Molecular mass spectrometry

Chapter 20

The study of “molecular ions”

\[ M + e^- \rightarrow M^+ + 2e^- \]
Ionization energy?
El Ionization??

Increasing energy content in ion

(a)

(d)
SOFT vs. HARD IONIZATION METHODS???
Mass Spectrum of Ethyl Benzene

MW = 106

Base peak

106 Molecular ion peak
# Ion Sources for Mass Spectrometers

*Unless you “create” an ion you won’t see it!*

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

Energy driven process $\Rightarrow$ HARD IONIZATION, SOFT IONIZATION
MS with “Hard” and “Soft” Sources

(a) Base peak $C_3H_7^+$

(b) Base peak $CH_3(CH_2)_3CH_2^+$

Relative abundance

$m/z$

41, 55, 70, 83, 91, 112

$CH_3(CH_2)_3CH_2OH$

$M^+$ 158

$CH_3(CH_2)_3CH_2OH$

$M - OH)^+$

$(M - 1)^+$ 157
Electron Impact Source

Electron Ionization (EI)  \[ M + e^- \rightarrow M^+ + 2e^- \]
Electron impact source

**Filament** - Typically made of Re. Our source of 70 eV electrons.

**Target** - Anode used in association with the filament to produce electrons.

**Repeller** - Positively charged electrode used to ‘push’ positive ions out of the ionization source.

**Lens stack** - Series of increasingly more negative electrodes used to accelerate our ions to constant kinetic energy.
Typical Reactions during Electron Impact

Molecular ion formation

Fragmentation

\[ \text{ABCD} + e^- \rightarrow \text{ABCD}^{*+} + 2e^- \]
\[ \text{ABCD}^{*+} \rightarrow \text{A}^+ + \text{BCD}^* \]
\[ \text{ABCD}^{*+} \rightarrow \text{A}^+ + \text{BCD}^+ \rightarrow \text{BC}^+ + \text{D} \]
\[ \text{ABCD}^{*+} \rightarrow \text{CD}^+ + \text{AB}^+ \rightarrow \text{B} + \text{A}^+ \]
\[ \text{ABCD}^{*+} \rightarrow \text{AB}^+ + \text{CD}^+ \rightarrow \text{D} + \text{C}^+ \]
\[ \text{ABCD}^{*+} \rightarrow \text{AB}^+ + \text{CD}^+ \rightarrow \text{C} + \text{D}^+ \]

Rearrangement followed by fragmentation

\[ \text{ABCD}^{*+} \rightarrow \text{ADBC}^{*+} \rightarrow \text{BC}^+ + \text{AD}^+ \]
\[ \text{ABCD}^{*+} \rightarrow \text{ADBC}^{*+} \rightarrow \text{AD}^+ + \text{BC}^+ \]

Collision followed by fragmentation

\[ \text{ABCD}^{*+} + \text{ABCD} \rightarrow (\text{ABCD})^{*2+} \rightarrow \text{BCD}^* + \text{ABCD}A^+ \]

Energy = 70eV \( \rightarrow \) 6700 kJ/mol

Typical bond energies \( \rightarrow \) 200 to 600 kJ/mol \( \rightarrow \) EXTENSIVE FRAGMENTATION
Electron Impact Spectra

- Different molecules behave differently
- Good molecular ion $\Rightarrow$ little fragmentation
- No molecular ion $\Rightarrow$ extensive fragmentation
- Isotopes are extremely important!
- Molecular ion isotopic cluster
Mass Numbers

- **Nominal Mass** = integer mass of the most abundant isotope
- **Mono-isotopic Mass** = accurate mass of the most abundant isotope
- **Average Mass** = atomic or molecular weight
# How many combinations?

