Topic 5 (Chapters 11&20) Mass Spectrometry

1 Mass Spectrometry

- Ionization of gas phase molecules followed by analysis of the mass-to-charge ratios (m/z) of the ions produced
- Mass spectrum: ion intensities vs. m/z

- Nominal MW = 28
  Actual MW $C_2H_4^+$ = 28.0313
  CH_2N^+ = 28.017
  N_2^+ = 28.0061

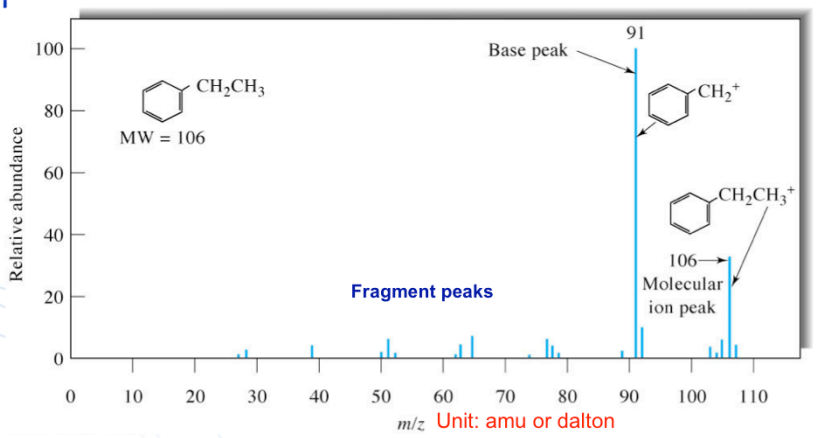


Fig. 20-1 (p551) Mass spectrum of ethyl benzene

2 Instrumentation

- Sample inlet system – vaporize sample
- Ion source – ionizes analyte gas molecules
- Mass analyzer – separates ions according to m/z
- Detector – counters ions
- Vacuum system – reduces collisions between ions and gas molecules

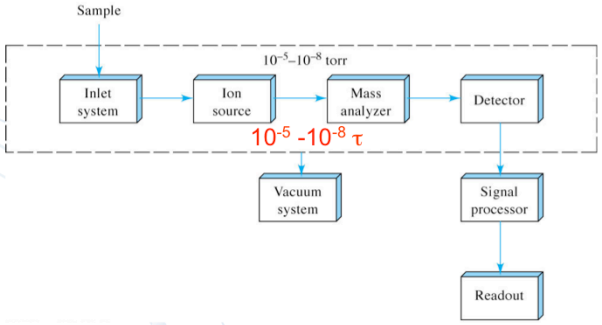


Fig. 20-11 (p564) Components of a mass spectrometer

2.1 Sample inlet

2.1.1 External (Batch) inlet systems

- Liquid
- Gas

2.1.2 Direct probe

- Non-volatile liquid
- Solid

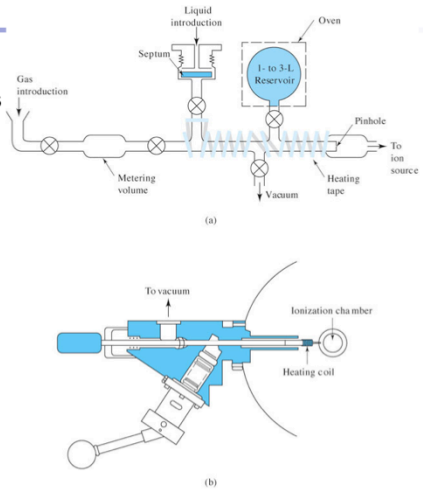


Fig. 20-12 (p564) Sample inlet

2.1.3 Chromatography/Electrophoresis

- Permits separation and mass analysis
- How to couple two techniques?
  GC/MS,

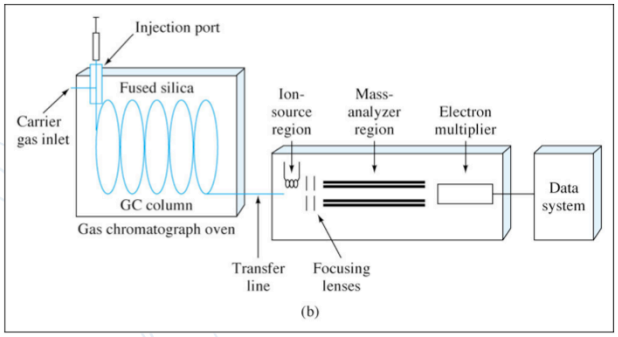
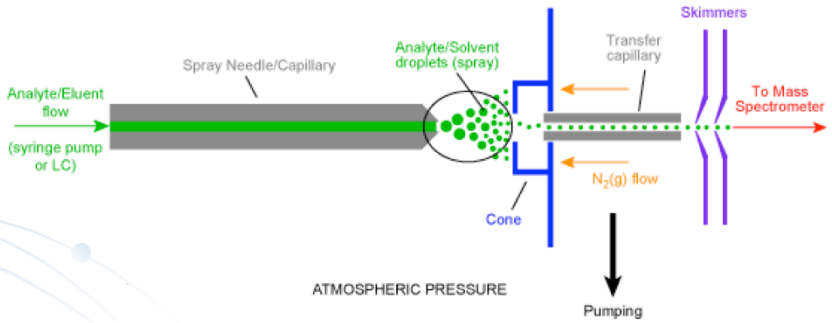


Fig. 27-14 (p799) Capillary GC-MS

HPLC/MS, nano flow, ESI



Adapted from http://www.bris.ac.uk/nerclsmsf/techniques/hplcms.html

2.2 Ion sources

TABLE 20-1 Ion Sources for Molecular Mass Spectrometry

Basic Type	Name and Acronym	Ionizing Agent
Gas phase	Electron impact (EI)	Energetic electrons
	Chemical ionization (CI)	Reagent gaseous ions
	Field ionization (FI)	High-potential electrode
Desorption	Field desorption (FD)	High-potential electrode
	Electrospray ionization (ESI)	High electrical field
	Matrix-assisted desorption-ionization (MALDI)	Laser beam
	Plasma desorption (PD)	Fission fragments from ^{252}Cf
	Fast atom bombardment (FAB)	Energetic atomic beam
	Secondary-ion mass spectrometry (SIMS)	Energetic beam of ions
	Thermospray ionization (TS)	High temperature

Hard ionization leaves excess energy in molecule – extensive fragmentation

Soft ionization little energy in molecule – reduced fragmentation

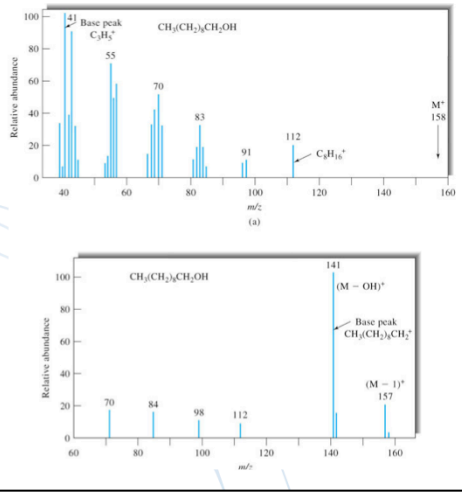


Fig. 20-2 (p553) Mass spectrum of 1-decanol from (a) a hard ionization source (electron impact) and (b) a soft ionization (chemical ionization)

2.2.1 Gas-phase ion source

(1) Electron Impact (EI)

