Spectroscopy vs spectrometry

**Spectroscopy**

- **Latin** specere
  - “to look at”

- **Greek** skopia
  - “to see”

**-metry**

- **Greek** metria
  - “process of measuring”

Spectroscopy traditionally involves the **absorption** of some type of energy leading to an “excited state” that is subsequently emitted - This returns the molecule to the initial state non-destructively.

Energy of excitation is just enough to promote a ground state to an excited state ... no more, no less because it is **quantized**

Typical examples: UV-vis, fluorescence, IR, NMR

Versus typically **destructive** techniques (mass spec) or those that involve the **scattering** of radiation (X-ray crystallography)
Spectroscopic methods: what are the goals?

Molecular information:

*Identity*
- Constitution: number and types of atoms in the molecule
- Configuration: position of the atoms in space
- Conformation: isomers derived from rotation about single bonds

*Purity*

Dynamic information:

*Rates*
- follow functional group changes with *in situ* IR
- UV-vis for enzyme kinetics

*Equilibria*
- temperature dependent NMR studies of interconverting isomers

*Reaction progress*
- workup and measure an aliquot from a reaction
What information do we ultimately want?

Molecular formula
Functional group presence
Carbon skeleton
Presence of heteroatoms
Presence of “unsaturation” (rings, multiple bonds)
Stereochemical relationships

What are the available techniques to give this information?
Basically, this section is about solving puzzles.

You must piece together bits of data ("givens") such that the molecule is consistent with the data ("the story checks out")

Sometimes, the data will give direct insight, and Other times you must make leaps of faith

Dan has 2 eggs, Sue has 2 eggs. How many does Dan have?

Vs.

Dan and Sue have 4 eggs. How many does Dan have?

The problem solving aspect makes this class a lot of fun, and very frustrating.
There is no “right way” to approach these … just as there is no “right way” to approach spectral interpretation. The best way to build proficiency is to do problems! I will show you what works for me along the way.

---

## Raking Leaves

by Shelly Hazard

November, 2010

Print n' Play Text
and Table of Results

Alex looked at the fallen leaves blowing around the yard last week and had a great idea. He went around to all the neighbors, offering his raking services to clean up their yards. He got five jobs for this week, a different neighbor each day. The neighbors all lived on different streets and each had a different yard size, so some days he made more than others. Determine the last name of each neighbor who hired him, what street each lived on, what day he worked for each neighbor, and how much each neighbor paid him.

1. Alex worked for the Jones family on Monday afternoon and he earned $10 more than the day he raked for the neighbor on West Street.

2. He earned $4 less working for the Bradley family than he did from the neighbor on School Street.

3. On Friday, he worked on Oak Street but not for the Hayes family. The family on Main Street paid him $10 more than the neighbor he raked for on Wednesday.

4. He got $29 from the May family but it wasn’t on Tuesday.

5. He worked for the Elliot family the day before he worked on Russell Street. He earned $39 on Thursday.

6. Alex raked the Elliot yard two days before the neighbor on Oak Street but one day after the neighbor who paid him $43.

<table>
<thead>
<tr>
<th>Last Name</th>
<th>Street</th>
<th>Day of the Week</th>
<th>Amount Earned</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bradley</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elliot</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hayes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jones</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>May</td>
<td></td>
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<table>
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<tr>
<th>Main Street</th>
<th>Oak Street</th>
<th>Russell Street</th>
<th>School Street</th>
<th>West Street</th>
<th>Monday</th>
<th>Tuesday</th>
<th>Wednesday</th>
<th>Thursday</th>
<th>Friday</th>
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<td>$35</td>
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<td></td>
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<td>C-13</td>
<td>MS</td>
<td>IR/RAMAN</td>
<td>UV-VIS</td>
<td>ORD/CD</td>
<td>X-RAY</td>
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<td>IR</td>
<td>UV to visible</td>
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<td>(\equiv 5) mg</td>
<td>(\equiv 1) mg</td>
<td>(\equiv 1) mg</td>
<td>(\equiv 1) mg</td>
<td>(\equiv 1) mg</td>
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<td>Very limited</td>
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<td>No</td>
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<td>No</td>
<td>Limited</td>
<td>No</td>
<td>No</td>
<td>Yes (if separate)</td>
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<td>(by GC/MS LC/MS)</td>
<td>Yes (by GC/IR)</td>
<td>No</td>
<td>No</td>
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<td>Yes</td>
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<td>Limited</td>
<td>Limited</td>
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<td>m/z</td>
<td>cm(^{-1})</td>
<td>nm</td>
<td>nm</td>
<td>nm</td>
<td>Relative atom positions, (R/S) absolute stereochemistry</td>
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<td>(\delta) (ppm)</td>
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<td>cm(^{-1})</td>
<td>nm</td>
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<td><strong>Typical representations</strong></td>
<td>[Graphs]</td>
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<td>[Graphs]</td>
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</tr>
</tbody>
</table>
Timeline of available techniques

