12-14. Structure Determination: IR, UV, NMR

Based on McMurry’s *Organic Chemistry*, 7th edition
12.5 The Electromagnetic Spectrum

![Electromagnetic Spectrum Diagram]

- **γ rays**
- **X rays**
- **Ultraviolet**
- **Infrared**
- **Microwaves**
- **Radio waves**

Frequency ($\nu$) in Hz:
- $10^{20}$
- $10^{18}$
- $10^{16}$
- $10^{14}$
- $10^{12}$
- $10^{10}$
- $10^{12}$
- $10^{-12}$
- $10^{-10}$
- $10^{-8}$
- $10^{-6}$
- $10^{-4}$
- $10^{-2}$

Wavelength ($\lambda$) in m:
- γ rays: $3.8 \times 10^{-7}$ m
- X rays: 500 nm
- Ultraviolet: 600 nm
- Infrared: 700 nm
- Microwaves: 780 nm
- Radio waves: $7.8 \times 10^{-7}$ m
Wavelength and Frequency

(a) 

![Wavelength and Amplitude Diagram]

(b) 400 nm

Violet light
\( (v = 7.50 \times 10^{14} \text{ s}^{-1}) \)

(c) 800 nm

Infrared radiation
\( (v = 3.75 \times 10^{14} \text{ s}^{-1}) \)
Absorption Spectra

- Organic compounds exposed to electromagnetic radiation can absorb photons of specific energies (wavelengths or frequencies).
- Changing wavelengths to determine which are absorbed and which are transmitted produces an **absorption spectrum**.
- Energy absorbed is distributed internally in a distinct and reproducible way (See Figure 12-11).
Continuum, Absorption, Emission
Infrared Absorption Spectrum of Ethanol
IR region and vicinity

\[ \lambda = 2.5 \times 10^{-4} \text{ cm} = 25 \mu\text{m} \]
\[ \tilde{\nu} = 4000 \text{ cm}^{-1} \]
Infrared Energy Modes

Symmetric stretching

Antisymmetric stretching

In-plane bending

Out-of-plane bending

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Regions of the Infrared Spectrum
12.8 Infrared Spectra of Hydrocarbons

- C-H, C-C, C=C, C≡C have characteristic peaks

**Alkanes**

\[ \text{C—H} \quad 2850–2960 \text{ cm}^{-1} \]

\[ \text{C—C} \quad 800–1300 \text{ cm}^{-1} \]

Hexane

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Alkenes

\[ \text{C} \equiv \text{C} \]

\[ \text{RCH} \equiv \text{CH}_2 \]

\[ \text{R}_2\text{C} \equiv \text{CH}_2 \]

1-Hexene

- \( \equiv \text{C} \equiv \text{H} \): \( 3020-3100 \text{ cm}^{-1} \)
- \( \text{C} \equiv \text{C} \): \( 1640-1680 \text{ cm}^{-1} \)
- \( \text{RCH} \equiv \text{CH}_2 \): \( 910 \text{ and } 990 \text{ cm}^{-1} \)
- \( \text{R}_2\text{C} \equiv \text{CH}_2 \): \( 890 \text{ cm}^{-1} \)
Alkynes

\[ \equiv C \equiv C \quad 2100-2260 \text{ cm}^{-1} \]