Electron bombardment of gas/vapor molecules

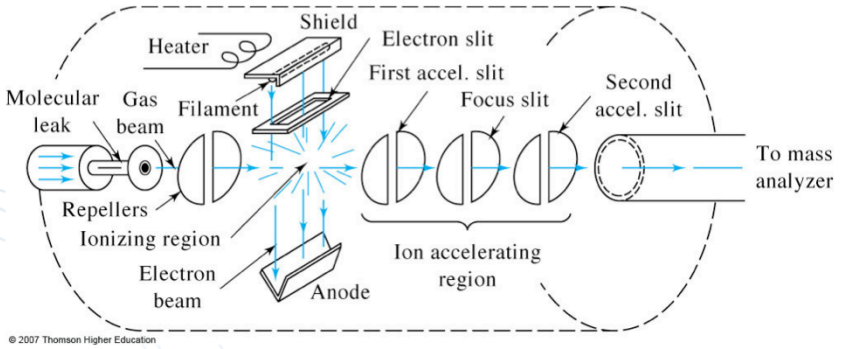


Fig. 20-3 (p553) An EI ion source

EI: **$M + e^- (\sim 70\ eV) \rightarrow M^+ + 2e^-$** **($\sim 10^{-4}$% ionized)**

Hard source (incident energy 70 eV >> chemical bond)

- Molecules excited {electronically, vibrationally and rotationally}
- Extensive fragmentation → fragment ions
- Base peak m/z << M^+

Advantages:	convenient & sensitive
	complex fragmentation helps identification of molecular structure
Disadvantages:	weak or absent M^+ peak inhibits determination of MW
	molecules must be vaporized (MW < 1000 amu), and
	must be thermally stable {during vaporization}

TABLE 20-2 Some Typical Reactions in an Electron-Impact Source

Molecular ion formation	$ABCD + e^- \rightarrow ABCD^{\bullet +} + 2e^-$
Fragmentation	$ABCD^{\bullet +} \rightarrow A^+ + BCD^\bullet$ $\rightarrow A^\bullet + BCD^+ \rightarrow BC^+ + D$ $\rightarrow CD^\bullet + AB^+ \rightarrow B + A^+$ $\rightarrow A + B^+$ $\rightarrow AB^\bullet + CD^+ \rightarrow D + C^+$ $\rightarrow C + D^+$
Rearrangement followed by fragmentation	$ABCD^{\bullet +} \rightarrow ADBC^{\bullet +} \rightarrow BC^\bullet + AD^+$ $\rightarrow AD^\bullet + BC^+$
Collision followed by fragmentation	$ABCD^{\bullet +} + ABCD \rightarrow (ABCD)_2^{\bullet +} \rightarrow BCD^\bullet + ABCDA^+$

(2) Chemical ionization (CI)

- EI ionization in excess (10^5 of analyte pressure) of reagent gas (methane) to generate CH_4^+ and CH_3^+, then

  $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$

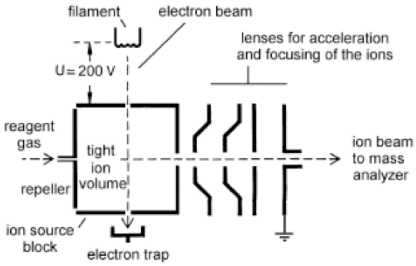
  $CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$

  Ions reacts with analyte

  $CH_5^+ + A \rightarrow CH_4 + AH^+$ proton transfer

  $C_2H_5^+ + A \rightarrow C_2H_4 + AH^+$ proton transfer

  $C_2H_5^+ + A \rightarrow C_2H_6 + (A\text{-}H)^+$ hydride elimination

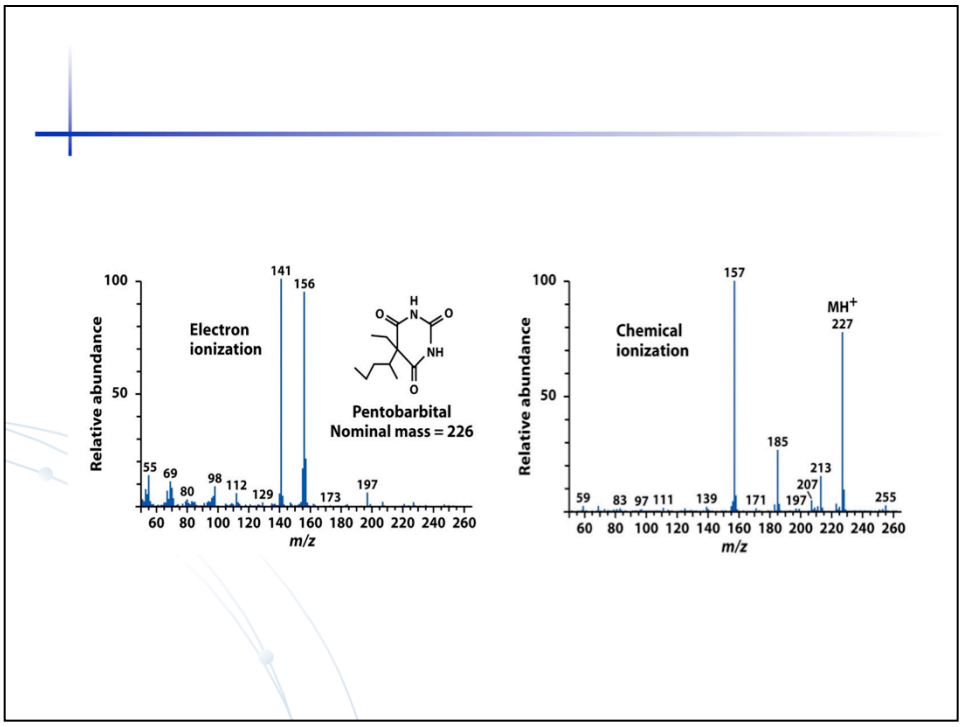


Adapted from Schröder, E. *Massenspektrometrie - Begriffe und Definitionen;* Springer-Verlag: Heidelberg, 1991.

- analyte

  most common ions $(M+1)^+$ and $(M-1)^+$

  sometimes $(M+17)^+$ addition of CH_5^+ or $(M+29)^+$ (addition of $C_2H_5^+$)


Electron ionization
Relative abundance
100
50
141
156
55
69
80
98
112
129
173
197
60 80 100 120 140 160 180 200 220 240 260
m/z
Pentobarbital
Nominal mass = 226
Chemical ionization
157
MH+
227
185
213
207
197
59
83
97
111
139
171
255

2.2 Ion sources

TABLE 20-1 Ion Sources for Molecular Mass Spectrometry

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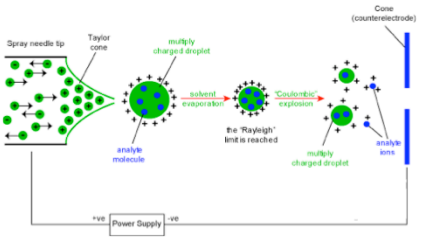
	Thermospray ionization (TS)	High temperature

2.2.2 Desorption/Ionization sources (For non-volatile or non-stable analytes)

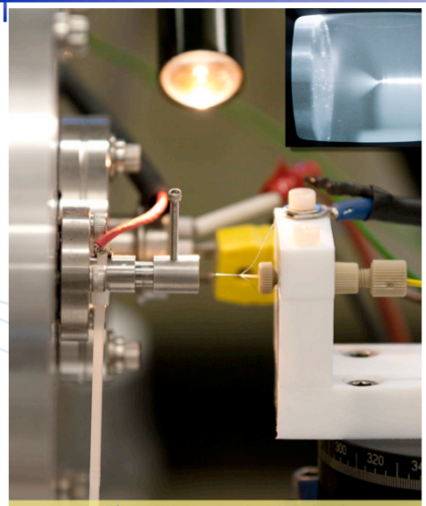
(1) Electrospray ionization (ESI): explosion of charged droplets containing analyte

- solution of analyte pumped through charged (1-5 kV) capillary
- small droplets become charged, (i.e. taylor cone), pushed to air
- solvent evaporates, drop shrinks, surface charge density increases
- charge density reduced by explosion of charged analyte molecules ("Coulomb explosion")



