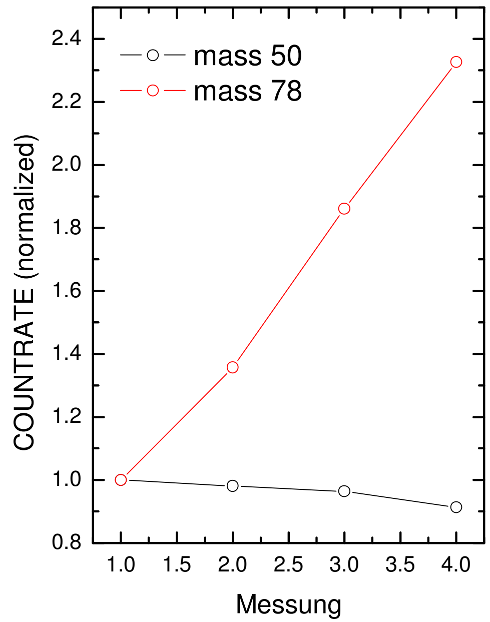
Berndt et al. Contributions to Plasma Physics, 2009 (rev)

Plasma chemistry: neutrals

ion source on



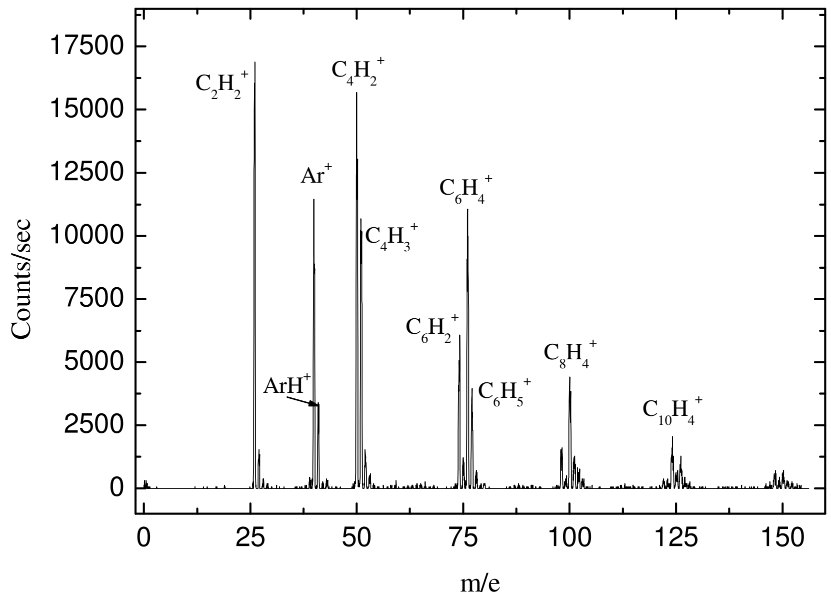
The ignition of the plasma leads to the formation of larger molecules as for example C_4H_2 (mass 50).



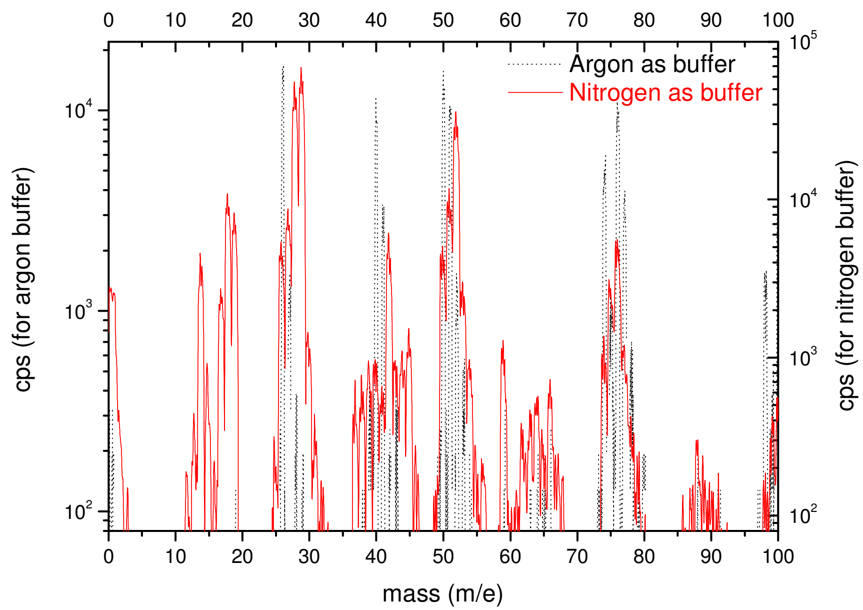
The production rate of these molecules is also affected by the formation of dust particles.