\[ \equiv C \equiv H \quad 3300 \text{ cm}^{-1} \]
IR: Alcohols

Alcohols

\[ \text{O} - \text{H} \quad 3400-3650 \text{ cm}^{-1} \text{ (broad, intense)} \]
Phenylacetylene
<table>
<thead>
<tr>
<th>Functional group class</th>
<th>Band position (cm⁻¹)</th>
<th>Intensity of absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes, alkyl groups</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C—H</td>
<td>2850–2960</td>
<td>Medium to strong</td>
</tr>
<tr>
<td>Alkenes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>=C—H</td>
<td>3020–3100</td>
<td>Medium</td>
</tr>
<tr>
<td>C=C</td>
<td>1640–1680</td>
<td>Medium</td>
</tr>
<tr>
<td>Alkynes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>=C—H</td>
<td>3300</td>
<td>Strong</td>
</tr>
<tr>
<td>—C≡C—</td>
<td>2100–2260</td>
<td>Medium</td>
</tr>
<tr>
<td>Alkyl halides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C—Cl</td>
<td>600–800</td>
<td>Strong</td>
</tr>
<tr>
<td>C—Br</td>
<td>500–600</td>
<td>Strong</td>
</tr>
<tr>
<td>C—I</td>
<td>500</td>
<td>Strong</td>
</tr>
<tr>
<td>Alcohols</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O—H</td>
<td>3400–3650</td>
<td>Strong, broad</td>
</tr>
<tr>
<td>C—O</td>
<td>1050–1150</td>
<td>Strong</td>
</tr>
<tr>
<td>Aromatics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[C—H]</td>
<td>3030</td>
<td>Weak</td>
</tr>
<tr>
<td>Compound</td>
<td>Wavenumber Range</td>
<td>Intensity</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Amines</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N–H</td>
<td>3300–3500</td>
<td>Medium</td>
</tr>
<tr>
<td>C–N</td>
<td>1030–1230</td>
<td>Medium</td>
</tr>
<tr>
<td>Carbonyl compounds(^a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>1670–1780</td>
<td>Strong</td>
</tr>
<tr>
<td>Carboxylic acids</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O–H</td>
<td>2500–3100</td>
<td>Strong, very broad</td>
</tr>
<tr>
<td>Nitriles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C≡N</td>
<td>2210–2260</td>
<td>Medium</td>
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<tr>
<td>Nitro compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO(_2)</td>
<td>1540</td>
<td>Strong</td>
</tr>
</tbody>
</table>

\(^a\)Carboxylic acids, esters, aldehydes, and ketones.
15.8 Spectroscopy of Aromatic Compounds

IR: Aromatic ring C–H stretching at 3030 cm\(^{-1}\) and peaks 1450 to 1600 cm\(^{-1}\) (See Figure 15-13)
Benzene: 30 Vibrational modes

Aromatic ring
C–H stretching
at 3030 cm$^{-1}$

And

peaks 1450 to 1600 cm$^{-1}$
14.7 Structure Determination in Conjugated Systems: UV Spectroscopy

- Conjugated compounds can absorb light in the ultraviolet region of the spectrum.
- The electrons in the highest occupied molecular orbital (HOMO) undergo a transition to the lowest unoccupied molecular orbital (LUMO).
- The region from $2 \times 10^{-7}$ m to $4 \times 10^{-7}$ m (200 to 400 nm) is most useful in organic chemistry.
- A plot of absorbance (log of the ratio of the intensity of light in over light transmitted) against wavelength in this region is an ultraviolet spectrum –

![UV Spectrum Diagram]

\[ \lambda = 2 \times 10^{-7} \text{ m} = 200 \text{ nm} \]
\[ \bar{\nu} = 5 \times 10^4 \text{ cm}^{-1} \]

\[ \lambda = 4 \times 10^{-7} \text{ m} = 400 \text{ nm} \]
\[ \bar{\nu} = 2.5 \times 10^4 \text{ cm}^{-1} \]
Ultraviolet Spectrum of 1,3-Butadiene

Example: 1,4-butadiene has four $\pi$ molecular orbitals with the lowest two occupied.

Electronic transition is from HOMO to LUMO at 217 nm (peak is broad because of combination with stretching, bending).

- The **Lowest Unoccupied Molecular Orbital**
- The **Highest Occupied Molecular Orbital**

![Diagram showing energy levels, orbitals, and electronic transitions](attachment:image.png)
Quantitative Use of UV Spectra

- Absorbance for a particular compound in a specific solvent at a specified wavelength is directly proportional to its concentration.
- You can follow changes in concentration with time by recording absorbance at the wavelength.