Adapted from http://www.bris.ac.uk/theory/fab-ionisation.html

Soft ionization – transfer existing ions from the solution to the gas phase, little fragmentation



Electrospray Ionization (ESI)

$V_{on}=(r_c\gamma\cos\theta/2\varepsilon_0)^{1/2}\mathrm{Ln}(4d/r_c)$

- r_c: outer radius of ESI needle
- γ: surface tension of solvent
- θ: half angle of the Taylor cone (49°)
- ε_0: relative dielectric constant of vacuum (8.85×10^{-12})
- d: distance between ESI tip and counter electrode (6 mm)

- Typical V_{on} = ~3 kV

J. S. Klassen, Y. Ho, A. T. Blades, and P. Kebarle, Adv. Gas-Phase Ion Chem., 1998, 3, 255-318

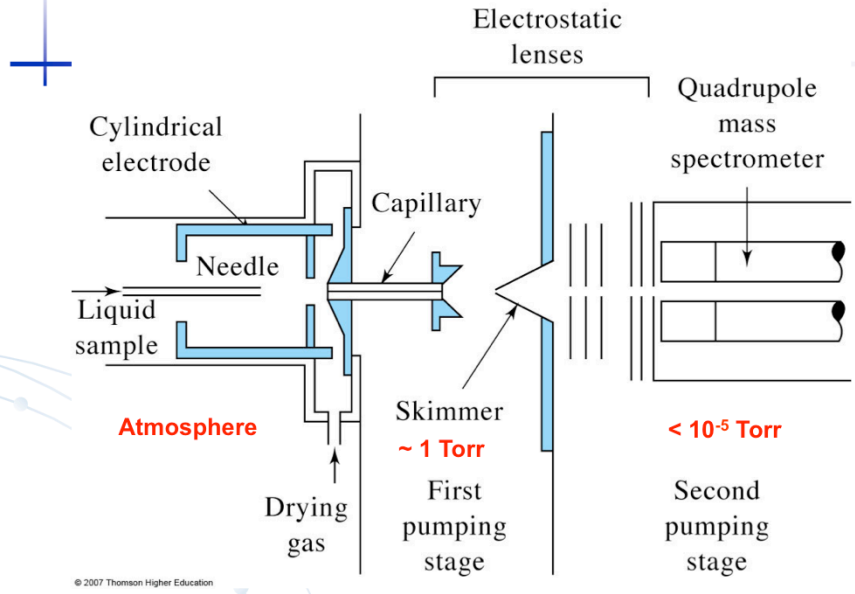


Fig. 20-9 (p562) Apparatus for ESI

- Important technique for large (10^5 Da) thermally fragile molecules, e.g., peptide, proteins
- produce either cations or anions.
- Analytes may accumulate multiple charges in ESI, M^{2+}, M^{3+} …
  molecular mass = m/z x number of charges

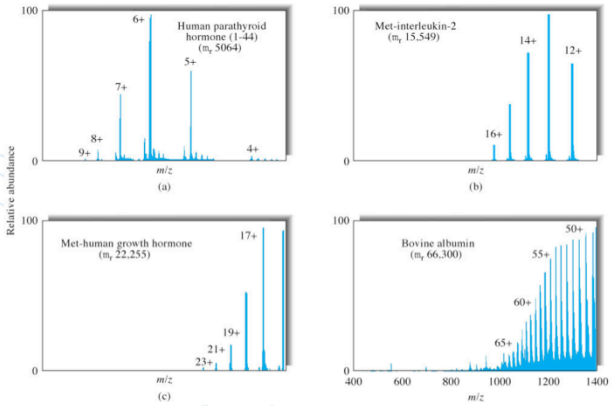


Fig. 20-10 (p563) Typical ESI MS of proteins and peptides.

- Easily coupled to HPLC

The Nobel Prize in Chemistry 2002

John B. Fenn

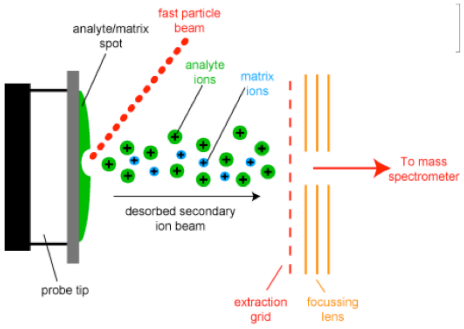
Koichi Tanaka

The Nobel Prize in Chemistry 2002 was awarded "for the development of methods for identification and structure analyses of biological macromolecules" with one half jointly to John B. Fenn and Koichi Tanaka "for their development of soft desorption ionisation methods for mass spectrometric analyses of biological macromolecules" and the other half to Kurt Wüthrich "for his development of nuclear magnetic resonance spectroscopy for determining the three-dimensional structure of biological macromolecules in solution".

(2) Fast atom bombardment (FAB)

- Sample in glycerol matrix
- Bombarded by high energy Ar or Xe atoms (few KeV)
- Atoms and ions sputtered from surface (ballistic collision)
- Both M^+ and M^- produced
- Applicable to small or large (>10^5 Da) unstable molecule

Comparatively soft ionization – less fragmentation



Adapted from http://www.bris.ac.uk/theory/fab-ionisation.html

(3) Matrix-assisted laser desorption/ionization (MALDI)

- analyte dispersed in UV-absorbing matrix and placed on sample plate

- pulsed laser struck the sample and cause desorption of a plume of ions,

- energy absorption by matrix, transfer to neutral analyte; desorption of matrix and neural analyte ionization via PT between protonated matrix ions and neutral analyte.

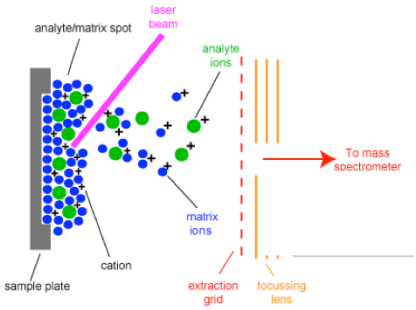


Fig. 20-7 (p560) Diagram of MALDI progress.

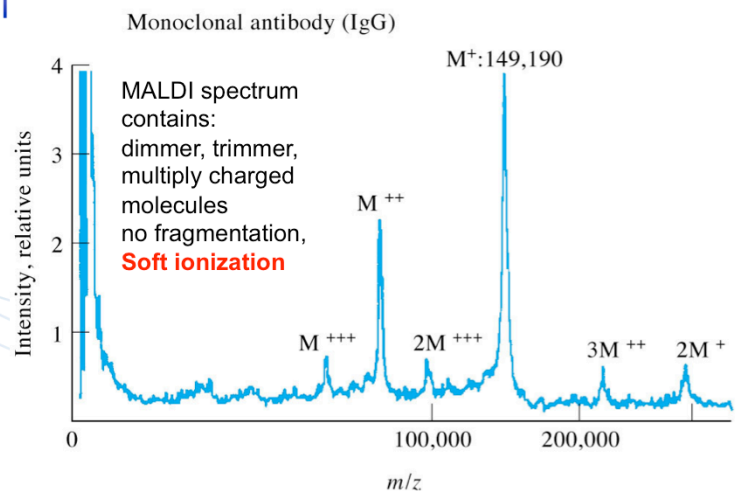


Fig. 20-8 (p561) MALDI-TOF spectrum from nicotinic acid matrix irradiated with a 266-nm laser beam