*Elemental analysis (combustion)*
*Melting point, boiling point*
*Chemical reactivity and degradation: derivatives*

**Ultraviolet-visible (UV-vis) - 1930s**
- Woodward-Fieser Rules ca. 1941
- Circular dichroism 1960s

**Infrared (IR) - 1940s**
- Functional groups, molecular fingerprints
- Raman spectroscopy 1960s

**Mass spectrometry (MS) - 1950s**
- Molecular weights, and observation of key fragments
- Characteristic reactivity … molecular fingerprints

**Nuclear magnetic resonance (NMR) - 1960s**
- Fourier Transform NMR 1970s
- 2-D correlation spectroscopies 1980s
A METHOD
FOR
THE IDENTIFICATION OF PURE ORGANIC COMPOUNDS
BY A SYSTEMATIC ANALYTICAL PROCEDURE BASED ON PHYSICAL PROPERTIES AND CHEMICAL REACTIONS

VOL. I
CONTAINING CLASSIFIED DESCRIPTIONS OF ABOUT 2300 OF THE MORE IMPORTANT COMPOUNDS OF CARBON WITH HYDROGEN AND WITH HYDROGEN AND OXYGEN

BY
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Assistant Professor of Organic Chemical Research at the Massachusetts Institute of Technology, Boston, Mass.

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SECOND THOUSAND

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LONDON: CHAPMAN & HALL, LIMITED
1914
CHAPTER VI
GENUS IV. PHENOLIC COMPOUNDS
OF
SUBORDER I, ORDER I.
(Colorless Compounds of Carbon, Hydrogen, and Oxygen.)

In this genus belong all the true phenols of the suborder not included in the foregoing genera, and many non-aromatic "enols."

GENERIC TEST IV.

OBTAIN PROCEDURE 1 OF THIS TEST FIRST TO EVERY COMPOUND, SOLID OR LIQUID.
APPLY PROCEDURE 2 TO EVERY SOLID COMPOUND THAT FAILS TO GIVE A COLORATION IN PROCEDURE 1; BUT NOT TO LIQUIDS. COMPOUNDS THAT SHOW A PHENOLIC BEHAVIOR IN THE FIRST PART OF THE TEST ARE CLASSIFIED AS PHENOLS IRRESPECTIVE OF THEIR BEHAVIOR IN PROCEDURE 2.

PROCEDURE 1.
(The Test with Ferric Chloride.)

Dissolve about 0.05 grm. of the substance in 1 cc. of cold water; or, if this should be found impossible, prepare a hot saturated aqueous solution; cool, filter, and reserve 1 cc. of the cold saturated filtrate. To this solution, in a narrow three-necked test-tube (small weighing-tube), held in front of a sheet of white paper, add one drop of the ferric-chloride reagent described below, pausing for a few seconds after the addition of each drop to note whether any color change occurs. If no coloration is noticed, repeat the test in the same way, except that alcohol is substituted for water as the solvent.

If any coloration, transient or permanent, other than a tone of yellow or orange-yellow (Y or OY), is observed, the substance is probably a phenol or an alkyl phenol.

PROCEDURE 2.
(The Test with Alkali.)

a. Place 0.10 grm. of the finely powdered substance in a narrow three-inch test-tube with 1 cc. of cold water, and ascertain by shaking and stirring whether it will dissolve. If it dissolves completely in the cold, and gives no color with ferric chloride, the procedure is not a phenol.