## Exact Masses and Natural Isotopic Abundance Ratios

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Integer Mass</th>
<th>Exact Mass</th>
<th>Abundance</th>
<th>X+1 Factor*</th>
<th>X+2 Factor*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>1</td>
<td>1.0078</td>
<td>99.99</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>D or $^2\text{H}$</td>
<td>2</td>
<td>2.0141</td>
<td>0.01</td>
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<td>Carbon</td>
<td>$^{12}\text{C}$</td>
<td>12</td>
<td>12.0000</td>
<td>98.91</td>
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<tr>
<td></td>
<td>$^{13}\text{C}$</td>
<td>13</td>
<td>13.0034</td>
<td>1.1</td>
<td>1.1$n_C$</td>
<td>0.0060$n_C$</td>
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<tr>
<td>Nitrogen</td>
<td>$^{14}\text{N}$</td>
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<td>14.0031</td>
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<tr>
<td></td>
<td>$^{15}\text{N}$</td>
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<td>15.0001</td>
<td>0.4</td>
<td>0.37$n_N$</td>
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<td>Oxygen</td>
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<td>16</td>
<td>16.9949</td>
<td>99.76</td>
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<tr>
<td></td>
<td>$^{17}\text{O}$</td>
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<td>16.9991</td>
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<td>0.20$n_O$</td>
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<td>Fluorine</td>
<td>F</td>
<td>19</td>
<td>18.9984</td>
<td>100</td>
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<tr>
<td>Silicon</td>
<td>$^{28}\text{Si}$</td>
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<td></td>
<td>$^{29}\text{Si}$</td>
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<td>28.9765</td>
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<td>Phosphorus</td>
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<td>Sulphur</td>
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<td>Chlorine</td>
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<td>Bromine</td>
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<td>Iodine</td>
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<td>127</td>
<td>126.9045</td>
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</tbody>
</table>


## Abundance, M + 1 Peak Height

<table>
<thead>
<tr>
<th>Formula</th>
<th>M + 1</th>
<th>M + 2</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_4\text{O}$</td>
<td>3.36</td>
<td>0.24</td>
<td>83.0120</td>
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<td>$\text{C}_2\text{H}_4\text{N}_2$</td>
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<td>0.06</td>
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<td>$\text{C}_2\text{H}_2\text{O}_2$</td>
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<td>0.45</td>
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<td>$\text{C}_2\text{H}_2\text{N}_2\text{O}$</td>
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<td>$\text{C}_2\text{H}_2\text{N}_2\text{O}$</td>
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<tr>
<td>$\text{C}_2\text{H}_2\text{O}_2$</td>
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<td>0.48</td>
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<td>83.0861</td>
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</table>

$M = 83$

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<th>Formula</th>
<th>M + 1</th>
<th>M + 2</th>
<th>Molecular Weight</th>
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</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_4\text{O}$</td>
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<td>$\text{C}_2\text{H}_4\text{N}_2\text{O}$</td>
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<td>$\text{C}_2\text{H}_2\text{N}_2\text{O}_2$</td>
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<td>$\text{C}_2\text{H}_2\text{N}_2\text{O}_2$</td>
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<td>$\text{C}_2\text{H}_2\text{N}_2\text{O}_2$</td>
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<td>$\text{C}_2\text{H}_2\text{N}_2\text{O}_2$</td>
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</table>

$M = 84$
Graphical representation of relative isotope peak intensities for any given ion containing the indicated number of chlorine and/or bromine atoms.

<table>
<thead>
<tr>
<th>CHLORINE-BROMINE ISOTOPE ABUNDANCE RATIOS</th>
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<tbody>
<tr>
<td>Cl-Br X X+2 X+4 X+6 X+8 X+10</td>
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<tr>
<td>Cl  100 32.5</td>
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<tr>
<td>Cl₂ 100 65.0 10.6</td>
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<tr>
<td>Cl₃ 100 97.5 31.7 3.4</td>
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<tr>
<td>Cl₄ 76.9 100 48.7 10.5 0.9</td>
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<tr>
<td>Cl₅ 61.5 100 65.0 21.1 3.4 0.2</td>
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<tr>
<td>Cl₆ 51.2 100 81.2 35.2 8.5 1.1</td>
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<tr>
<td>C#</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>C₁</td>
</tr>
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<td>C₂</td>
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<td>C₅</td>
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<td>M - 44</td>
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<tr>
<td>M - 60</td>
</tr>
<tr>
<td>M - 90</td>
</tr>
</tbody>
</table>
Chemical ionization

A soft ionization method.

