STRUCTURE DETERMINATIONS USING IR AND NMR SPECTROSCOPY

Spectroscopy is a branch of chemistry that deals with graphical representations of a molecule’s energy absorption pattern. The instruments used to measure absorption of energy are known as spectrometers. All spectroscopic techniques are based on absorption of energy by a molecule.

<table>
<thead>
<tr>
<th>Spectroscopic method</th>
<th>Transitions between</th>
<th>Structural clues</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMR</td>
<td>Spin states of an atom’s nucleus</td>
<td>Carbon-hydrogen skeleton</td>
</tr>
<tr>
<td>IR</td>
<td>Vibrational states</td>
<td>Presence or absence of functional groups</td>
</tr>
<tr>
<td>UV-VIS</td>
<td>Electronic transitions</td>
<td>Electronic bonding</td>
</tr>
</tbody>
</table>

The two atoms of greatest interest to an organic chemist are hydrogen and carbon. The $^1\text{H}$ isotope is 99.9% in abundance while the $^{13}\text{C}$ isotope is only 1% in nature. Therefore, the $^1\text{H}$ NMR is easy and a more sensitive technique compared to $^{13}\text{C}$ NMR.

When electromagnetic radiation strikes a molecule, some wavelengths, but not all, are absorbed. For absorption to occur, the energy of the photon must match the difference between two energy states in the molecule (ground state to excited state).

For absorption to occur, the energy of the incident electromagnetic radiation must match $\Delta E$.

$\Delta E = \text{the energy difference between two states in a molecule}$

The larger the energy difference between two states, the higher the energy of radiation needed for absorption.

Higher energy light (UV-visible) causes electronic excitation.
Lower energy radiation (infrared) causes vibrational excitation.

In order to determine and confirm the complete structure of a given compound, you will need the molecular formula of the compound, IR spectrum (Infrared) and $^1\text{H}$ NMR spectrum (Proton
Magnetic Resonance), $^{13}$C NMR spectrum, UV-VIS spectrum and the mass spectrum of the substance.

You must first use the molecular formula of the compound to calculate the index of hydrogen deficiency.

**Index of Deficiency = # of Carbon atoms – # of Hydrogen atoms/2 – # of Halogen atoms/2 + # of Nitrogen atoms/2 + 1**

**Problem**
Calculate the index of hydrogen deficiency for each of the following compounds.
Aspirin, C$_9$H$_8$O$_4$; Vitamin C, C$_6$H$_8$O$_6$; Pyridine, C$_5$H$_5$N; Urea, CH$_4$N$_2$O; Cholesterol, C$_{27}$H$_{46}$O; Dopamine, C$_8$H$_{11}$NO$_2$ (Answers – 6,3,4,1,5,4)

Degrees of unsaturation may be interpreted as follows.

<table>
<thead>
<tr>
<th>Degrees of unsaturation</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Only single bonds</td>
</tr>
<tr>
<td>1</td>
<td>One π bond or one ring</td>
</tr>
<tr>
<td>2</td>
<td>Two π bonds or one π bond and one ring</td>
</tr>
<tr>
<td>3</td>
<td>3 π bonds or 2 π bonds and 1 ring or 3 rings or 1 π bond and 2 rings</td>
</tr>
<tr>
<td>4</td>
<td>Any combination of rings and π bonds; one example is an</td>
</tr>
</tbody>
</table>
PROTON MAGNETIC RESONANCE SPECTROSCOPY

A proton will absorb in the radiofrequency region, when placed in a strong magnetic field. This will cause the nucleus to change its spin and jump from a lower energy state to a higher state. This flipping of the proton spin is known as “resonance”.

When the nuclei return to their original state (known as “relaxation”), they emit electromagnetic radiation whose frequency depends on the difference in energy between α and β states. The NMR spectrometer detects these signals and displays them as a plot of frequency versus intensity. This plot is known as an NMR (nuclear magnetic resonance) spectrum.

A typical $^{1}$H NMR and $^{13}$C NMR spectra will look as follows.
A simple model of a NMR instrument looks like the one showed in the figure below.

An NMR spectrometer. The sample is dissolved in a solvent, usually CDCl₃ (deuterochloroform), and placed in a magnetic field. A radiofrequency generator then irradiates the sample with a short pulse of radiation, causing resonance. When the nuclei fall back to their lower energy state, the detector measures the energy released, and a spectrum is recorded. The superconducting magnets in modern NMR spectrometers have coils that are cooled in liquid helium and conduct electricity with essentially no resistance.