Matrix:
small MW
absorb UV
able to crystallize

TABLE 20-4 Common Matrices for MALDI and Usable Wavelengths

Matrix	Analytes	Wavelength, nm
Nitropyridines:		
2-Amino-4-methyl-5-nitropyridine	Proteins, oligonucleotides	355
2-Amino-5-nitropyridine	Oligonucleotides	355
Nicotinic acid	Proteins, glycoproteins, oligonucleotides	266, 220–290
Benzoic acid derivatives:		
2,5-Dihydroxybenzoic acid	Proteins	266, 337, 355, 2940
Vanillic acid	Proteins	266
2-Aminobenzoic acid	Proteins	266, 337, 355
2-(4-Hydroxyphenylazo) benzoic acid	Proteins, gangliosides, polymers	266, 377
2-Pyrazinecarboxylic acid	Proteins	266
3-Aminopyrazine-2-carboxylic acid	Proteins	337
Cinnamic acid derivatives:		
Ferulic acid	Proteins, oligonucleotides	266, 337, 355, 488
Sinapinic acid	Proteins, industrial polymers	337, 355
Caffeic acid	Proteins, oligonucleotides	266, 337, 355, 10600
α-Cyano-4-hydroxy cinnamic acid	Proteins, oligosaccharides	337
3-Nitrobenzyl alcohol	Proteins	266
3-Nitrobenzyl alcohol with rhodamine 6G	Proteins	532
3-Nitrobenzyl alcohol with 1,4-diphenyl-1,3-butadiene	Proteins	337
3-Hydroxypicolinic acid	Oligonucleotides, glycoproteins	266, 308, 355
Succinic acid	Proteins	2940, 10600

2.3 Mass analyzer (separate ions to measure m/z and intensity)

Resolution:

- ability to differentiate peaks of similar mass
  R = mean mass two peaks / separation between peaks
  = $[(m_1+m_2)/2] / \Delta m$
- Resolution depends on mass
  R=1000, able to separate 1000 & 1001,
  or 100.0 & 100.1,
  or 10000& 10010
- High resolution necessary for exact MW determination
  - Nominal MW = 28
  - Actual MW $C_2H_4^+$ = 28.0313
    CH_2N^+ = 28.017
    N_2^+ = 28.0061, R > 2570

2.3.1 magnetic sector analyzer

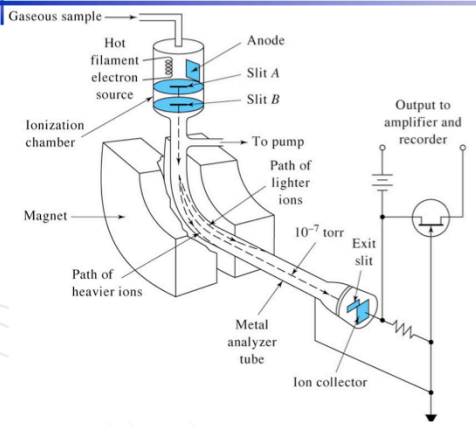


Fig. 20-13 (p567) Schematic of a magnetic sector spectrometer. Single-focusing spectrometer: ions of the same m/z but with a small diverging directional distribution are focused at a point after the exit.

Kinetic energy of ion:

$KE = z \cdot e \cdot V = 1/2 \cdot m \cdot v^2$

Magnetic force:

$F_B = B \cdot z \cdot e \cdot v$

Centripetal force:

$F_c = mv^2/r$

Only for ions with

$F_B = F_C$ can exit the slit

$m/z = B^2r^2e/2V$

For fixed radius & charge

- use permanent magnet, and vary A and B potential V
- Fixed V, vary B of electromagnet

Double-focusing vs. single focusing analyzer

single-focusing magnetic sector analyzers R_{max} < 2000,
Because 1) ions *have initial translational energy (Boltzmann distribution)*
2) angular distribution

Double focusing spectrometer: adding an electrostatic analyzer to focus ions of unique m/z at entrance slit to magnetic sector,

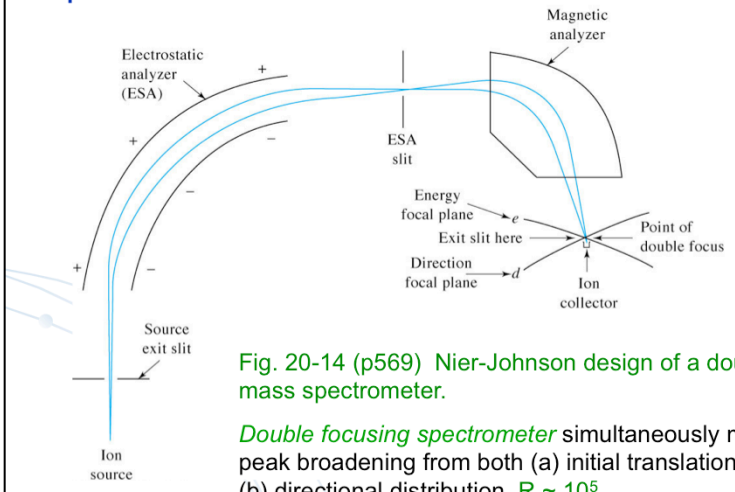
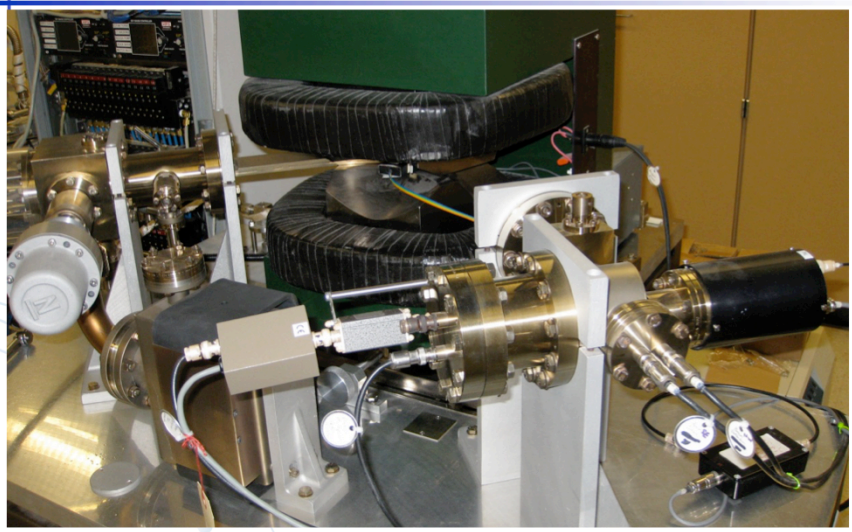


Fig. 20-14 (p569) Nier-Johnson design of a double-focusing mass spectrometer.

Double focusing spectrometer simultaneously minimizes ion peak broadening from both (a) initial translation energy and (b) directional distribution. R ~ 10^5



2.3.2 Quadrupole analyzer

Ions travel parallel to four rods
Opposite pairs of rods have opposite
VRFcos(2πft) and **U_{DC}**
Ions try to follow alternating field in helical trajectory

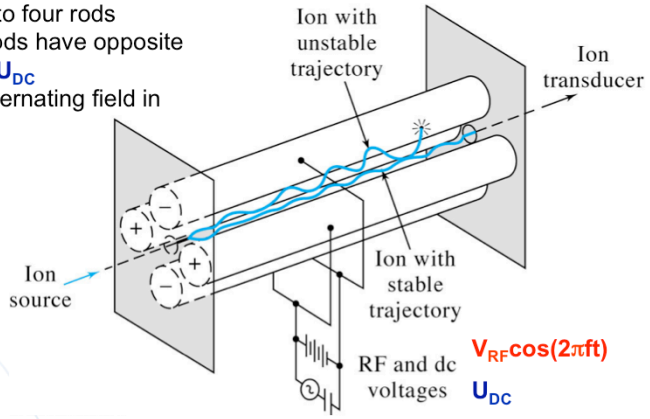
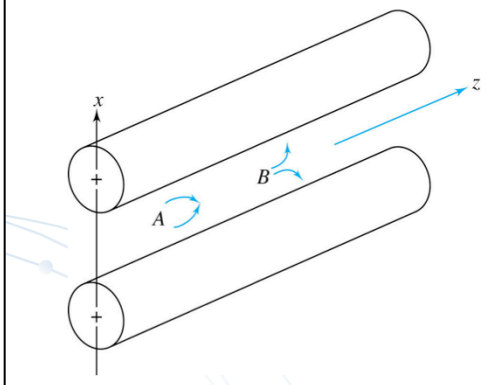


