Objective 4. Determine (characterize) the structure of a compound using IR, NMR, MS.

**Skills:** Draw structure
IR: match bond type to IR peak
NMR: ID number of non-equivalent H’s, relate peak splitting to number of H’s on adjacent C
MS: ID molecular ion peak = molecular weight

**Key ideas:**
Given structure, determine # of non-equivalent H’s.
Given structure, determine multiplicity.
Given simple organic compound, draw H NMR spectrum (# of peaks and splitting).
Given NMR, IR, MS spectra, determine structure.
There Are Many Ways To Identify A Substance

It is fairly easy to identify a substance if you are given a few choices.

**Objective:** Choose an identification method.

You are given a sample of a colorless liquid and told it is either ethanol ($\text{C}_2\text{H}_5\text{OH}$) or rubbing alcohol ($\text{CH}_3\text{CHOHCH}_3$). What method would you use to identify this liquid? Give reasons.

a) IR
b) Boiling point
c) Density
Objective: Choose an Identification method

You are given a sample of a colorless liquid and told it is C₄H₁₀. C₄H₁₀ has two isomers. What method would you use to determine which isomer of C₄H₁₀ you were given? Give reasons.

a) IR
b) Boiling point
c) Density
To Determine the **Structure** of a Compound, IR, NMR, MS, and UV/VIS Are Used

- **IR (Infrared Spectroscopy)** is used to identify **Bond Types** and Functional Groups.
- **NMR (Nuclear Magnetic Resonance Spectroscopy)** is used to identify the **Carbon Skeleton** and the Number of H’s Bonded to C.
- **MS (Mass Spectrometry)** is used to determine the **Molecular Weight** of a Compound => determine chemical formula.
- **UV/VIS (Ultraviolet/Visible Spectroscopy)** is used to study **Conjugated** Systems.
Mass Spectrometry
http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch13/ch13-ms.html

1 inject sample
2 heater to vapourise sample
3 electron beam ionises sample
4 particles accelerated into magnetic field
5 magnetic field separates particles based on mass/charge ratio

ionisation fragmentation
\[ \tilde{M} \rightarrow \tilde{M}^+ \rightarrow m_1^+ + m_2^\cdot \]

molecule molecular ion fragment ion
Mass Spectrometry (MS) - the *Molecular Ion (M+•) peak tells you the molecular weight*

Molecular Ion (M+•) peak = peak (often the largest) with highest m/z ratio.

http://www.chemguide.co.uk/analysis/masspec/fragment.html
Which peak is the Molecular Ion peak?
### Molecular Weight ==> Chemical Formula

From Chemical Formula ==> determine *Hydrogen Deficiency Index* (HDI) for number of pi bonds or rings

From molecular weight, you can determine the chemical formula of a compound.
E.g., alkane \((C_nH_{2n+2})\) \(MW = 16 + 14 \times (n-1)\)

<table>
<thead>
<tr>
<th>Formula</th>
<th>Treat X the same as H. Ignore O.</th>
<th># of (\pi) bonds or rings or combo = HDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_nH_{2n+2})</td>
<td>0 bonds or rings: alkane</td>
<td></td>
</tr>
<tr>
<td>(C_nH_{2n})</td>
<td>1 bond (alkene) or 1 ring (cycloalkane)</td>
<td></td>
</tr>
<tr>
<td>(C_nH_{2n-2})</td>
<td>2 (\pi) bonds or rings or combo equaling 2</td>
<td></td>
</tr>
<tr>
<td>(C_nH_{2n-4})</td>
<td>3 (\pi) bonds or rings or combo equaling 3</td>
<td></td>
</tr>
<tr>
<td>(C_nH_{2n-6})</td>
<td>4 (\pi) bonds or rings or combo equaling 4</td>
<td></td>
</tr>
</tbody>
</table>
HDI for compounds with O, N, X

Reduce chemical formula to $C_xH_y$ formula:
- Ignore O
- Treat X (F, Cl, Br, I) like H
- For each N, subtract one H