* The Ferric-Chloride Reagent.—Prepare the reagent as required for use by diluting three parts of the 10 per cent stock solution of ferric chloride with 1 cc. of water. 

| PHENOLIC COMPOUNDS.—Colorless and Solid. |
|---|---|
| C₆H₅O₄ | Anhydridobisphenoxybenzoic, C₆H₅(OH)₂. Sol. in alcohols intense red to violet; ppt’d by CO₂. Oxide d. at 210° without melting. |
| Phosphitaldehyde, C₆H₅O₡ | S. alc. or eth.; s. alc. w. pale yellow and in conc. H₂SO₄ w. intense violet color. |
| Hydrochlorophenol, C₆H₅H(OH)(CH₃)₂ | Sbd. in h. aqua. Sbd. with d. C₆H₅OH. Bpd. w. FeCl₃ or dil. HNO₃ gives phlorin. Reduces Ag sol. |
| Acetone, Me.C₆H₅, | Sbd. in h. aqua. Sbd. with d. C₆H₅OH. |
| Hydrochloroaceto phenol, C₆H₅(OH)CH₃ | Sbd. in h. aqua. Sbd. with d. C₆H₅OH. |
| 2, 4, 5-Tetrahydroxybenzene, C₆H₅(CHO)₃ | Sbd. in h. aqua. Sbd. with d. C₆H₅OH. |
| Phenol, C₆H₅OH | Sbd. in h. aqua. Sbd. with d. C₆H₅OH. |

† Phloroglucin, C₆H₅(OH)(CH₃)₂ | Sbd. in h. aqua. Sbd. with d. C₆H₅OH. |

β-Binaphthol, (HO.C₆H₅)₂ | Distillation gives β-naphthol (Test 413). |

Fustin, C₆H₅(OH)₂ | Sbd. faintly fr. alc. t. aqua.; s. alc.; e. eth. Gives greenish color w. FeCl₃, becoming bright red on heating. Pcrate, e. s. alc., has m. p. 174°. |

Fustin, C₆H₅(OH)₂ | Sbd. faintly fr. alc. t. aqua.; s. alc.; e. eth. Gives greenish color w. FeCl₃, becoming bright red on heating. Pcrate, e. s. alc., has m. p. 174°. |

Methyleneediphenol, CH₃[CH₃(OH)]₂ | D. s. alc. or eth. Dip-Oxyhydrobenzoin, C₆H₅.O₂H | Cryst., w. h. aqua.; s. alc.; i. ethyl. (Forms a Na salt.) |

Umbelliferone, C₆H₅.O₂H | I. c. aqua.; s. alc. and h. aqua.; S. w. intense blue fluorescence in conc. H₂SO₄. When warmed has odor like camphor. S. in cold KOH, but on heating the sol. to 60° gives umbelliferone n. |


β-Triphenylmethane, (C₆H₅.CO)₂ | Sbd. with d. s. alc. |

Hydroquinonephemthalein, C₆H₅.Na₂ | Sbd. fr. alc. Sbd. in alcohols w. deep-violet color. |
What energies are involved?

\[ E = h \nu = \frac{hc}{\lambda} \]

Frequency
Hz or \( s^{-1} \)

Wavelength
m

We \textit{can} and \textit{will} think of these units as “energies.”

\[ \sigma^* \]
\[ \pi^* \]
\[ \pi \]
\[ \sigma \]

XPS
10s-100s of eV

UV-vis
100s of nm

IR
1000s of cm\(^{-1}\)

… to NMR
100s of ppm

\( h \): Planck’s constant (Js)
\( c \): speed of light (m/s)
Step 1: obtain compound
Step 2: molecular formula

Having the molecular formula will allow us to start making guesses of the structure (or more regally, proposing structures)

How? By drawing *constitutional isomers*! (this was not simply an exercise in busy work)

How do we obtain a molecular formula?