Fig. 11-6 (p283) A quadrupole mass spectrometer

$V_{RF}\cos(2\pi ft) + U_{DC}$



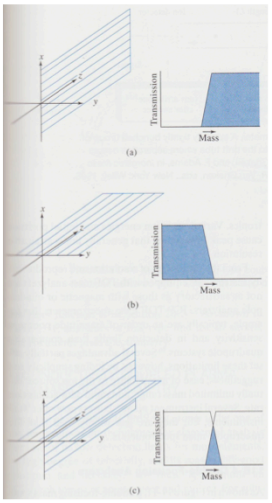


Fig. 11-7 (p288) operation of a quadrupole in xz plane

A video

https://www.youtube.com/watch?v=8AQaFdI1Yow

- Stable path only for one m/z value for each field frequency

$U_{DC} = 1.212 m f^2 r_0^2$

$V_{RF} = 7.219 m f^2 r_0^2$

$U_{DC} / V_{RF} = 1.212/7.219 = 0.1679$

$R = 0.126/(0.16784 - U_{DC}/V_{RF})$

- Harder to push heavy molecule – $m/z_{max} < 4000$
- $R_{max} \sim 500$

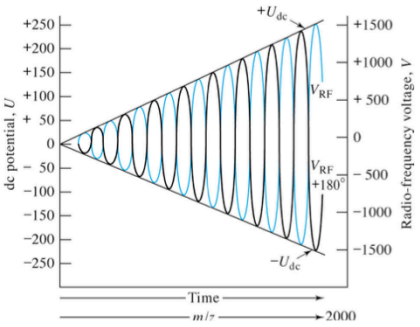
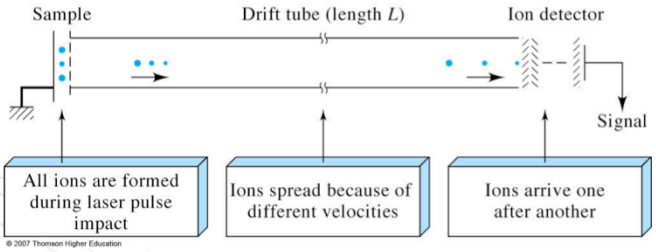


Fig. 11-7 (p288) Change of U_{DC} and V_{RF} during mass scan

2.3.3 Time-of-flight (TOF) analyzer



$$t_{TOF} = \frac{L}{v}$$

$$v = \sqrt{2KE/m}$$

$$KE = zeV$$

$$t_{TOf} = L\sqrt{\frac{m}{2ZeV}}$$

Fig. 11-10 (p290) A TOF mass spectrometer

Mass resolution of TOF

$$t_{TOf} = L\sqrt{\frac{m}{2ZeV}}$$

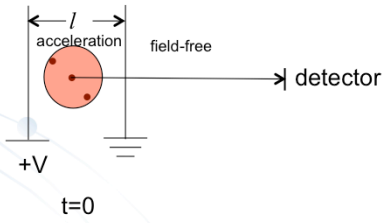
$$\frac{m}{dm} = \frac{t}{2dt}$$

$$R = \frac{m}{\Delta m} = \frac{t}{2\Delta t} = \frac{L}{\Delta x}$$

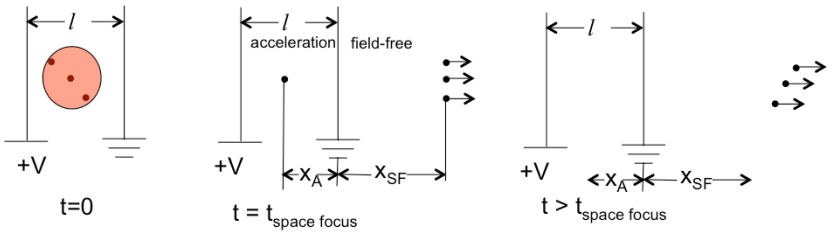
where Δx is the thickness of an ion packet approaching the detector

Spatially indefinite ion production due to a finite Laser focus size:

1) formation of ions at different potential energies which are converted into different KE after acceleration, causing different $t_{TOF.}$
2) Different flight length due to this spatial distribution also causes different $t_{TOF.}$



First-order space focus in two-electrode, single-stage ion source linear TOF



$$\frac{1}{2}mv_A^2 = qV\frac{x_A}{L},\ \text{so}\ v_A = \sqrt{2qV/mL}\cdot\sqrt{x_A} = K\sqrt{x_A}$$

$$t_{TOF} = t_A + t_{SF} = \frac{2x_A}{K\sqrt{x_A}} + \frac{x_{SF}}{K\sqrt{x_A}} = \frac{1}{K}\left(2\sqrt{x_A} + \frac{x_{SF}}{\sqrt{x_A}}\right)$$

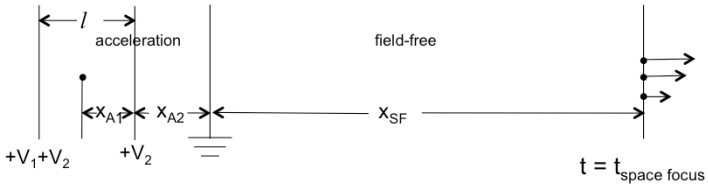
requiremnt for space focus: $\frac{dt_{TOF}}{dx_A} = \frac{1}{K}\left(2\cdot\frac{1}{2}\cdot\frac{1}{\sqrt{x_A}} + x_{SF}\left(-\frac{1}{2}\right)\frac{1}{\sqrt[3]{x_A}}\right) = \frac{1}{K}\left(\frac{1}{\sqrt{x_A}} - \frac{x_{SF}}{2x_A\sqrt{x_A}}\right) = 0$

$$x_{SF} = 2x_A$$

For a simple two-electrode ion source, the distance $x_A + x_{SF} = 3x_A$ is too short for mass resolution by flight time

2nd-order space focus
in three-electrode, two stage ion source linear TOF

(W. C. Wiley and I. H. McLaren, *Rev. Sci. Instru.* 1955, **26**, 1150-1157)



$$x_{A1} = \frac{1}{2} v_1 t_1$$

$$x_{A2} = \frac{1}{2}(v_1 + v_2) t_2$$

$$x_{SF} = v_2 t_3$$

$$t_{TOF} = t_1 + t_2 + t_3 = \frac{2x_{A1}}{v_1} + \frac{2x_{A2}}{v_1 + v_2} + \frac{x_{SF}}{v_2}$$

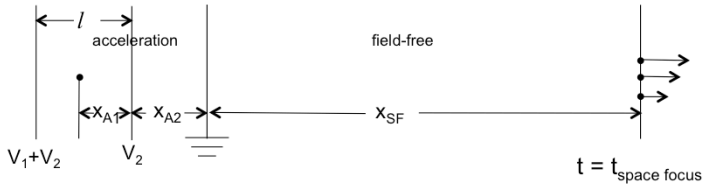
Look for x_{SF} so that $(dt_{TOF} / dx_{A1} = 0)$,

which leads to $x_{A1} = \frac{x_{SF} - 2x_{A2}}{2(x_{SF} + x_{A2})}\left(x_{SF}\left(\frac{x_{SF} - 2x_{A2}}{3x_{SF}}\right)^{3/2} + x_{A2}\right)$