Positive ions

ions source off!!!



Argon-acetylene plasma



Nitrogen-acetylene plasma

(same conditions)

Kovacevic et al 2009, J.Appl.Phys.

Negative ions

- **Positive ions - accelerated by the sheath field**

(orifice floating, grounded, negative bias –last one can disturb plasma)

- **Negative ions - confined in the bulk**

  extraction complicated!

- **In DC glow discharges – simple**

  extraction through an orifice in the anode (see literature)

- **In RF discharges sheath must be (locally) cancelled**

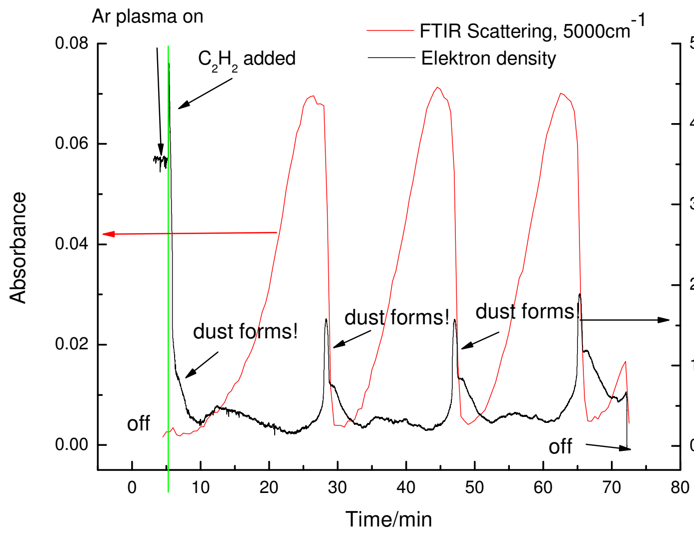
Experimental tricks:

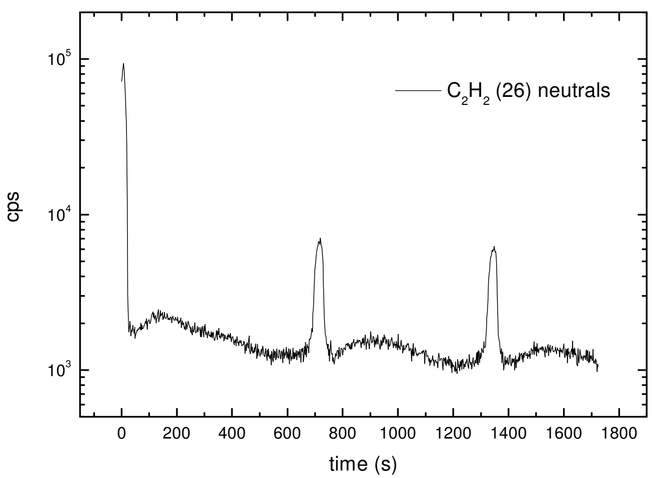
1. positively biased extraction orifice (disturbs plasma)
2. pulsed plasma, detection in the afterglow

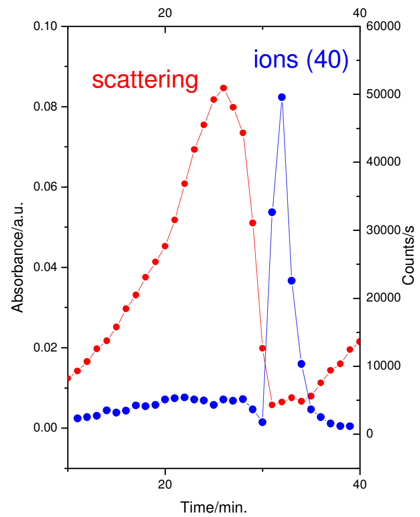
See e.g. E. Stoeffels et al. J. Vac. Sci & Technol.A **5**,2109, (2001) , Hollenstein et al. J. of Vac.Sci.&Technol.A-**14**, 535, (1996), J. Meichsner et al. Contrib. Plas. Phys. **25**, 503 (1985), Leukens, A. 1998, Doctoral Thesis, L Overzet et al. Jpn. J. Appl. Phys. **36**, 2443 (1997) …