It relies on our charge being transferred from a reagent molecule to our sample.

\[
\text{Reagent ion + molecule} \quad \downarrow \\
\text{molecular ion + reagent ion}
\]

This results in reduced fragmentation and increased production of the molecular ion.
Field Ionization Source

- Molecular leak
- Gas beam
- Repellers
- Ionizing region
- Electron beam
- Filament
- Shield
- Electron slit
- First accel. slit
- Focus slit
- Second accel. slit
- Anode
- Ion accelerating region
- To mass analyzer
- CI REAGENT GAS
Chemical Ionization MS Sources

High Energy electrons →

\[ \text{CH}_4 \quad \text{CH}_4^+ \quad \text{CH}_3^+ \quad \text{CH}_2^+ \]

\[ \text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CH}_3 \]

\[ \text{CH}_3^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2 \]

Sample Molecule MH →

\[ \text{CH}_5^+ + \text{MH} \rightarrow \text{MH}_2^+ + \text{CH}_4 \]

\[ \text{C}_2\text{H}_5^+ + \text{MH} \rightarrow \text{MH}_2^+ + \text{C}_2\text{H}_4 \]

\[ \text{C}_2\text{H}_5^+ + \text{MH} \rightarrow \text{M}^+ + \text{C}_2\text{H}_6 \]

Molecule Ions →
EI vs. Cl

**EI (Electron Impact):**
- **Step 1:** M → M⁺
- **Step 2:** M⁺ → M⁺, A⁺, B⁺ etc. (Mass Spectrum)

**Cl (Chemical Ionization):**
- **Step 1:** R → R⁺
- **Step 2:** R⁺ → RH⁺
- **Step 3:** M → MH⁺ + R (Mass Spectrum)
Cl vs El data

Note reduced fragmentation of the Cl spectrum.

There is a larger M+1 peak and less fragmentation.

There is also a reduced amount of information regarding structure.
Desorption Methods

- Laser
- Energetic ion
- Energetic atom
- Fission fragment

Atoms on a surface → Ions
Field Ionization / Field Desorption Sources

- Apply large electric fields to carbon dendrites on a tungsten wire
- **Field Ionization** – gas is passed over ionization source
- **Field Desorption** – dipped in solution containing sample and placed back in spectrometer
Ionization vs. Desorption?
Field Ionization and Field Desorption

FIELD IONIZATION

\[ F = \frac{V}{k \cdot r} \]

\( K = \) shape factor (Sphere = 1, others = 1)

If \( V = 5000 \text{V}, r = 1 \mu \) \( \Rightarrow F = 500,000,000 \text{V/m} !!! \)
Field Ionization Sources

Apply large electric fields to carbon dendrites on a tungsten wire

Fig. 6.1 Scanning electron micrograph (×500) of high temperature activated FD emitter. (Reprinted with permission from W.D. Reynolds Anal. Chem., 51, 283A[4]: Copyright (1979) American Chemical Society)
Electron Impact (EI)

Field Ionization

Field Desorption

Glutamic Acid
Matrix Assisted Laser Desorption/Ionization (MALDI)

- MWs of polar biopolymers ranging from a few thousand to several hundred thousand daltons
- Solution of analyte is mixed with a large amount of radiation absorbing matrix material
- The solid material was placed on a metallic probe and inserted into a Time-of-Flight MS
- Mixtures exposed to a pulsed laser beam
- Complete MS measured between each pulse
MALDI
# Solid Matrix Materials for MALDI

## TABLE 20-4  Matrices Most Frequently Used for MALDI Together with the Usable Wavelengths*

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nicotinic acid</td>
<td>266, 220–290</td>
</tr>
<tr>
<td>Benzoic acid derivatives:</td>
<td></td>
</tr>
<tr>
<td>2,5-Dihydroxybenzoic acid</td>
<td>266, 337, 355</td>
</tr>
<tr>
<td>Vanillic acid</td>
<td>266</td>
</tr>
<tr>
<td>2-Amino-benzoic acid</td>
<td>266, 337, 355</td>
</tr>
<tr>
<td>Pyrazine-carboxylic acid</td>
<td>266</td>
</tr>
<tr>
<td>3-Aminopyrazine-2-carboxylic acid</td>
<td>337</td>
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<tr>
<td>Cinnamic acid derivatives:</td>
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<tr>
<td>Ferulic acid</td>
<td>266, 377, 355</td>
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<td>Sinapinic acid</td>
<td>266, 337, 355</td>
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<tr>
<td>Caffeic acid</td>
<td>266, 337, 355</td>
</tr>
<tr>
<td>3-Nitrobenzylalcohol</td>
<td>266</td>
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</tbody>
</table>