Advantages and disadvantages of linear TOF mass spectrometer

Advantages	Disadvantages
Pulsed mode of operation makes it suitable for use with MALDI (paves the way for new applications not only for biomolecules but also for synthetic polymers and polymer/biomolecule conjugates)	Low resolution power (R = 100 – 2000)
Capacity to acquire spectra rapidly for averaging	Requires higher vacuum than most other types of mass spectrometers
No upper limit for the m/z scale. Can detect neutrals in linear mode, which greatly increases signal from fragile compounds, *e.g.* carbohydrates	Operates at a constant resolving power (R); *i.e.*, resolution changes with m/z value

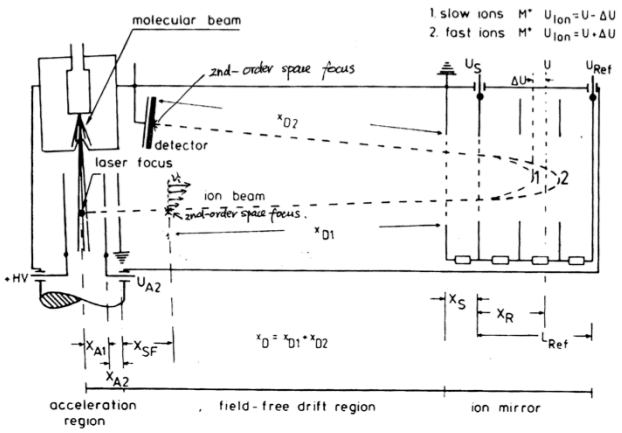
2nd-order space focus
in three-electrode, two stage ion source linear TOF



Take the space focus as the starting point, ions have no spatial temporal distributions, but with different kinetic energy

flight-time broads in the drift region behind the space focus due to the pure kinetic energy → this can be corrected for by a “Reflectron TOF”

Reflectron TOF: to correct for flight-time broadening in the drift region behind the space focus due to the pure kinetic energy distribution

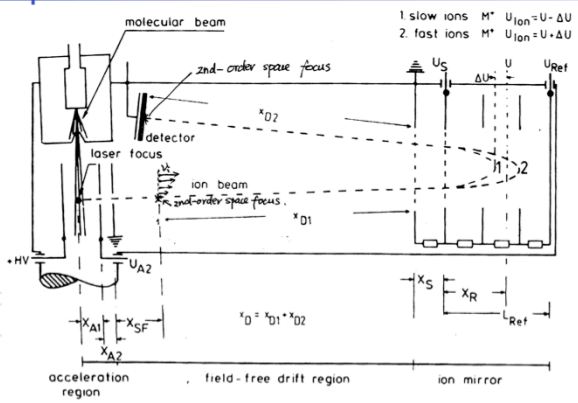


Ion mirror consisting of two successive homogeneous electric fields (three electrodes) for decelerating, reflecting & accelerating

After drifting x_{D1}, the ions w/ high kinetic energy first enter into the ion mirror, followed by those w/ lower kinetic energy.

The former penetrates deeper into the reflecting filed than the later, resulting in a larger residence time within the reflector for high energy ions than for the lower energy ions.

Reflectron TOF: 2nd order space focus



1) Choosing appropriate x_{D1}, x_{D2}, x_S, x_R, U_S, U_{Ref}, the shorter TOF of high energy ions in the field-free drift region is compensated for by their longer residence time within the reflector.

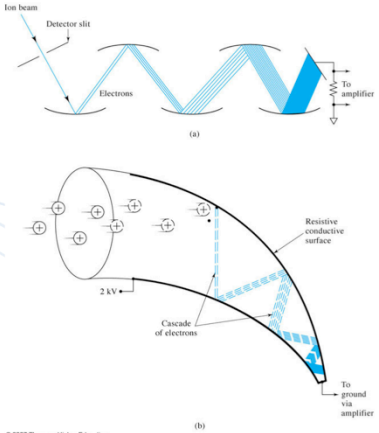
2) Assume $x_{D1}=x_{D2}$, and take the point when ions of one m/z are stopped within the reflector before being reflector as the starting time, the reflector acts as an ion source. This ion source can be constructed to have a 2nd-order space focus

$$x_R = \frac{x_D - 2x_S}{2(x_D + x_S)}\left(x_D\left(\frac{x_D - 2x_S}{3x_D}\right)^{3/2} + x_S\right), where\ x_D = x_{D1} = x_{D2}$$

Advantages and disadvantages of the reTOF mass spectrometer

Advantages	Disadvantages
Pulsed mode of operation makes it suitable for use with MALDI	Limited m/z range compared to that of the linear TOF instrument
Capacity to acquiring spectra rapidly for averaging and good definition of narrow chromatograohic peaks	Requires higher vacuum than some other types of mass spectrometers
Not only lengthens the ion flight path, but it aids in reducing the angular dispersion of the ion trajectories; R= 20,000: Higher resolving power results in accurate mass measurements to the nearest 0.1 millimass unit for determining elemental compositions for ions less than 500 Da.	Pulsed mode of operation is not necessarily ideal for use as chromatograhic detector
No problems with spectral skewing in GC/MS	High price partially due to the requirement of a high vacuum

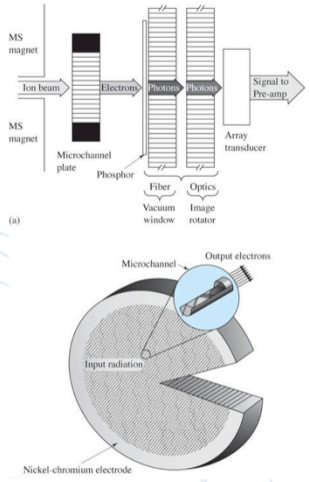
2.4 Detector
Electron Multipliers



Each ions produces 10^5 - 10^8 electrons, this is the gain for the multiplier

Fig. 11-2 (p284) Electron multiplier

Microchannel Plates (MCP)



Consist of an array of tiny tubes (ϕ 6 μm) made of lead glass

Each tube acts as an electron multiplier, gain ~1,000

Combined with phosphorescence screen behind the MCP, cascade of electrons produces a flash of light → **ion imaging**

Fig. 11-4 (p286) MCP

3 Application of MS

3.1 Identification of pure compounds

1) Nominal M^+ (or MH^+, $[M-H]^-$) peak gives MW (not EI)
2) Exact m/z (fractional m/z resolution obtained from double-focusing magnetic sector, R-TOF, etc) can give stoichiometry () but not molecular structure
3) Fragment peaks give evidence for functional groups, *e.g.*,

   $[M - 15]^+$ peak → methyl

   $[M - 18]^+$ → OH or water

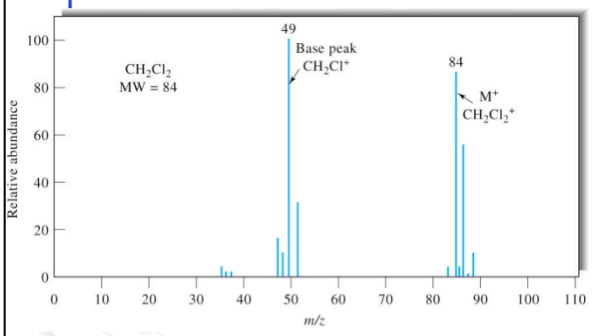
   $[M - 45]^+$ → COOH

   series $[M - 14]^+$, $[M - 28]^+$, $[M - 42]^+$… → sequential CH_2 loss in alkanes
4) Isotopic peaks can indicate presence of certain atoms Cl, Br, S, Si, etc.

   Isotopic ratios also suggest plausible molecules from M^+, $(M+1)^+$ and $(M+2)^+$ peaks.

   $^{13}C/^{12}C = 1.08\%$, $^{2}H/^{1}H = 0.015\%$

   For C_2H_6, $(M+1)^+$ peak intensity should be (2 x 1.08) + (6 x 0.015) = 2.25% of the M^+ peak
5) Comparison with library spectra



What about peaks at greater m/z than M^+?