Falzone, Townsend and Tovar will not always be around oo give you one on an exam …
### Table 1.1
**Calculation of Percentage Composition from Combustion Data**

| C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> + excess O<sub>2</sub> → x CO<sub>2</sub> + y/2 H<sub>2</sub>O |
|---|---|---|
| 9.83 mg | 23.26 mg | 9.52 mg |

\[
\text{millimoles CO}_2 = \frac{23.26 \text{ mg CO}_2}{44.01 \text{ mg/mmole}} = 0.5285 \text{ mmoles CO}_2
\]

\[
\text{mmoles CO}_2 = \text{mmoles C in original sample} \]
\[
(0.5285 \text{ mmoles C})(12.01 \text{ mg/mmole C}) = 6.35 \text{ mg C in original sample}
\]

\[
\text{millimoles H}_2\text{O} = \frac{9.52 \text{ mg H}_2\text{O}}{18.02 \text{ mg/mmole}} = 0.528 \text{ mmoles H}_2\text{O}
\]

\[
(0.528 \text{ mmoles H}_2\text{O})\left(\frac{2 \text{ mmoles H}}{1 \text{ mmole H}_2\text{O}}\right) = 1.056 \text{ mmoles H in original sample}
\]

\[
(1.056 \text{ mmoles H})(1.008 \text{ mg/mmole H}) = 1.06 \text{ mg H in original sample}
\]

\[
\% \text{ C} = \frac{6.35 \text{ mg C}}{9.83 \text{ mg sample}} \times 100 = 64.6\%
\]

\[
\% \text{ H} = \frac{1.06 \text{ mg H}}{9.83 \text{ mg sample}} \times 100 = 10.8\%
\]

\[
\% \text{ O} = 100 - (64.6 + 10.8) = 24.6\%
\]

---

### Table 1.2
**Calculation of Empirical Formula**

Using a 100-g sample:

64.6% of C = 64.6 g
10.8% of H = 10.8 g
24.6% of O = \(\frac{24.6 \text{ g}}{100.0 \text{ g}}\) = 5.38 moles C

\[
\text{moles C} = \frac{64.6 \text{ g}}{12.01 \text{ g/mole}} = 5.38 \text{ moles C}
\]

\[
\text{moles H} = \frac{10.8 \text{ g}}{1.008 \text{ g/mole}} = 10.7 \text{ moles H}
\]

\[
\text{moles O} = \frac{24.6 \text{ g}}{16.0 \text{ g/mole}} = 1.54 \text{ moles O}
\]

giving the result:

\[
\text{C}_{5.38}\text{H}_{10.7}\text{O}_{1.54}
\]

Converting to the simplest ratio:

\[
\text{C}_{5.38}^{1.54}\text{H}_{10.7}^{1.54}\text{O}_{1.54}^{1.54} = \text{C}_{3.59}\text{H}_{7.00}\text{O}_{1.00}
\]

which approximates

\[
\text{C}_{3.50}\text{H}_{7.00}\text{O}_{1.00}
\]

or

\[
\text{C}_7\text{H}_{14}\text{O}_2
\]

---

Pavia et al, *Introduction to Spectroscopy*
Problem

What is the formula of our molecule?

\[ \text{C}_7\text{H}_{14}\text{O}_2? \]

\[ \text{C}_{14}\text{H}_{28}\text{O}_4? \]

\[ \text{C}_{21}\text{H}_{42}\text{O}_6? \]

...?
Types of mass and their decimal needs

Unit Mass vs. exact mass:
SWK Chapter 1 Appendix A

\begin{align*}
\text{e.g. } 55 \\
\text{C}_2\text{H}_3\text{N}_2 & \quad 55.0297 \\
\text{C}_3\text{H}_3\text{O} & \quad 55.0184 \\
\text{C}_3\text{H}_5\text{N} & \quad 55.0422 \\
\text{C}_4\text{H}_7 & \quad 55.0548
\end{align*}

A high resolution exact mass determination is now acceptable to verify identity and to establish purity!

Silverstein, *Spectrometric Identification of Organic Compounds*

Unit mass: integral values

\begin{align*}
\text{C} & = 12 \\
\text{O} & = 16
\end{align*}

Molecular weight for stoichiometry:
two decimals

based on *natural abundance*

\begin{align*}
\text{C} & = 12.011 (^{12}\text{C} \ 98.9 \ + \ ^{13}\text{C} \ 1.1\%) \\
\text{O} & = 15.9994
\end{align*}

Exact mass: four decimals

weight of a specific isotope

\begin{align*}
^{12}\text{C} & = 12.0000 \\
^{13}\text{C} & = 13.00336 \\
^{16}\text{O} & = 15.9949 \\
^{18}\text{O} & = 17.9992
\end{align*}
Basics of mass spectrometry

Using a mass spectrometer, we will ionize an analyte and then detect it (the details of this will not be covered here).

