mass spectrometry (MS)
bruice chapter 13

- does not involve electromagnetic radiation, ∴ spectrometry not spectroscopy
- gives MM, molecular formula & structural features of molecule
- sample injected into mass spectrometer
- vaporized, & bombarded by stream of high energy (70 eV) e⁻
  - e⁻ bombardment removes e⁻ from sample molecule, producing **positively charged radical cation** called **molecular ion**, which then **fragments** further, producing
  - positively charged fragments, repelled by positively charged **repeller plate**, pass between two negatively charged **focusing & accelerating plates** into **analyser tube**
  - magnet surrounding tube produces magnetic field, causing positively charged fragments to move in a curved path; **radius** of curve determined by **mass/charge ratio** (\(m/z\))
  - as charge is constant (e⁺), \(m/z\) ratio is molecular mass of fragment
- if fragment path, as determined by m/z ratio, matches curvature of analyser tube, fragment passes down tube, through ion exit slit, & strikes collector
- collector records relative number of fragments of that m/z passing through slit
- by slowly increasing magnetic field strength, fragments of increasing m/z values are guided down tube & through slit onto collector
- plot of relative abundance of each fragment versus its m/z value (& ∴ molecular mass) known as mass spectrum (ms)
- only (stable) positively charged particles reach detector & appear on ms
- fragmentation pattern determined by
  - bond strength
  - fragment stability
- all C-C bonds in pentane are of ~same strength
- C-2/C-3 bond fragmentation gives $1^\circ$ C$^+$ & $1^\circ$ radical
  C-1/C-2 bond fragmentation gives $1^\circ$ C$^+$ & CH$_3$ radical
- $1^\circ$ radical more stable than methyl radical
- C-2/C-3 bond more likely to break than C-1/C-2 bond
- C-2/C-3 bond fragmentation gives ions of m/z 43 & 29
  C-1/C-2 bond fragmentation gives ions of m/z 57 & 15
- base peak at m/z 43 indicates preference for C-2/C-3 bond fragmentation
- only (stable) positively charged particles reach detector & appear on ms

\[
[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3]^+ \quad \text{m/z} = 72
\]

\[
\rightarrow \text{CH}_3\text{CH}_2\text{CH}_2^+ \quad + \quad \text{CH}_3\text{CH}_2
\quad \text{m/z} = 43
\]

\[
\rightarrow \text{CH}_3\text{CH}_2^+\text{CH}_2 \quad + \quad \text{CH}_3\text{CH}_2
\quad \text{m/z} = 29
\]

\[
\rightarrow \text{CH}_3\text{CH}_2\text{CH}_2^+\text{CH}_2 \quad + \quad \text{CH}_3
\quad \text{m/z} = 57
\]

\[
\rightarrow \text{CH}_3\text{CH}_2\text{CH}_2^\cdot\text{CH}_2 \quad + \quad \text{CH}_3^\cdot
\quad \text{m/z} = 15
\]
- fragmentation pattern of 2-methylbutane very similar to that of pentane

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{CH}_3\text{CHCH}_2\text{CH}_3
\]

- single notable exception is intensity of peak at \( m/z \) 57; is more likely to lose \( \text{CH}_3 \) radical, as \( 2^\circ \text{C}^+ \) formed more stable than \( 1^\circ \text{C}^+ \)

\[
\text{CH}_3 \\
\text{[CH}_3\text{CHCH}_2\text{CH}_3]^+ \\
\quad \text{molecular ion} \\
\quad m/z = 72
\]

\[
\rightarrow \text{CH}_3^+\text{CHCH}_2\text{CH}_3 + \cdot\text{CH}_3 \\
\quad m/z = 57
\]
- peaks of 1 or 2 units less than carbocation m/z values due to further fragmentation involving loss of H atoms

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+ \xrightarrow{-\text{H}^+} [\text{CH}_3\text{CHCH}_2]^+ \xrightarrow{-\text{H}^+} \text{CH}_2\text{CH}==\text{CH}_2^+ \]

- peak at 1 unit more than molecular ion m/z (M+1 peak) due to isotopic effect of $^{13}\text{C}$
  - as 1.11% of naturally occurring C is $^{13}\text{C}$, relative abundance of M+1 peak in spectrum of compound of formula $\text{C}_n$ should be $n(1.1\%)$ of molecular ion
alkyl halides
- isotopic effect particularly useful in identifying presence of halogens Br & Cl

bromine
- has two isotopes $^{79}\text{Br}$ 50.69% $^{81}\text{Br}$ 49.31% ratio ~1:1
  - presence of Br ⇔ appearance of 2 peaks, 2 mass units apart, of equal rel.ab.
- nonbonding (lone pair) e\(^-\) in molecule less tightly held & more easily dislodged by e\(^-\) bombardment than bonding e\(^-\)
- C-Br bond is weakest bond in resulting radical cation & ∴ most easily broken
  - bond breaks heterolytically
    - both e\(^-\) leave with more E\(_{\text{neg}}\) Br, forming propyl cation and neutral Br atom
  - base peak is \(m/z\) 43 [M\(^+\) - 79 or (M+2)^+ - 81]
**chlorine**

- has two isotopes $^{35}\text{Cl}$ 75.77%  $^{37}\text{Cl}$ 24.23% ratio ~3:1
- presence of Cl $\Leftrightarrow$ appearance of 2 peaks 2 mass units apart, with rel.ab. of 3:1

- base peak $m/z$ 43 [$\text{M}^+ - 35$ or $(\text{M}+2)^+ - 37$] arises from heterolytic cleavage of C-Cl bond to give propyl cation