**Number of NMR signals (or peaks)**

Some protons lie in the same chemical environment in a molecule and these are known as **chemically equivalent protons**. Each set of chemically distinct protons in a molecule gives rise to a signal.
1,1-dichloroethylene
- 1 type of H
- 1 NMR signal

1-bromo-1-chloroethylene
- 2 types of H's
- 2 NMR signals

chloroethylene
- 3 types of H's
- 3 NMR signals

cyclopropane
- All H's are equivalent.
- 1 NMR signal

chlorocyclopropane
- 3 types of H's
- 3 NMR signals

Draw NOT

Cl

NOT
ClCH=CH₂
Problem
How many signals would you expect to see in the $^1$H NMR spectrum of each of the following compounds?

a) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \)

b) \( \text{BrCH}_2\text{CH}_2\text{Br} \)

c) 

\[
\text{CH}_3
\]

d) \( \text{CH}_3\text{OCH}_3 \)

e) \( \text{CH}_3\text{CH}_3 \)
Position of peaks or Chemical Shifts

A small amount of inert reference compound is usually added to the sample when an NMR spectrum is taken. The positions of the signals are defined with respect to the reference sample. The most common reference is TMS (tetramethylsilane). It is inert and volatile. The TMS signal is defined as the zero position on the spectrum. The position at which a proton appears as a signal in an NMR spectrum is known as the chemical shift of that particular proton. It is a measure of how far the signal is from the TMS signal. The frequency is expressed as δ (ppm). Most protons have chemical shifts that range from 0 to 11 ppm. The characteristic chemical shifts are indicated in Appendix PROTON AND CARBON-13 NMR VALUES.

Protons in an electron rich environment (shielded nuclei) will give signals at a lower frequency; protons in an electron poor environment (deshielded nuclei) will give signals at a higher frequency. If electronegative atoms are close to a proton, they withdraw electron density and the proton is deshielded.

The protons (or hydrogens) that are located adjacent to an electronegative element appear at a higher chemical shift value (higher δ ppm).
• The Hₕ protons are deshielded because they are closer to the electronegative Cl atom, so they absorb downfield from Hₐ.

• Because F is more electronegative than Br, the Hₖ protons are more deshielded than the Hₐ protons and absorb farther downfield.

• The larger number of electronegative Cl atoms (two versus one) deshields Hₖ more than Hₐ, so it absorbs downfield from Hₐ.

Important Regions in the NMR Spectrum

• Shielded protons absorb at lower chemical shift (to the right).
• Deshielded protons absorb at higher chemical shift (to the left).
**Signal Intensity**

The area under each signal corresponds to the # of protons. A computer can integrate the areas under each peak and give the chemist the # of protons each peak corresponds to. The integrals are represented as lines superimposed on the peaks. The height of the line is equal to the area. The area is proportional to the # of protons.
**Peak Multiplicity**

Signals on an NMR spectrum may not be split (appear as singlets) or may be split as doublets, triplets (known as multiplets) etc. This is known as peak multiplicity. Splitting can be determined using \((n + 1)\) rule, where \(n\) = # of equivalent protons on adjacent carbons. Splitting occurs because different kinds of protons are close enough to influence each other’s magnetic fields. The protons that influence each other’s magnetic field are known as **coupled protons**.

The intensity of the multiplets follows Pascal’s triangle.

<table>
<thead>
<tr>
<th>Number of equivalent protons causing splitting</th>
<th>Multiplicity of the signal</th>
<th>Relative peak intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>singlet</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>doublet</td>
<td>1:1</td>
</tr>
<tr>
<td>2</td>
<td>triplet</td>
<td>1:2:1</td>
</tr>
<tr>
<td>3</td>
<td>quartet</td>
<td>1:3:3:1</td>
</tr>
<tr>
<td>4</td>
<td>quintet</td>
<td>1:4:6:4:1</td>
</tr>
<tr>
<td>5</td>
<td>sextet</td>
<td>1:5:10:10:5:1</td>
</tr>
</tbody>
</table>

The intensity of multiplets follows Pascal’s triangle.

\[
\begin{align*}
5 + 1 &= 6 \\
\text{sextet} \\
2 + 1 &= 3 \\
\text{triplet} \\
2 + 1 &= 3 \\
\text{triplet} \\
0 + 1 &= 1 \\
\text{singlet}
\end{align*}
\]
Characteristic spin-spin coupling for common organic fragments