Examples: $C_2H_6O$ reduces to $C_2H_6$ so HDI = 0.5 (6-6) = 0

$C_3H_7Cl$ reduces to $C_3H_8$ so HDI = 0

$C_2H_7N$ reduces to $C_2H_6$ so HDI = 0

HDI = 0.5 (# of H’s in alkane chain - # of H’s in formula)
Use $C_nH_{2n+2}$ to determine # of H’s in alkane chain
Infrared (IR) radiation causes a bond to *vibrate* (stretch/bend)


Bond Types are determined by IR Spectroscopy
# Use an IR Correlation Table to Interpret IR Spectra

<table>
<thead>
<tr>
<th>Bond</th>
<th>Base Value, cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Strength / Shape</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C=O</td>
<td>1715</td>
<td>s, &quot;finger&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Exact position depends on type of carbonyl</td>
</tr>
<tr>
<td>2</td>
<td>O-H</td>
<td>3200-600</td>
<td>s, broad</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Broad due to H bonding</td>
</tr>
<tr>
<td>3</td>
<td>N-H</td>
<td>3500</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Can tell primary from secondary</td>
</tr>
<tr>
<td>4</td>
<td>C-O</td>
<td>1100-1300</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Also check for OH and C=O</td>
</tr>
<tr>
<td>5</td>
<td>C=C</td>
<td>1650</td>
<td>w alkene</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>m-s aromatic</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Alkene w due to low polarity</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aromatic usually in pairs</td>
</tr>
<tr>
<td>6</td>
<td>C≡C</td>
<td>2150</td>
<td>w, sharp</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Most obvious in terminal alkynes</td>
</tr>
<tr>
<td>7</td>
<td>C-H</td>
<td>3000 (stretch)</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>As hybridisation of C changes sp&lt;sup&gt;3&lt;/sup&gt;-sp&lt;sup&gt;2&lt;/sup&gt;-sp, the frequency increases</td>
</tr>
<tr>
<td></td>
<td>1375 and 1450 (bend)</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>C≡N</td>
<td>2250</td>
<td>m, sharp</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Characteristic since little else around it</td>
</tr>
</tbody>
</table>
**Objective:** interpret an IR spectrum

When I interpret an IR spectrum, I look at:

3200-3500 cm\(^{-1}\) region ==> O-H bond ==> alcohol or ___

1600-1700 cm\(^{-1}\) region ==> C=O bond ==> aldehyde or ____
   ==> C=C bond ==> alkene

1100-1300 cm\(^{-1}\) region ==> C-O bond ==> ________

I know most organic compounds have C-H bond at around 3000 cm\(^{-1}\).
> 3000 cm\(^{-1}\) ==> alkene, alkyne, or aromatic C-H
< 3000 cm\(^{-1}\) ==> alkyl C-H
The IR spectrum of _____ is shown below. The compound is:

a) Ethanol
b) Butane
c) acetone

http://www.bluffton.edu/~bergerd/classes/cem222/infrared/oxygen.html
Nuclear Magnetic Resonance (NMR) spectroscopy

[Image of a diagram showing a RF (60 MHz) oscillator, an RF detector, and a recorder, with labels indicating 'No magnetic field' and 'With magnetic field']

http://www.avogadro.co.uk/analysis/nmr/nmr.htm
$^1$H and $^{13}$C Are The Most Common Nuclei Studied Using NMR

Electrons have spin. So do some nuclei. See Nuclear spin:
NMR basics:
http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch13/ch13-0.html
http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/nmr/nmr1.htm
Doing an NMR experiment:
http://arrhenius.rider.edu:16080/nmr/NMR_tutor/pages/nmr_tutor_home.html