Plasma answer to the dust particle formation

Dust particles change the plasma characteristics





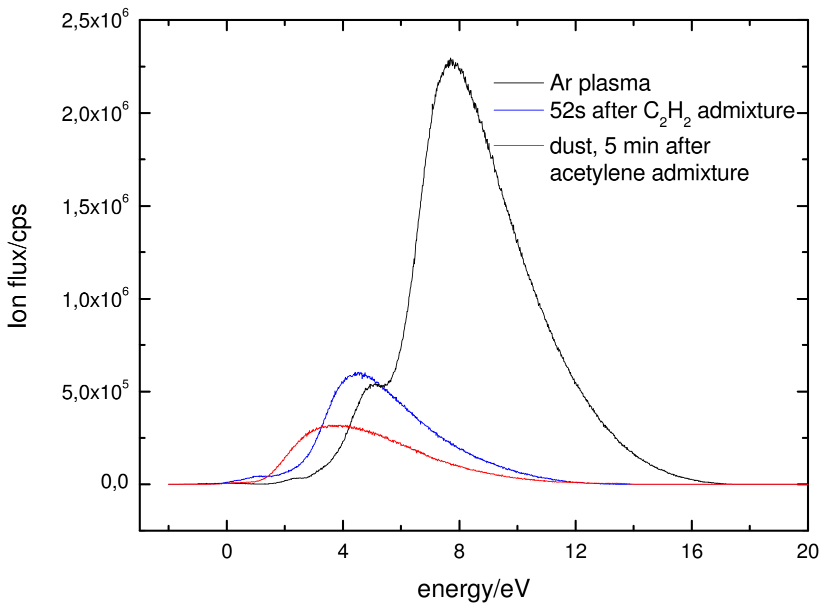


Time resolved behavior of scatter IR and electron density

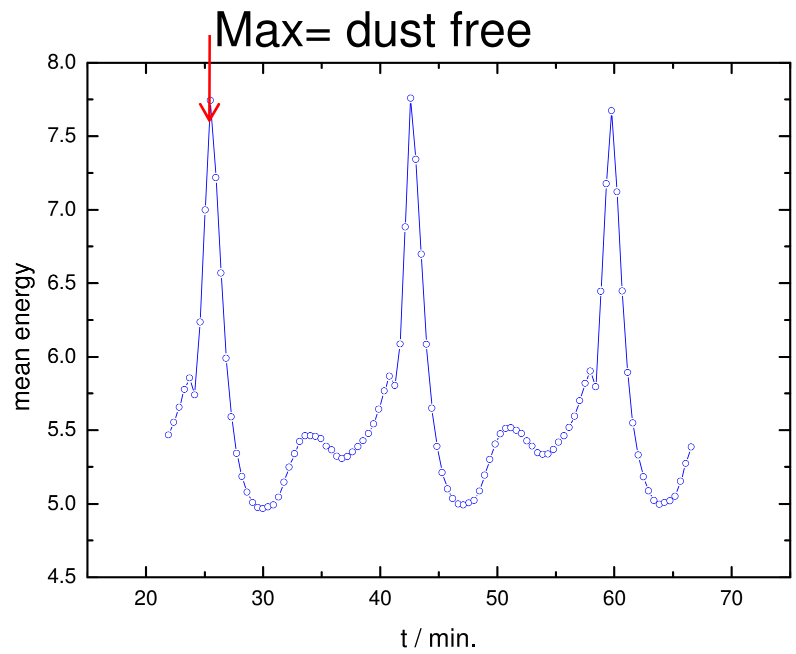
Time resolved behavior of the neutrals: mass 26 (acetylen)

Plasma answer to the dust particle formation
* ion source off!