Table 14.4 Common Splitting Patterns Observed in $^1$H NMR

<table>
<thead>
<tr>
<th>Example</th>
<th>Pattern</th>
<th>Analysis ($H_a$ and $H_b$ are not equivalent.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td><img src="image1.png" alt="Image 1" /></td>
<td>$H_a$: one adjacent $H_b$ proton $\rightarrow$ two peaks $\rightarrow$ a doublet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H_b$: one adjacent $H_a$ proton $\rightarrow$ two peaks $\rightarrow$ a doublet</td>
</tr>
<tr>
<td>[2]</td>
<td><img src="image2.png" alt="Image 2" /></td>
<td>$H_a$: two adjacent $H_b$ protons $\rightarrow$ three peaks $\rightarrow$ a triplet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H_b$: one adjacent $H_a$ proton $\rightarrow$ two peaks $\rightarrow$ a doublet</td>
</tr>
<tr>
<td>[3]</td>
<td><img src="image3.png" alt="Image 3" /></td>
<td>$H_a$: two adjacent $H_b$ protons $\rightarrow$ three peaks $\rightarrow$ a triplet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H_b$: two adjacent $H_a$ protons $\rightarrow$ three peaks $\rightarrow$ a triplet</td>
</tr>
<tr>
<td>[4]</td>
<td><img src="image4.png" alt="Image 4" /></td>
<td>$H_a$: three adjacent $H_b$ protons $\rightarrow$ four peaks $\rightarrow$ a quartet*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H_b$: two adjacent $H_a$ protons $\rightarrow$ three peaks $\rightarrow$ a triplet</td>
</tr>
<tr>
<td>[5]</td>
<td><img src="image5.png" alt="Image 5" /></td>
<td>$H_a$: three adjacent $H_b$ protons $\rightarrow$ four peaks $\rightarrow$ a quartet*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H_b$: one adjacent $H_a$ proton $\rightarrow$ two peaks $\rightarrow$ a doublet</td>
</tr>
</tbody>
</table>

*The relative area under the peaks of a quartet is 1:3:3:1.

CH$_3$Br  
**bromomethane**

ClCH$_2$CH$_2$Cl  
**1,2-dichloroethane**

Both compounds have an NMR spectrum that shows one singlet because equivalent protons do not split each other’s signals.

Three C–H protons are chemically equivalent; no splitting occurs.

Four C–H protons are chemically equivalent; no splitting occurs.
Problem
Indicate the # of signals and the multiplicity of each signal in the $^1$H NMR spectrum of each of the following compounds.

a) $\text{BrCH}_2\text{CH}_2\text{Br}$

b) $\text{BrCH}_2\text{CH}_2\text{CHCl}_2$

c) $\text{H}_3\text{C} - \text{C} - \text{O}$

 d) $\text{CH}_3\text{CCH}_2\text{CH}_2\text{CCH}_3$

Splitting observed
Splitting not usually observed
Analyze the splitting pattern in the following $^1$H NMR spectra.
Important points to note.....

1. NMR absorptions generally appear as sharp peaks.
2. Most protons absorb between 0-10 ppm.
3. The terms “upfield” and “downfield” describe the relative location of peaks.
   a. Upfield means to the right (higher magnetic field).
   b. Downfield means to the left (lower magnetic field).
4. An external standard, (CH₃)₄Si (tetramethylsilane) is added to the sample tube prior to the NMR measurement.
5. NMR absorptions are measured relative to the position of a reference peak at 0 ppm on the δ scale due to tetramethylsilane (TMS).
6. TMS is a volatile inert compound that gives a single peak upfield from typical NMR absorptions.

PROTON NMR provides information on
   a) **Chemical shift**, given by location along the x-axis. It gives an idea of the amount of electron density around a proton. The closer the hydrogen (or proton) is to an electronegative element, the more deshielded it is and therefore the higher the chemical shift (farther left on the spectrum)
   b) **Number of signals**, which tells us the how many types of protons are present within a given molecule
   c) **Integration of signals**, the peak area, tells us the ratio of the various kinds of protons.
   d) **Splitting patterns, or multiplicity** gives us the relation between the protons in a given molecule. This results from proton-proton coupling. Splitting patterns provides us with the number of nonequivalent neighbor hydrogens within three bonds.
THE $^{13}$C NMR SPECTRUM

1. The two features of a $^{13}$C NMR spectrum that provide the most structural information are the number of signals observed and the chemical shifts of those signals.

2. The number of signals in a $^{13}$C spectrum gives the number of different types of carbon atoms in a molecule.

3. Because $^{13}$C NMR signals are not split, the number of signals equals the number of lines in the $^{13}$C spectrum.

4. In contrast to the $^1$H NMR situation, peak intensity is not proportional to the number of absorbing carbons, so $^{13}$C NMR signals are not integrated.

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1. $^1^{13}$C NMR signal
Both C’s are equivalent.