In one typical example, the molecule is bombarded with high energy Electrons, that cause an electron to be ejected from the analyte. (called “electron impact” mass spec)

In mass spec, we can only detect charged species

The energy of this impact renders the ionized molecule subject to Fragmentation chemistries leading to smaller but still charged structures
Electron impact MS

High energy (ca. 70 eV) electrons bombard a vaporized analyte. This collision strips an electron from the analyte:

$$M + e^- \rightarrow M^{++} + 2 e^-$$ (M^{++} is the “molecular ion”)

The ionization potential of most organics is ca. 15 eV, so the M^{++} has a lot of excess energy.

Recall that a covalent bond is ca. 3-10 eV ... this excess energy leads to bond cleavages and molecular rearrangements.

How likely is the observation of M^{++}?

Can anything useful be deduced from these reactions?
Relative energies, apologies to a fly

This is IR

This is UV-vis

This is MS
The mass spectrum

**Benzamide**

\[ C_7H_7NO \]

Mol. Wt.: 121

O\(\text{C}N\text{H}_2 \)

\[ \text{Ph} + e^- - 2e^- \rightarrow \text{Ph} \]

\[ [\text{O} \text{C} \text{NH}_2]^+ \]

\[ m/z \ 121 \]

---

**O\(\text{C}\)N\(\text{H}_2 \)**

\[ \text{Ph} \]

\[ m/z \ 105 \]

---

**[M-16]+ or [M-NH\(_2\)]+**

**Molecular ion**

**Base peak**

**Fragment ions:**

*Characteristic for a particular functional group or compound!*

---

**FIGURE 1.1** The EI mass spectrum of benzamide above which is a fragmentation pathway to explain some of the important ions.

**SWK**

\([\text{M-16}]^+ \) or \([\text{M-NH}_2]^+ \)
Predicting molecular formulae

If we don’t know the identity of the analyte, we can use the M+ in many situations to start our search for a molecular formula.

“Rule of 13” … given that this is an organic chemistry course, it is fair to assume that we will have at least a CH group = 13 amu

Observe M+, divide it by 13. The integral portion of the quotient (n) defines the number of CH groups to give (CH)ₙ

The remainder (m) (remember your long division) is added to the formula as extra hydrogens giving CₙHₙ+m

M+ = 78 … 78/13 = 6 … C₆H₆ is a candidate formula

M+ = 92 … 92/13 = 7r1 … C₇H₈ is a candidate formula
Heteroatoms

Make replacements from the hydrocarbon candidate formula on the basis of unit mass equivalencies

\[ ^{16}\text{O replaces CH}_4 (12+1+1+1+1) \]

\[ ^{14}\text{N replaces CH}_2 \]

\[ ^{35}\text{Cl replaces C}_2\text{H}_{11} \quad \text{etc} \]

\[ M+ = 108 \ldots 108/13 = 8r4 \ldots \text{C}_8\text{H}_{12} \]

\[ \text{OR C}_7\text{H}_8\text{O} = \text{C}_8\text{H}_{12} - \text{CH}_4 + \text{O} \]

\[ \text{OR C}_5\text{H}_1\text{O}_3 \ldots \text{OR} \ldots \]

This gives possible molecular formulae, we need other data to narrow down our choices.
Hydrogen deficiency

aka “degrees of unsaturation”

Consider the following:

\[ \text{H}_3\text{C}-\text{CH}_3 \rightarrow \text{H}_2\text{C} = \text{CH}_2 + \text{H}_2 \]

Ethylene is deficient 1 molecule of hydrogen

\[ \text{H}_3\text{C}-\text{CH}_2\text{CH}_3 \rightarrow \text{H}_2\text{C} = \text{C} = \text{H} + \text{H}_2 \]

Cyclohexane is deficient 1 molecule

\[ \text{[benzene]} \text{ Deficient 4 molecules} \]

\[ \text{[acetone]} \text{ Deficient 1 molecule} \]
INDEX OF HYDROGEN DEFICIENCY for the molecular formula $\alpha w \beta \gamma \delta z$:

\[ \text{Index} = (z) - (w/2) + (y/2) + 1 \]

Where $\alpha$ represents all monovalent atoms (H, D, halogen), $\beta$ divalent (O, S), $\gamma$ trivalent (N, P) and $\delta$ tetravalent (C, Si, Sn).