Two sources

-Isotope peaks –same chemical formula but different masses

- $^{12}C^1H_2{}^{35}Cl_2$ m=84
- $^{13}C^1H_2{}^{35}Cl_2$ m=85
- $^{12}C^1H_2{}^{35}Cl^{37}Cl$ m=86
- $^{13}C^1H_2{}^{35}Cl^{37}Cl$ m=87
- $^{13}C^1H_2{}^{37}Cl_2$ m=88

CH_2Cl_2,

^{13}C, 1 x 1.08 = 1.08 **^{37}Cl, 2 x 32.5%**

^2H, 2 x 0.015 = 0.030%

$(M+1)^+/M^+$ = 1.21% **$(M+2)^+/M^+$ =65%**

- Heights vary with isotope abundance ^{13}C 1.08%,

^2H is 0.015%, ^{37}C is 32.5%

Fig. 20-4 (p556) EI mass spectra of methylene chloride and 1-pentanol

For C_nH_m, the probablilty to have $(M+1)^+/M^+$ is $C_n^1p + C_m^1q$

p is the isotope ratio for ^{13}C, p = 1.08%; q is the isotope ratio for 2H, q = 0.015%

case:	Probability
one ^{13}C	C_n^1p
one ^1H	C_m^1q

For C_nH_m, $(M+2)^+/M^+$ is $C_n^2p^2 + C_n^1p \times C_m^1q + C_m^2q2$

case:	Probability
two ^{13}C x 2	$C_n^2p^2$
one ^{13}C + one ^1H	$C_n^1p \times C_m^1q$
two ^1H x 2	$C_m^2q^2$

cyclohexne C_8H_{12}

(M+1)+/M+		
^{13}C	C_n^1p	6.48%
^1H	C_m^1q	0.18%
Total		6.66%

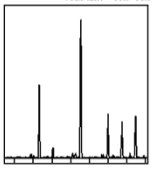
$(M+2)^+/M^+$		
^{13}C x 2	$C_n^2p^2$	0.18%
^{13}C + ^1H	$C_n^1p \times C_m^1q$	0.01%
^1H x 2	$C_m^2q^2$	0.00%
Total		0.19%

$C_a^b = ax(a-1)x(a-2)\ldots x(a-b)/b!$

3.2 Reaction kinetics and dynamics

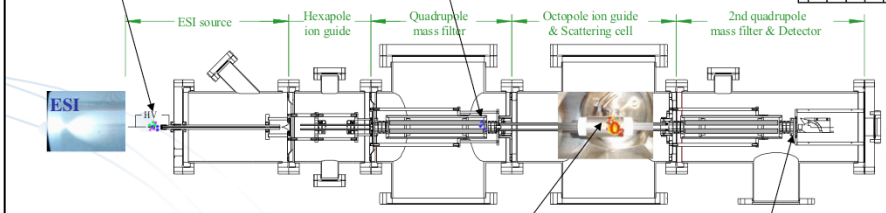
$$\sigma = k / v_{rel} = \frac{I_{product} k_B T}{I_{reactant} P_{cell} l_{cell}}$$

Guided-Ion-Beam Tandem Mass Spectrometer



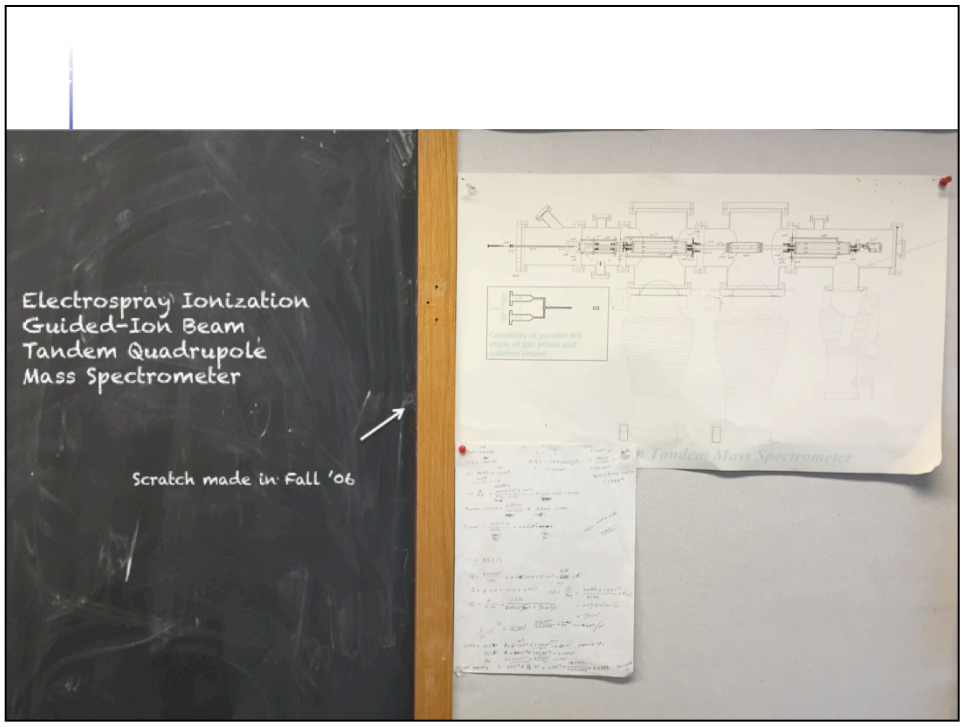
1. Generation of biomolecular ions by ESI

2. Ions are passed into a quadrupole for mass selection

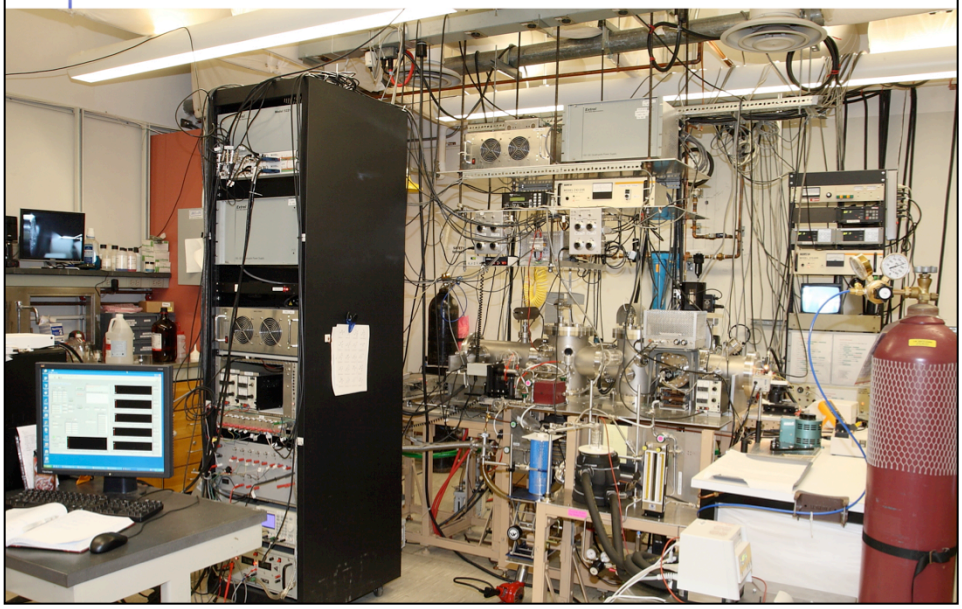


3. Mass-selected ions are guided into an octopole surrounded by a collision cell, and scattered from $^1O_2$ contained within

4. Product ions are mass analyzed & counted


Electrospray Ionization
Guided-Ion Beam
Tandem Quadrupole
Mass Spectrometer
Scratch made in Fall '06