Energy spectra : fast escaping ions



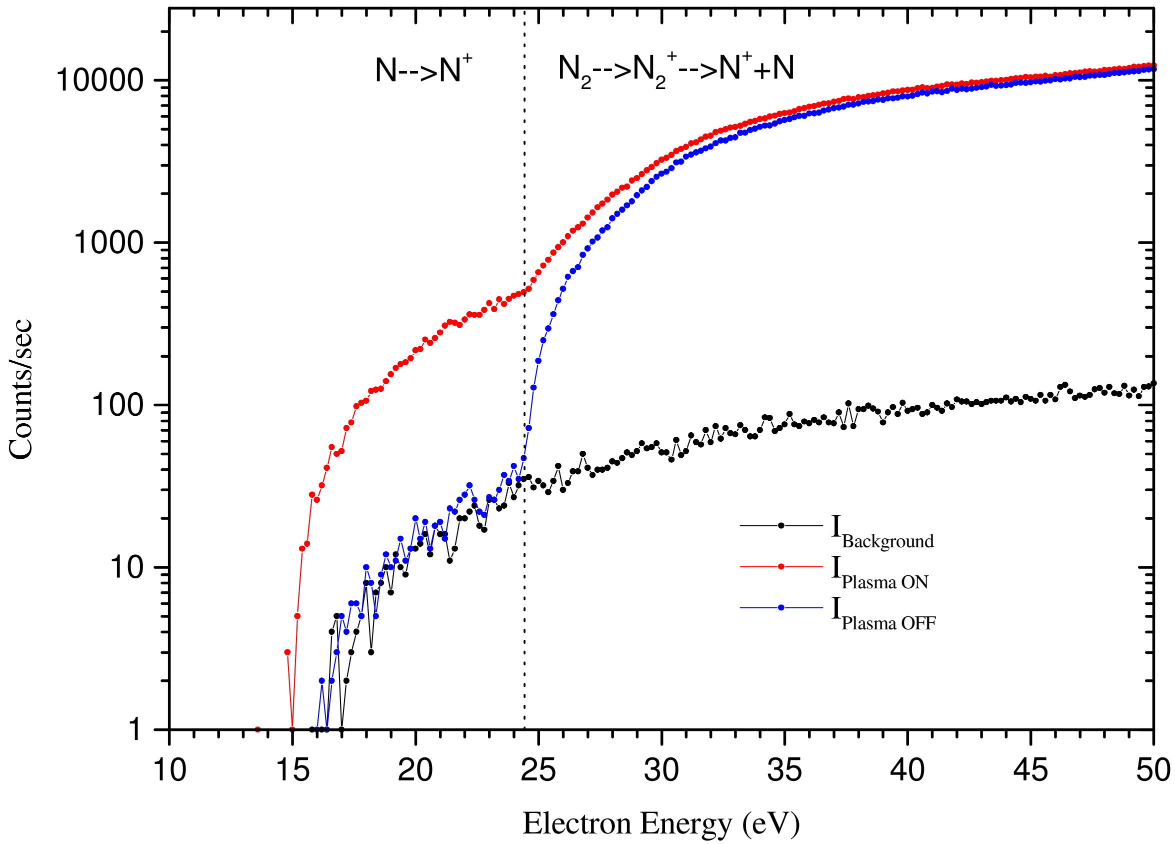
Energy spectra: time developement



$$\int f(E)\,E\,dE \;/\; \int f(E)\,dE$$

Ref: Kovacevic et al, Berndt et al 2003,2009; Stefanović et al NJP2003,PPCF2005; Denysenko et al Phys Plas. 2006, Hippler et al J. Phys D2007