Linear alkanes: $C_nH_{2n+2}$ … hexane $C_6H_{14}$ … $2n+2$ is the maximum # of H

Divalent (such as oxygen): consider hexanol, butyl ethyl ether
… $C_6H_{14}O$ no change in H

Trivalent (nitrogen): consider hexyl amine … $C_6H_{15}N$ add one H to max

Monovalent (halides): hexyl bromide … $C_6H_{13}Br$ less one H to max

Then, subtract existing protons in the formula … each less one H
But first divide by 2 (one $H_2$ has 2 H!)

It can’t be negative without violating standard valencies
It can’t be used for charged species
Example $C_7H_7NO$

Mono: $H$ \quad w = 7
Di: $O$ \quad x = 1
Tri: $N$ \quad y = 1
Tetra: $C$ \quad z = 7

Hydrogen deficiency = $7 - (7/2) + (1/2) + 1 = 5$

Possibilities:

![Chemical structures]

Need other data to determine, but this gives us a start …
Issues in interpretation

You may not always have the luxury of knowing a molecular formula and will need to use mass spectrometry to determine the mass.

Are we seeing the true molecular ion, or simply a large fragment?

Does the absence of a molecular ion imply that the desired/expected compound is not present in the analyte?

When in doubt, use *multiple* ionization techniques!
Isotopes in mass spectrometry

Remember, we are presumably looking at individual molecules, So we must consider isotopic abundance!

“C” = 12.011 = 12.00000(0.989) + 13.00336(0.011)

$^{12}$C = 12.00000 (ca. 98.9%)

$^{13}$C = 13.00336 (ca. 1.1%) a one-unit difference

So, there is a one percent chance of a $^{13}$C being in a given molecule, And a .01% chance of two $^{13}$C and …

$^{12}$C$_4$H$_7$: M$^{\ddagger\ddagger}$ = 55

$^{12}$C$_3$$^{13}$CH$_7$: M$^{\ddagger\ddagger}$ = 56

$^{12}$C$_2$$^{13}$C$_2$H$_7$: M$^{\ddagger\ddagger}$ = 57

If my powerpoint skills were any good, the intensities of these should be ca 1: 0.01: 0.0001
More pronounced isotopic effects

**S:**
- $^{32}$S (100)
- $^{33}$S (0.78)
- $^{34}$S (4.4)

M
- M+1
- M+2 (noticeable!)

**Si:**
- $^{28}$Si (100)
- $^{29}$Si (5.1)
- $^{30}$Si (3.35)

M
- M+1
- M+2

**Cl:**
- $^{35}$Cl (100)
- $^{37}$Cl (32.5)

M
- M+2

"relative intensities” in parentheses

**Br:**
- $^{79}$Br (100)
- $^{81}$Br (98)

M
- M+2

(equal intensities!)

**FIGURE 1.29** Predicted patterns of M, M + 2, M + 4, . . . for compounds with various combinations of chlorine and bromine.
EI-MS Ionization and fragmentation

Since EI provides high probabilities of fragment formation, we will refer to this often in our discussion of fragmentation.

\[
\begin{align*}
\text{M} & \xrightarrow{\text{e}^-} \text{M}^{+\cdot} & \text{What is the fate of this ion?} \\
& \xrightarrow{2 \text{e}^-} \text{M} + \cdot
\end{align*}
\]

persists? … leads to molecular ion decomposition pathways? Gas phase organic chemistry.

Where does the electron come from? Molecular “hot spots” as most likely sources for an ionizable electron heteroatoms, pi-systems, or even sigma bonds!

Consider where these electrons are relative to vacuum.

Delocalized: no indication of charge location

Localized: explicit assignment of radicals and ions
Typical bond cleavages

KEEP PROPER TRACK OF ELECTRONS!

CAREFUL ACCOUNTING IS KEY!

Notice how these two suggestions are written in all caps.