- alternative fragmentation involves homolytic $\alpha$ cleavage of C-C bond & loss of methyl radical; remaining fragment, still containing Cl in isotopic 3:1 ratio, forms resonance stabilised cation
Mass spectrometry

2-chloropropane

\[ \text{CH}_3 \text{CH} \] + \cdot \text{Cl} \\
\text{m/z} = 43

\[ \text{CH}_3 \text{CH}^{35\text{Cl}}^+ \] + \[ \text{CH}_3 \text{CH}^{37\text{Cl}}^+ \]
\[ \text{m/z} = 78 \] \[ \text{m/z} = 80 \]

\[ \text{CH}_3 \] \[ \text{CH}_3 \text{CH} - \text{Cl} \]

\[ \text{CH}_3 \text{CH}^{35\text{Cl}}^- \] + \[ \text{CH}_3 \text{CH}^{37\text{Cl}}^- \]
\[ \text{m/z} = 78 \] \[ \text{m/z} = 80 \]

\[ \text{CH}_3 \text{CH}^{35\text{Cl}}^+ \] + \[ \text{CH}_3 \text{CH}^{37\text{Cl}}^+ \] + \cdot \text{CH}_3
\[ \text{m/z} = 63 \] \[ \text{m/z} = 65 \]
ethers

- fragmentation pattern similar to that of alkyl halides
- lone pair e\(^-\) dislodged from oxygen atom
- fragmentation of the resulting M\(^+\) ion can occur in two ways:
  - heterolytic C-O bond cleavage; both e\(^-\) leave with E\(_\text{neg}\) O
  - homolytic \(\alpha\) cleavage of C-C bond, forming resonance stabilised cation
    - largest \(\alpha\) substituent \(\Leftrightarrow\) most readily cleaved
Sec-butyl isopropyl ether

\[ \text{CH}_3 \text{CH}_3 \text{CH}_2 \text{CH}_3 \text{O} \text{CHCH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_2 \text{CH} \rightarrow \text{CH}_3 \text{CH}_2 \text{CH}_3 \text{O} \text{CHCH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_2 \text{CH} \rightarrow \text{CH}_3 \text{CH}_2 \text{CH}_3 \text{O} \text{CHCH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_2 \text{CH} \]

\[ \text{m/z} = 116 \]

\[ \alpha \text{-cleavage} \]

\[ \text{CH}_3 \text{CH}_2 \text{CH} \text{O} \text{CHCH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_2 \text{CH} \rightarrow \text{CH} = \text{O} \text{CHCH}_3 + \text{CH}_3 \text{CH}_2 \text{CH} \]

\[ \text{m/z} = 87 \]

\[ \alpha \text{-cleavage} \]

\[ \text{CH}_3 \text{CH}_2 \text{CH} \text{O} \text{CHCH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_2 \text{CH} \rightarrow \text{CH}_3 \text{CH}_2 \text{CH} = \text{O} \text{CHCH}_3 + \text{CH}_3 \text{H} \]

\[ \text{m/z} = 101 \]

\[ \alpha \text{-cleavage} \]

\[ \text{CH}_3 \text{CH}_2 \text{CH} \text{O} \text{CHCH}_3 \text{CH}_3 \text{CH}_3 \text{CH}_2 \text{CH} \rightarrow \text{CH}_3 \text{CH}_2 \text{CH} = \text{O} \text{CHCH}_3 + \text{CH}_3 \text{H} \]

\[ \text{m/z} = 101 \]
match spectra below with one of

1-methoxybutane, 2-methoxybutane, 2-methoxy-2-methylpropane
alcohols

- alcohol M⁺ ions fragment so readily that few survive to reach collector
  - MS of 1° & 2° alcohols show weak M⁺ peaks
  - M⁺ of 3° alcohols not detectable
- undergo homolytic α cleavage; largest α substituent most readily cleaved
- alcohols also show a peak at $M^+ - 18$ arising from loss of $H_2O$
  - OH group & H from $\gamma$ position

\[
\text{CH}_3\text{CH}_2\text{CH}\text{CH}_2\text{CHCH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CHCHCH}_2\text{CHCH}_3^+ + \text{H}_2\text{O} \\
m/z = (102 - 18) = 84
\]

**ketones**
- unlike alcohols, have **strong** molecular ion peak
- undergo homolytic $\alpha$ cleavage; largest $\alpha$ substituent most readily cleaved
given following reaction

Identify reaction products from spectra below
- can also undergo McLafferty arrangement
  - requires H in γ position
  - involves homolytic β cleavage, H migration from γ C to O, & extrusion of ethene to produce resonance stabilised cation
identify two isomeric ketones from spectra given below
alkyl halides, ethers & alcohols show similar fragmentation behaviour:
1. bond between C & more E\textsubscript{neg} atom (O, hal) breaks \textit{heterolytically}
2. $\alpha$ bond between C & atom of similar E\textsubscript{neg} (C, H) breaks \textit{homolytically} ($\alpha$ cleavage)
   - bonds most easily broken those that lead to resonance-stabilised cations

**ketones**
1. $\alpha$ cleavage
2. $\beta$ cleavage, involving McLafferty rearrangement & ethene extrusion

**similarity in MS of alkanes, ethers, alcohols & ketones**
- alkanes have peaks at $m/z = 15, 29, 43$ etc. due to methyl, ethyl, propyl C\textsuperscript{+} etc.
- ethers & alcohols, due to O atom, have peaks of $m/z$ 16 units greater than alkanes
  at 31 (methoxy), 45 (ethoxy), 59 (propoxy)
- ketones also have O atom, but form ions 2 $m/z$ units less than those of alcohols & ethers, because of C=O
  - have peaks at $m/z$ 29, 43, 57
  - coincide with $m/z$ values of alkanes