In $^1$H NMR, look at
1. **Number and Location of signal** (peak) – **equivalent** H’s.
2. **Intensity of peak** relative to other peaks - # of H’s bonded to each C (or other atom)
3. **Multiplicity** (splitting of main peak into multiple peaks) - # of H’s bonded to adjacent C are “coupled”
$^1\text{H}$ nmr spectrum shows:

Relative # of equiv H’ s = integration

Splitting of main peak = # of H’ s on adjacent C

Downfield - “deshielded” H’ s
Inductive effect

$\delta$ = chemical shift, ppm

Upfield - “shielded” H’ s

http://lsc.ucdavis.edu/~hollieste/jim118A/ProtonNMR.Probs.html
**Objective**: Determine which H’s are *Equivalent* by Replacing H with X

If the 2 structures are the same, then H’s are equivalent

E.g., Are the H’s in CH₄ equivalent? YES

Which H’s in C₃H₈ are equivalent?

(i) A and B  (ii) A and C  (iii) B and C
Objective: Given structure, what does the H NMR spectrum look like?

Problem solving method:
(i) Determine the number of equivalent and non-equivalent H’ s (to determine number of peaks and ratio of non-equiv H’ s).
(ii) Determine peak splitting by H’ s on adjacent C (3 bonds away) using (n+1) rule, where n = # of equivalent H’ s on adjacent C.

1. For CH₄,
a. How many equivalent H’ s?
   (i) 1    (ii) 2    (iii) 3    (iv) 4
b. How many peaks? (i) 1    (ii) 2    (iii) 3    (iv) 4
c. If 2 or more peaks, what is ratio of non-equivalent H’ s?
d. If 2 or more peaks, what is splitting?

USE ChemDoodle to look at predicted NMR spectrum
A H is affected by a Non-Equivalent H on an Adjacent Carbon

Multiplicity - splitting of main peak into two or more peaks

$H_a$ is 3 bonds away from $H_b$

$H_b$ affects the shielding (environment) around $H_a$

$H_a$ Signal (peak) is split into two or more peaks:

\[ n + 1 \text{ rule} \]

where $n$ is the number of equivalent H’s coupled to $H_a$ signal
For $\text{C}_3\text{H}_8$

http://www.muhlenberg.edu/depts/chemistry/chem201nmrexamples.html

a. How many non-equivalent H’s?
   (i) 1   (ii) 2   (iii) 3   (iv) 4

b. How many peaks? (i) 1   (ii) 2   (iii) 3   (iv) 4

c. If 2 or more peaks, what is ratio of non-equivalent H’s?

d. If 2 or more peaks, what is splitting?
For $\text{C}_2\text{H}_5\text{OH}$

http://www.muhlenberg.edu/depts/chemistry/chem201nmrexamples.html

a. How many non-equivalent H’s?
   (i) 1  (ii) 2  (iii) 3  (iv) 4

b. How many peaks? (i) 1  (ii) 2  (iii) 3  (iv) 4

c. If 2 or more peaks, what is ratio of non-equivalent H’s?

d. If 2 or more peaks, what is splitting?
For $(\text{CH}_3)_2\text{CO}$

http://www.muhlenberg.edu/depts/chemistry/chem201nmrexamples.html

a. How many non-equivalent H’s?
   - (i) 1
   - (ii) 2
   - (iii) 3
   - (iv) 4

b. How many peaks?
   - (i) 1
   - (ii) 2
   - (iii) 3
   - (iv) 4

c. If 2 or more peaks, what is ratio of non-equivalent H’s?

d. If 2 or more peaks, what is splitting?
Can H NMR be used to distinguish between Butane \((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3)\) and isobutane \((\text{CH}_3)_3\text{CH}\)?
Can you use H nmr to distinguish between the following compounds?
Hint: Determine the number of non-equivalent hydrogens.
How many signals (peaks) will you see in a H nmr spectrum?
Given $^1\text{H}$ NMR Spectrum (and chemical formula), Determine Structure

$^1\text{H}$ NMR Correlation Table Helps Us Interpret Spectra

Deshielded H
Downfield

Shielded H
Upfield
When I interpret a $^1$H NMR spectrum, I look at:

**Number of peaks** ==> tells me how many non-equivalent H’ s
E.g., 2 peaks ==> 2 different types of H’ s

**Peak integration** ==> tells me ratio of non-equivalent H’ s
E.g., 2:1 ratio ==> 2:1 or 4:2 or 6:3 ratio of the different H’ s

**Splitting (multiplicity) of peaks** ==> tells me how many H’ s on adjacent C
E.g., Peak is split into a quartet ==> 3 H on adjacent C using (n+1) rule so -CH$_3$ group
Peak is split into a triplet ==> 2 H on adjacent C so -CH$_2$- group

Put the puzzle together so the NMR data fit the structure ==> structure solved!
Given $^1$H NMR Spectrum (and chemical formula), Determine Structure

$C_8H_{18}$; 1 peak at $\delta = 0.9$
How many non-equivalent H’ s?

(i) 1  (ii) 2  (iii) 3  (iv) 4

Which structure fits the data?

A
B
C
Given $^1\text{H}$ NMR Spectrum (and chemical formula), Determine Structure

C$_8$H$_{10}$; 3 peaks at $\delta = 1.2$ (triplet, 3 H), $\delta = 2.6$ (quartet, 2 H), $\delta = 7.1$ (broad singlet, 5 H)

How many rings or pi bonds?

(i) 2  (ii) 3  (iii) 4  (iv) 5

Which structure fits data?

A  B  C
\textsuperscript{13}C NMR is a Little Different Than \textsuperscript{1}H NMR

In \textbf{\textsuperscript{13}C NMR}, look at:

1. Number and Location of signal (peak) – equivalent C’s.
2. Intensity of peak relative to other peaks
3. Multiplicity – splitting of main peak into multiple peaks

\textsuperscript{13}C NMR Correlation Table

Interpret \textsuperscript{13}C NMR spectrum: Klein, Ch. 16
Review: Each Characterization Method Gives Different Information

1. a. What information does MS tell you?
   b. What information does IR tell you?
   c. What information does $^1$H NMR tell you?
   d. What information does $^{13}$C NMR tell you?

2. a. What information does the chemical formula tell you?
   b. What method tells you about the chemical formula?

3. a. What method tells you whether a pi bond is present?
   b. Can your method in part 3a tell you whether a ring is present?
   c. Can you method in part 3a tell you whether a methylene ($\text{CH}_2$) group is next to a methyl group? If not, which method gives you this information?
Structure Characterization Often Requires A Combination of IR, NMR, and MS

1. Determine the structure:
   http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch13/ch13-0.html
(i) Use H and C nmr, IR, MS spectra:
(ii) Chemical formula: index of H deficiency
   a. Spectra Problem #1
   b. Interactive Spectroscopy Problem 1

2. Webspectra
   http://www.chem.ucla.edu/~webspectra/
   a. Problem 1
A compound (C₈H₁₀O) has the IR and ¹H NMR spectra data below.

IR:

<table>
<thead>
<tr>
<th>Peak</th>
<th>Wavenumber, cm⁻¹</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3400</td>
<td>Strong, broad</td>
</tr>
<tr>
<td>2</td>
<td>3000</td>
<td>Strong</td>
</tr>
<tr>
<td>3</td>
<td>1100</td>
<td>Strong</td>
</tr>
</tbody>
</table>

¹H NMR:

<table>
<thead>
<tr>
<th>Chemical Shift, ppm</th>
<th>Intensity</th>
<th>Splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>3</td>
<td>doublet</td>
</tr>
<tr>
<td>4.2</td>
<td>1</td>
<td>singlet</td>
</tr>
<tr>
<td>4.9</td>
<td>1</td>
<td>quartet</td>
</tr>
<tr>
<td>7.5</td>
<td>5</td>
<td>singlet</td>
</tr>
</tbody>
</table>

Draw the structure of this compound.