1) Homolytic

\[
\text{R-} \quad \text{C-} \quad \text{C-} \quad \text{R} \quad \xrightarrow{\text{}} \quad \text{R-} \quad \text{C-} \quad \text{.} \quad \text{.} \quad \text{C-} \quad \text{R}
\]

\[
\text{Use proper arrow notation:}
\text{Full vs barbed}
\]

2) Heterolytic

\[
\text{R-} \quad \text{C-} \quad \text{C-} \quad \text{R} \quad \xrightarrow{\text{}} \quad \text{R-} \quad \text{C} \quad \text{.} \quad \text{C-} \quad \text{R}
\]
General molecular ion lifetimes

The lifetimes of typical ions are on the order of $10^{-5}$ s but within this range there are some general structural trends to guide us to predict the likelihood of fragmentation for a molecule with particular functional groups

**High Chance:**
- Aromatics
- Conjugated alkene and alkyne
- Sulfides
- Unbranched hydrocarbons
- Ketones
- Amines
- Esters
- Ethers

**Low Chance:**
- Carboxylic acids (– CO$_2$)
- Branched hydrocarbons (stable cations)
- Alcohols (– H$_2$O)
General comments

1) Gas phase! Assume unimolecular decomposition and no collisions among fragments or ions (except Cl of course!)

2) Remember atomic valences and oxidation states!

3) When guessing the arrow pushing for ion formation, fragment *ion* stability trumps fragment *radical* stability
Alkane fragmentation 1: linear, branched

Only options are C-C and C-H $\sigma$ bond rupture

\[
\text{C-C: } \begin{array}{c}
\cdot \hspace{2cm} + \hspace{2cm} \cdot \\
\end{array}
\text{ or } \\
\begin{array}{c}
\cdot \hspace{2cm} + \\
\end{array}
\]

Consider \textit{dodecane} and \textit{methyl undecane} $\text{C}_{12}\text{H}_{26}$ MW 170

\[\text{C}_{29} \text{H}_{57} \text{C}_{49} \text{H}_{13} \hspace{2cm} \text{15} \text{C}_{3} \text{H}_{7} \text{C}_{5} \text{H}_{11} \hspace{2cm} \text{71} \text{C}_{5} \text{H}_{11} \]

\[\text{m/z 127} \hspace{2cm} \text{C}_{9} \text{H}_{19} \hspace{2cm} \text{m/z 71} \]

\[\text{m/z 170} \hspace{2cm} \text{m/z 71} \hspace{2cm} \text{CRJ 6.18} \]
Alkane fragmentation 2: cyclic

\[ \text{C}_6\text{H}_{13} \rightarrow \text{C}_6\text{H}_6 + \text{H}_2 \]

\[ \text{m/z} = 97 \]

\[ \text{H}^+ \text{H} \rightarrow \text{H}_2 \text{H} \]

\[ \text{m/z} = 41 \]

\[ \text{H}_2 \text{H} + \text{H}_2 \]

\[ \text{m/z} = 55 \]

\[ \text{H}_2 \text{H} \rightarrow \text{H}_2 \]

\[ \text{m/z} = 69 \]

\[ \text{H}_2 \text{H} + \text{H}_2 \]

\[ \text{m/z} = 168 \]

\[ \text{H}_2 \text{H} \rightarrow \text{H}_2 \]

\[ \text{m/z} = 29 \]

\[ \text{H}_2 \text{H} \rightarrow \text{H}_2 \]

\[ \text{m/z} = 3 \]

\[ \text{H}_2 \text{H} \rightarrow \text{H}_2 \]

\[ \text{m/z} = 97 \]
The most stable initial intermediate need not be formed preferentially if a less stable structure can lead to a highly stabilized fragment!
Alkene EI-MS: fingerprint for MW 98

CRJ Fig 6.19
Alkyne and arene fragmentation

\[
\begin{align*}
\text{[R-CH=CH]}^+ & \rightarrow \text{[R-H]}^+ + \text{[H-CH=CH]}^+ \\
\text{[R-CH=CH]}^+ & \rightarrow \text{[R-H]}^+ + \text{[C=CH]}^+ \\
n/m = 39 & \text{ (how??)} \\
n/m = 91 &
\end{align*}
\]

CRJ 8.14,15
Isomeric alkanols

**FIGURE 1.18** EI mass spectra of isomeric pentanols.
Aliphatic and aromatic ethers

**FIGURE 1.20**  
EI mass spectrum of ethyl sec-butyl ether.

**FIGURE 1.21**  
EI mass spectrum of anisole.

SWK Fig 1.20, 1.21