MALDI-TOF
MALDI Spectrum from Nicotinic Acid Matrix of Monoclonal Antibody (IgG)
Electrospray Ionization MS of Proteins and Peptides
FAB Ionization: Fast Atom Bombardment

(a) $\text{Xe} + e^- \xrightarrow{\text{ionization}} \text{Xe}^+ + 2e^-$

(b) $\text{Xe}^+ \xrightarrow{\text{acceleration}} \text{Xe}^+$

(c) $\text{Xe}^+ + \text{Xe} \xrightarrow{\text{charge exchange}} \text{Xe} + \text{Xe}^+$

SECONDARY ION MASS SPECTROMETRY $\rightarrow$ SIMS
FAB Ionization

Xe\(^+\)

Primary Ion Beam

Atom Gun

Xe\(^0\)

(a) Neutral atom beam

(b) Sample

Probe

±kV

(c) Probe tip

(d) Extraction and focusing

Secondary ion Beam to MS

Fig. 5.4  Schematic diagram of fast ion bombardment ion source
MS Instrument Components

Sample

10^{-5} - 10^{-8} \text{ torr}

Inlet system \rightarrow \text{Ion source} \rightarrow \text{Mass analyzer} \rightarrow \text{Detector}

Vacuum system

Signal processor

Readout
Gas/Liquid Inlet System

- Gas introduction
- Septum
- Liquid introduction
- Oven
- 1 to 3 L Reservoir
- Pin hole
- Metering volume
- Heating tape
- Vacuum
- To ion source
Solid/Matrix Inlet Systems

Sample

To vacuum

Ionization chamber

Heating coil
Magnetic Sector Analyzer

**Diagram**

- **Gaseous sample**
- **Ionization chamber**
- **Hot filament electron source**
- **Anode**
- **Slit A**
- **Slit B**
- **To pump**
- **Path of heavier ions**
- **Path of lighter ions**
- **Magnet**
- **10^-7 torr**
- **Exit slit**
- **Metal analyzer tube**
- **Ion collector**
- **Output to amplifier and recorder**
KE = \( z eV = \frac{1}{2} m v^2 \)

Magnetic Force = \( F_M = BzeV \)

Centripetal Force = \( F_c = \frac{m v^2}{r} \)

\( F_M = F_c \)

\( BzeV = \frac{m v^2}{r} \)

\( v = \frac{Bzer}{m} \)

\( \frac{m}{z} = \frac{B^2 r^2 e}{2V} \)

\( r = \text{radius of curvature} \)
Single Focusing Magnetic Sector

- Ions at source with same mass-to-charge ratio
- Ions with diverging directional distribution will be acted upon in the same way
- Brings ions with different directional orientations to focus
- Limits the resolution
Double Focusing Mass Spectrometers

- Passes ions through an electrostatic analyzer (ESA) which limits the range of the kinetic energy of ions reaching the magnetic sector
- Only ions with the same average kinetic energy pass through the ESA slits into the magnetic sector
- Two focal planes at the ion collector
  - Energy focal plane
  - Directional focal plane
- Increases resolution
Double Focusing Mass Spectrometer
**Quadrupole operation:** What goes where and when?

- **U** = DC component, amplitude only
- **V** = AC component, sinus wave form!
Mass Analyzers: ION TRAPS

• Three-dimensional quadrupole field
• Wolfgang Paul Nobel Prize 1989
• MS^n capability.
Time of Flight Analyzers

Time-of-flight mass spectrometry (TOF for short)

Although, first commercially introduced only seven years ago (1995), TOF-MS has rapidly been embraced by the analytical community.