TIMS
Threshold Ionisation Mass-Spectroscopy: radicals, metastables



1. Threshold:

Ionisation of N-atoms

$$\mathbf{N + e^- \rightarrow N^+ + 2\,e^-}$$

2. Threshold:

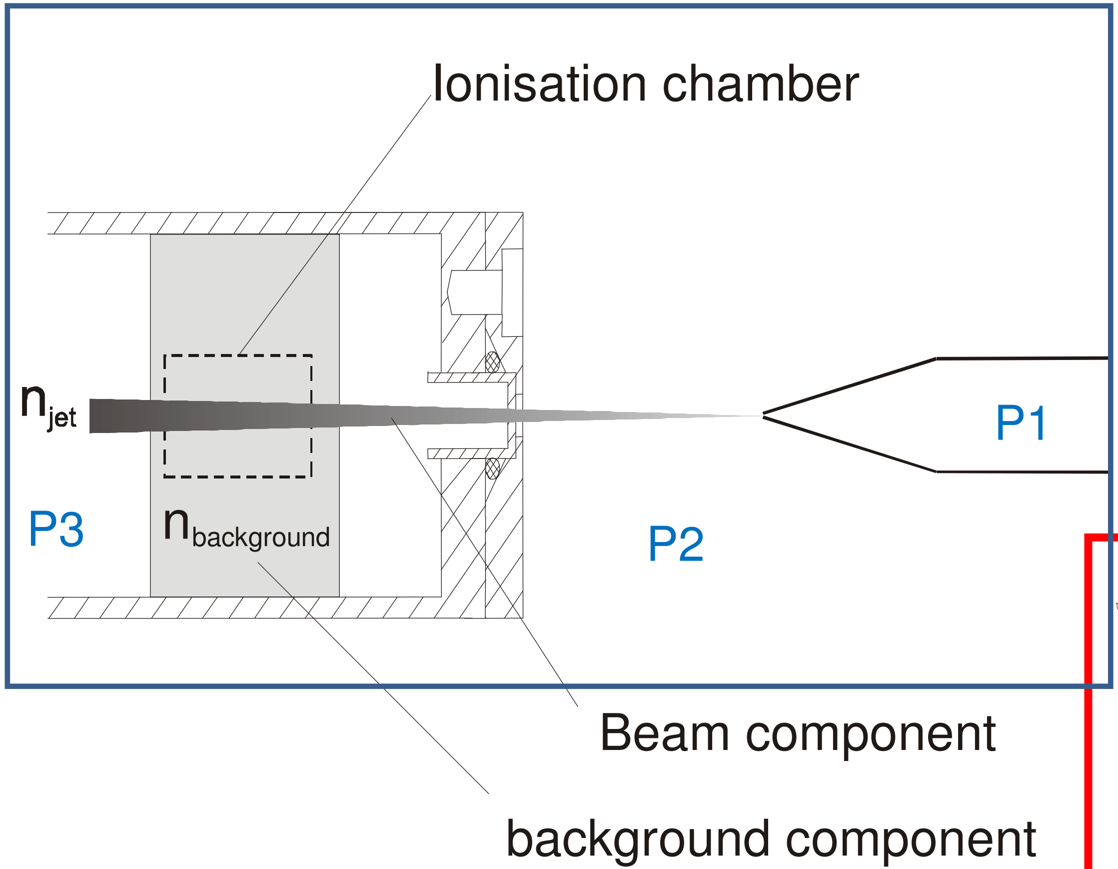
Dissociative ionisation of N_2

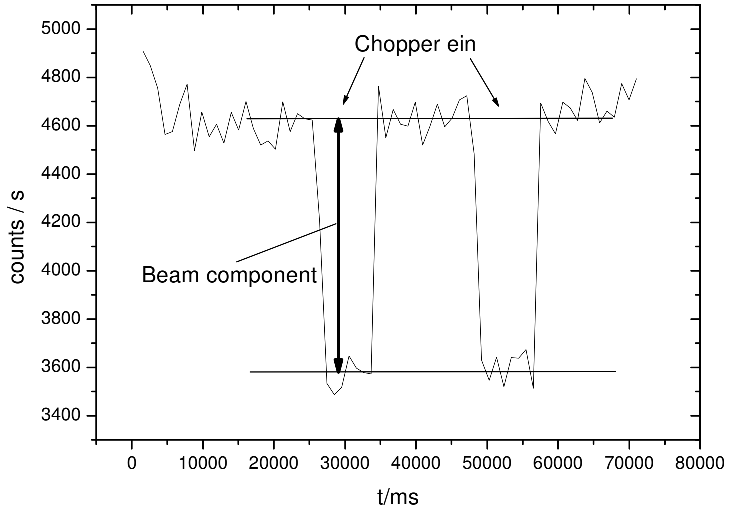
$$\mathbf{N_2 + e^- \rightarrow N^+ + N + 2\,e^-}$$