2. $^2^{13}$C NMR signals

3. $^3^{13}$C NMR signals
<table>
<thead>
<tr>
<th>Type of carbon</th>
<th>Chemical shift (ppm)</th>
<th>Type of carbon</th>
<th>Chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="sp3 C-H" /></td>
<td>5–45</td>
<td><img src="image" alt="sp2 C=C" /></td>
<td>100–140</td>
</tr>
<tr>
<td><img src="image" alt="sp3 C-Z" /></td>
<td>30–80</td>
<td><img src="image" alt="benzene" /></td>
<td>120–150</td>
</tr>
<tr>
<td>Z = N, O, X</td>
<td></td>
<td><img src="image" alt="C=O" /></td>
<td>160–210</td>
</tr>
<tr>
<td><img src="image" alt="C≡C" /></td>
<td>65–100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**INFRARED SPECTROSCOPY**

The infrared region of the spectrum corresponds to frequencies just below the visible region. IR radiation causes groups of atoms to vibrate with respect to the bonds that connect them. Absorption of IR light causes changes in the vibrational motions of a molecule. The different vibrational modes available to a molecule include stretching and bending modes.

A bond can stretch. Two bonds can bend.

The vibrational modes of a molecule are quantized, so they occur only at specific frequencies which correspond to the frequency of IR light. When the frequency of IR light matches the frequency of a particular vibrational mode, the IR light is absorbed, causing the amplitude of the particular bond stretch or bond bend to increase.

- Different kinds of bonds vibrate at different frequencies, so they absorb different frequencies of IR light.
- IR spectroscopy distinguishes between the different kinds of bonds in a molecule, so it is possible to determine the functional groups present.

In an IR spectrometer, light passes through a sample. Frequencies that match the vibrational frequencies are absorbed, and the remaining light is transmitted to a detector. An IR spectrum is a plot of the amount of transmitted light versus its wavenumber. Most bonds in organic molecules absorb in the region of 4000 cm\(^{-1}\) to 400 cm\(^{-1}\).
1. The \( x \)-axis is reported in frequencies using a unit called wavenumbers (\( \nu \)).
2. Wavenumbers are inversely proportional to wavelength and reported in reciprocal centimeters (cm\(^{-1}\)).
3. The \( y \)-axis is % transmittance: 100% transmittance means that all the light shone on a sample is transmitted and none is absorbed.
4. 0% transmittance means that none of the light shone on the sample is transmitted and all is absorbed.
5. Each peak corresponds to a particular kind of bond, and each bond type (such as O – H and C – H) occurs at a characteristic frequency.
6. Infrared (IR) spectroscopy is used to identify what bonds and what functional groups are in a compound.
7. The IR spectrum is divided into two regions: the functional group region (at \( \geq 1500 \text{ cm}^{-1} \)), and the fingerprint region (at \(< 1500 \text{ cm}^{-1} \)).
8. For a bond to absorb in the IR, there must be a change in dipole moment during the vibration. Symmetrical nonpolar bonds do not absorb in the IR. This type of vibration is said to be IR inactive.
• **A** and **B** show peaks in the same regions for their C=O group and sp\(^3\) hybridized C–H bonds.
• **A** and **B** are different compounds, so their fingerprint regions are quite different.

Bonds absorb in four predictable regions of an IR spectrum.
<table>
<thead>
<tr>
<th>Bond type</th>
<th>Approximate $v$ (cm$^{-1}$)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H</td>
<td>3600–3200</td>
<td>strong, broad</td>
</tr>
<tr>
<td>N-H</td>
<td>3500–3200</td>
<td>medium</td>
</tr>
<tr>
<td>C-H</td>
<td>~3000</td>
<td>medium</td>
</tr>
<tr>
<td>C$_{sp^3}$-H</td>
<td>3000–2850</td>
<td>strong</td>
</tr>
<tr>
<td>C$_{sp^2}$-H</td>
<td>3150–3000</td>
<td>medium</td>
</tr>
<tr>
<td>C$_{sp}$-H</td>
<td>3300</td>
<td>medium</td>
</tr>
<tr>
<td>C≡C</td>
<td>2250</td>
<td>medium</td>
</tr>
<tr>
<td>C≡N</td>
<td>2250</td>
<td>medium</td>
</tr>
<tr>
<td>C=O</td>
<td>1800–1650 (often ~1700)</td>
<td>strong</td>
</tr>
<tr>
<td>C=C</td>
<td>1650</td>
<td>medium</td>
</tr>
<tr>
<td></td>
<td>1600, 1500</td>
<td>medium</td>
</tr>
</tbody>
</table>