While originally used as mass analyzers for use with peptides, they are now applied to problems which range nanospray analysis of biological samples to liquid chromatography (LC/MS/MS) of pharmaceutical preparations.

The rapid acceptance of TOF analyzers is due to their attractive combination of high sensitivity and high mass accuracy, not to mention their simplicity.
**Mass Analyzers:** ICR-MS, the sound of ions

\[ F = qVB \]
\[ F' = \frac{mv^2}{r} \]

**Centripetal**

\[ qB = \frac{mv}{r} \]

**Centrifugal**

**Frequency**

\[ \nu = \frac{v}{2\pi r} \]

**Angular velocity**

\[ \omega_c = 2\pi \nu = \frac{v}{r} = \frac{q}{m} B \]

\[ \frac{m}{q} = \frac{B}{2\pi \omega_c} \]

*Excitation*

*Detection*

*Trapping*

*Intensity → Fourier transform → Twelve frequencies*
ICR: Let the magic begin!

1) Ions before excitation. They are in their natural cyclotron radius within the magnetic field.

2) Ions during excitation with a radio frequency. This excites the ions to a larger cyclotron radius.

3) Ions after excitation. The cyclotron radius remains in its larger state.

\[
m = \frac{B}{q} \frac{B}{2\pi \omega_c}
\]
Mass Analyzers: ICR

a. RF Excitation

b. Detected Time Domain Image Current

c. Fourier Transform

d. Resulting Mass Domain Spectrum
Tandem Mass spectrometry

Diagram showing the components of a tandem mass spectrometer:
- Ion source
- Quadrupole 1: first-stage mass separation
- Quadrupole 2: collision focusing
- Quadrupole 3: second-stage mass separation
- Electron multiplier: detection
- Sample inlets
- Ionizer
- Turbomolecular pumps
- Analyzer
- Collision gas inlet

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Figure 1-1 - A diagram of an MS/MS experiment depicting the two different stages of mass dispersion.
MSMS Experiments

Quadrupole 1 (MS1)  
Quadrupole 2 (CID Collision cell)  
Quadrupole 3 (MS2)

(1) select m/z  
product ion scan

(2) scanning  
precursor ion scan (selected m/z)

(3) scanning  
neutral loss scan
Faraday Collector

Single Collector (faraday cage or cup)

- Defining slit
- Secondary electron suppressor (-90 V)
- Guard ring (reduces leakage current to collector)
- Magnets - prevent electron loss from collector
- Faraday cage
- To Amplifier
• Extending the principle used with a Faraday cup.

• Series of dynodes maintained at ever increasing potentials.

• Ions strike the dynode surface, resulting in the emission of electrons.

• These secondary electrons are then attracted to the next dynode.

• Typical amplification or current gain of an electron multiplier is one million.
• Ions initially strike a dynode, resulting in the emission of electrons.

• Electrons then strike a phosphorus screen.

• The phosphorus screen, much like the screen on a television set, releases photons once an electron strikes.

• The primary advantage of the conversion dynode setup is that the photomultiplier tube is sealed in a vacuum (photons pass through sealed glass).
## Typical vacuum pumps

<table>
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<tr>
<th>Pump</th>
<th>Lowest Attainable Pressure</th>
<th>Typical Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical pump</td>
<td>$10^{-3} - 10^{-4}$ torr</td>
<td>roughing or backing pump</td>
</tr>
<tr>
<td>Diffusion pump</td>
<td>$10^{-6}$ torr</td>
<td>vacuum lines</td>
</tr>
<tr>
<td>Turbomolecular pump</td>
<td>$10^{-9}$ torr</td>
<td>high-vacuum systems</td>
</tr>
</tbody>
</table>
Oil diffusion pump

A diffusion pump is another commonly used type of high vacuum pump.

- inlet
- water cooling coils
- vents
- stacks
- heater
  to roughing pump
Turbomolecular pump

A turbomolecular pump relies on a series of blades or airfoils that spin at 30,000 - 90,000 RPM. This tends to deflect gas molecules down and out the outlet.