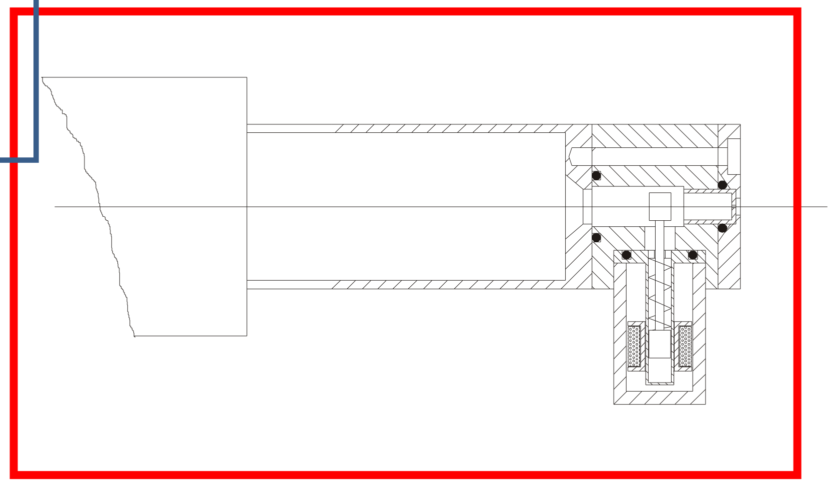
Example:HIDEN HALPSM 300

D.Douai, J. Berndt, J. Winter , J. Appl. Phys. 2002

MBMS
Modulated Beam Mass-Spectroscopy: radicals, metastables



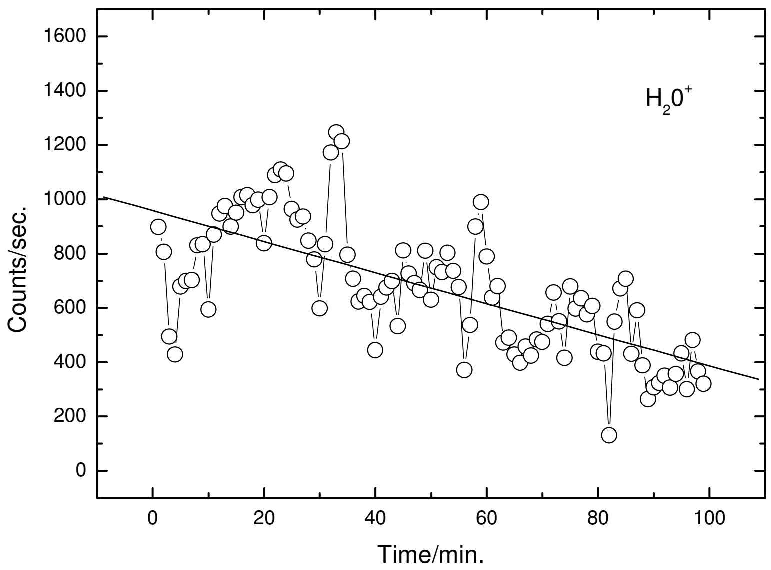




D.Douai, J. Berndt, J. Winter , J. Appl. Phys. 2002

Example:HIDEN HALPSM 300

Impurities



Water (impurities): from discharge chamer, from mass spectrometer

Spectrum can be contaminated in different ways, e.g. by the oil from the vacuum pump

For more see e.g.
John F. O'Hanlon, "A User's Guide to Vacuum Technology," John Wiley & Sons, New York, 1989.

Conclusions

- Powerful tool for the dusty plasma analysis:

Plasma chemistry+plasma response to the formation of dust particles

- Not a straightforward method

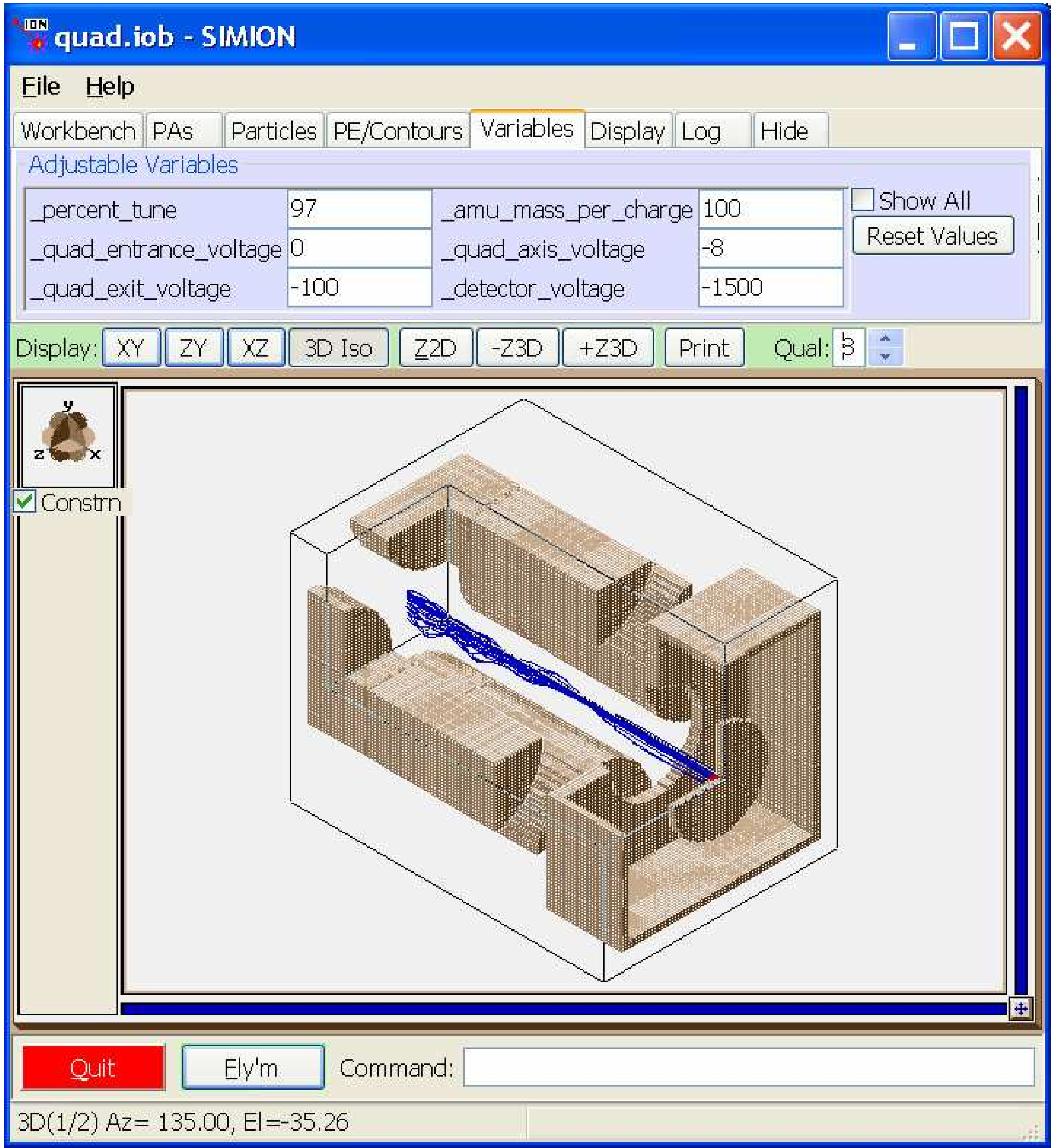
Literature, links:

- http://www.massbank.jp, NIST webbook.org
- http://www.dmoz.org/Science/Chemistry/Analytical/Mass_Spectrometry/
- http://library.med.utah.edu/masspec/elcomp.htm
- http://www.dmoz.org/Science/Chemistry/Analytical/Mass_Spectrometry/

- HMDSO: e.g. Magni et al.2001, *J. Phys. D: Appl. Phys* **34** 87
- SiH4: e.g. C Hollenstein *et al* 1994 *Plasma Sources Sci. Technol.* **3** 278
- Effects of positioning: works of S. Radovanov (NIST group)

- Acknowledgments:

J. Berndt, I. Stefanovic, D. Douai, J.Winter, L. Boufendi, Ch. Hollenstein, E&W Stoffels
Balzers (Infineon ag), HIDEN, SIMION



http://simion.com/

Calculation of fields and ion trajectories