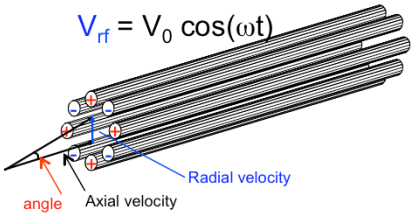
Guided-Ion-Beam Tandem Mass Spectrometer



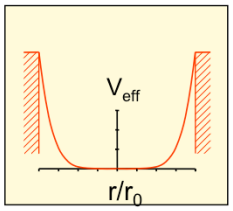
Radical Frequency Ion Guide
Transfer ions from one segment of a mass spectrometer to another

$V_{eff} = 4q^2V_{rf}^2(r/r_0)^6/(mr_0^2\omega^2)$

$V_{rf} = V_0 \cos(\omega t)$



r_0: radius of inscribed circle by rods



The ion guide traps ions in the radial direction, minimizes losses of reactant and product ions resulting from scattering off neutral molecules, and guides the ions to the next stage of the instrument

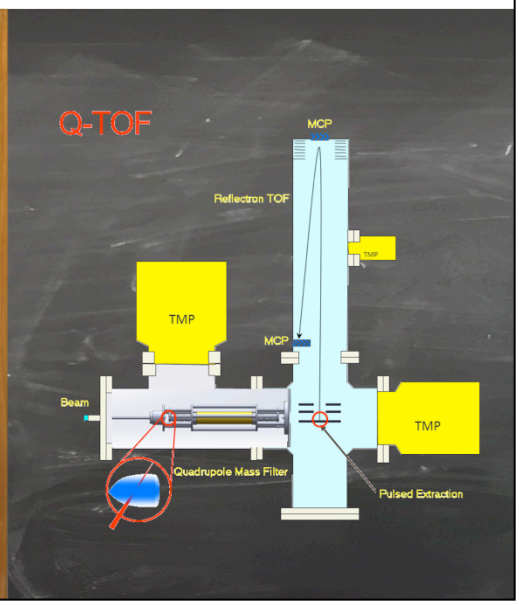
Quadrupole-ReTOF Tandem Mass Spectrometer

Q-TOF in NSB D319, ongoing

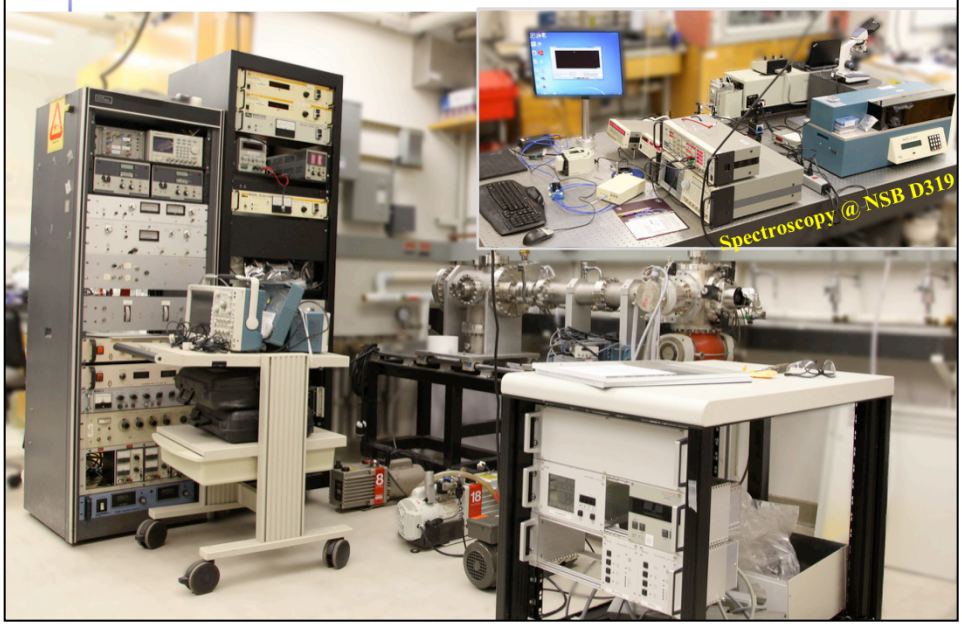
Quadrupole
Reflectron Time-of-Flight
Tandem Mass Spectrometer

Coupled with Time-Resolved
Emission/Absorption
Spectroscopy

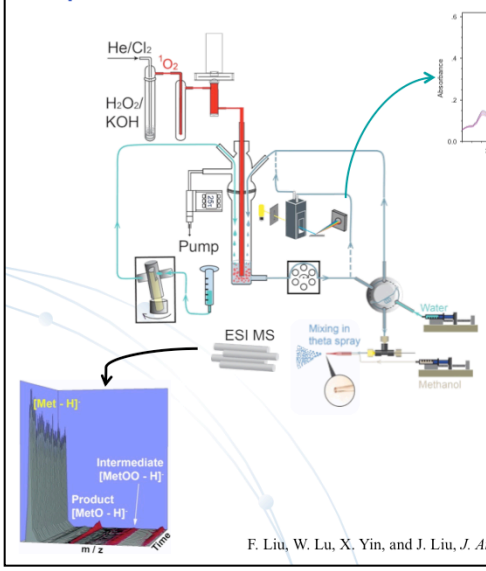
*A project for MS and
undergraduates,
from Fall'14

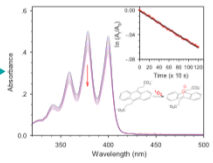


Quadrupole-ReTOF Tandem Mass Spectrometer



On-Line Kinetics using MS and Spectroscopy





Our on-line ESI MS

- **Sample air-tight and low pressure system**
- **Short the lag between sampling and MS, to help detect short-lived species**
- **Negative ESI of water solution**

Conventional ESI MS (on-line or off-line)

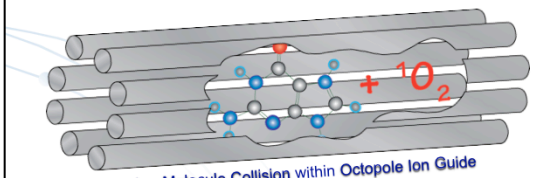
- Sample at open-air, atmosphere
- Long transfer time
- Cannot ESI water in negative mode (discharge at lower V than electrospray)

F. Liu, W. Lu, X. Yin, and J. Liu, *J. Am. Soc. Mass Spectrom. doi:*10.1007/s13361-015-1237-4, 2015.

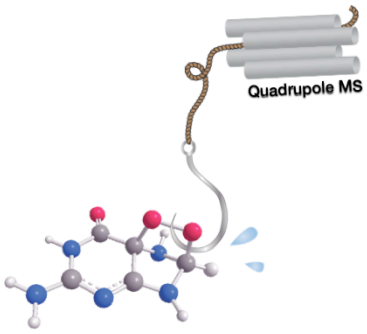
S.

Capture Transient Species in The Gas-Phase MS

Transient **endoperoxide**, which initiates the singlet O2-induced lesions of the guanine base of DNA, was captured in **gas-phase ion-molecule collision mass spectrometry**. The experiment, corroborated with kinetic modeling and dynamics simulations, tells about the early-stage dynamics of guanine oxidation which is missing from conventional condensed-phase study.



Ion-Molecule Collision within Octopole Ion Guide



4 Summary

One of the most powerful analytical tools
Sensitive (10^{-6} -10^{-13}g)
Range of ion sources for different situation
Element comparison for small and large MW – biomolecules
Structural information
Qualitative and quantitative analysis of mixtures
Composition of solid surfaces
Isotopic information in compounds
Reaction kinetics and applications
….., etc.

But
Complex instrumentation
Expensive: high resolution
Structures obtained indirectly
Complex spectra/fragmentation for hard ionization sources
Simple spectra for soft ionization sources