Beers’ law: \( A = \varepsilon cl \)
- “A” = absorbance
- “\( \varepsilon \)” is molar absorptivity (extinction coefficient) = amount of UV light absorbed
- “c” is concentration in mol/L
- “l” is path of light through sample in cm
14.8 Interpreting UV Spectra: The Effect of Conjugation

- $\lambda_{\text{max}}$: wavelength where UV absorbance for a compound is greatest. The energy difference between HOMO and LUMO decreases as the extent of conjugation increases.

- $\lambda_{\text{max}}$ increases as conjugation increases (lower energy)
  - 1,3-butadiene: 217 nm, 1,3,5-hexatriene: 258 nm
Substituents on $\pi$ system increase $\lambda_{\text{max}}$

1,3-buta diene: $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$ 217 nm

Table 14.2 Ultraviolet Absorptions of Some Conjugated Molecules

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methyl-1,3-buta diene</td>
<td>$\text{H}_2\text{C}=\text{C}-\text{CH}=\text{CH}_2$ CH$_3$</td>
<td>220</td>
</tr>
<tr>
<td>1,3-Cyclohexadiene</td>
<td></td>
<td>256</td>
</tr>
<tr>
<td>1,3,5-Hexatriene</td>
<td>$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$</td>
<td>258</td>
</tr>
<tr>
<td>1,3,5,7-Octatetraene</td>
<td>$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}=\text{CH}_2$</td>
<td>290</td>
</tr>
<tr>
<td>3-Buten-2-one</td>
<td>$\text{H}_2\text{C}=\text{CH}=\text{C}=\text{CH}_3$ O</td>
<td>219</td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td>203</td>
</tr>
</tbody>
</table>
Calculations of $\lambda_{\text{max}}$

The $\lambda_{\text{max}}$ of the $\pi \rightarrow \pi^*$ transition for compounds with $\leq 4$ conjugated double bonds can be calculated using Woodward-Fieser rules.

Start with a base number:

- $\text{CH}_2=\text{CH} - \text{CH}=\text{CH}_2$

  $\lambda_{\text{max}} = 217 \text{ nm}$

To the base add:

1. 30 for each extra conjugated double bond
2. 5 each time a conjugated double bond is an exocyclic double bond
3. 36 for each conjugated double bond frozen s-cis
4. 5 for each alkyl group or halogen bonded to conjugated system of polyene
5. 10 for an $\alpha$-substituent of a conjugated aldehyde or ketone
6. 12 for a $\beta$-substituent of a conjugated aldehyde or ketone
Example:

Calculate expected $\lambda_{\text{max}}$ for following:

\[
\text{CH}_2=\text{CH} - \text{CH}=\text{CH}_2
\]

$\lambda_{\text{max}} = 217 \text{ nm}$

Base = 217

3 alkyl substituents @ 5 each = 15

Calculated = 232

Observed = 232
CH$_2$=CH–CH=CH$_2$

$$\lambda_{\text{max}} = 217 \text{ nm}$$

\[ \text{C} = \text{C} - \text{H} \]

$$\lambda_{\text{max}} = 210 \text{ nm}$$

\[ \text{C} = \text{C} - \text{R} \]

$$\lambda_{\text{max}} = 215 \text{ nm}$$
Learning Check:

Calculate expected $\lambda_{\text{max}}$ for following:

To the base add:
1. 30 for each extra conjugated double bond
2. 5 each time a conjugated double bond is an exocyclic double bond
3. 36 for each conjugated double bond frozen s-cis
4. 5 for each alkyl group or halogen bonded to conjugated system of polyene
5. 10 for an $\alpha$-substituent of a conjugated aldehyde or ketone
6. 12 for a $\beta$-substituent of a conjugated aldehyde or ketone
Solution:

- Calculate expected $\lambda_{\text{max}}$ for following:

  Base = 215

  $\alpha$ substituent = 10

  $\beta$ substituent = 12

  Exocyclic db bd = 5

  **Calculated** = 242

  Observed = 241

CH$_2$=CH−CH=CH$_2$

$\lambda_{\text{max}} = 217$ nm

Base = 217

Additional db bd = 30

Locked s-cis = 36

2 alkyl substituents = 10

**Calculated** = 293

Observed = 293
15.8 Spectroscopy of Aromatic Compounds

- **UV:**
  Peak near 205 nm and a less intense peak in 255-275 nm range
NMR
The spin state of a nucleus is affected by an applied magnetic field.
Larmor Precession

Spinning particle precesses about the external field axis with an angular frequency known as the Larmor frequency

$$\omega_L = \gamma B_0$$

When radio frequency energy matching the Larmor frequency is introduced at a right angle to the external field, it would cause a transition between the two energy levels of the spin. In other world, the precessing nucleus will absorb energy and the magnetic moment will flip to its $I = -1/2$ state.
The energy difference between the two spin states depends on the strength of the magnetic field (that the atom “feels”)

![Diagram showing energy levels and magnetic field strength](image)
Signals detected by NMR
The electrons surrounding a nucleus affect the effective magnetic field sensed by the nucleus.

- Electron poor environment (shielded nuclei) sense a smaller effective magnetic field, so come into resonance at a lower frequency.
- Electron rich environment (deshielded nuclei) sense a larger effective magnetic field, so come into resonance at a higher frequency.

Intensity vs. Frequency:
- "Downfield" (shielded) region
- "Upfield" (deshielded) region
Electrons in bonds **shield** nuclei from magnetic field.

Different signals appear for nuclei in different environments.
Nuclear Magnetic Resonance Spectroscopy

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.
1 scan of conc. sample

200 scans of same sample
Spectrum of 2-butanone is illustrative- signal for C=O carbons on left edge
13.9 Chemical Shifts in $^1$H NMR Spectroscopy

- Proton signals range from $\delta$ 0 to $\delta$ 10
- Lower field signals are H’s attached to $sp^2$ C
- Higher field signals are H’s attached to $sp^3$ C
- Electronegative atoms attached to adjacent C cause downfield shift
<table>
<thead>
<tr>
<th>Type of hydrogen</th>
<th>Chemical shift (δ)</th>
<th>Type of hydrogen</th>
<th>Chemical shift (δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>Si(CH₃)₄</td>
<td>Alcohol</td>
<td>2.5–5.0</td>
</tr>
<tr>
<td>Alkyl (primary)</td>
<td>–CH₃</td>
<td>Alcohol, ether</td>
<td>3.3–4.5</td>
</tr>
<tr>
<td>Alkyl (secondary)</td>
<td>–CH₂</td>
<td>Vinylic</td>
<td>4.5–6.5</td>
</tr>
<tr>
<td>Alkyl (tertiary)</td>
<td>–CH</td>
<td>Aryl</td>
<td></td>
</tr>
<tr>
<td>Allylic</td>
<td>C≡C – C</td>
<td>Methyl ketone</td>
<td>2.0–2.4</td>
</tr>
<tr>
<td>Aromatic methyl</td>
<td>Ar – CH₃</td>
<td>Aldehyde</td>
<td>9.7–10.0</td>
</tr>
<tr>
<td>Alkynyl</td>
<td>–C≡C – H</td>
<td>Carboxylic acid</td>
<td>11.0–12.0</td>
</tr>
<tr>
<td>Alkyl halide</td>
<td>–C–Hal</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The relative intensity of a signal (integrated area) is proportional to the number of protons causing the signal.

This information is used to deduce the structure.

For example in ethanol (CH₃CH₂OH), the signals have the integrated ratio 3:2:1.

For narrow peaks, the heights are the same as the areas and can be measured with a ruler.

![NMR Spectrum](image.png)
Simple Spin-Spin Splitting

- An adjacent CH$_3$ group can have four different spin alignments as 1:3:3:1.
- This gives peaks in ratio of the adjacent H signal.
- An adjacent CH$_2$ gives a ratio of 1:2:1.
- The separation of peaks in a multiplet is measured is a constant, in Hz $J$ (coupling constant).
Chemical shift ($\delta$, ppm)

BrCH$_2$CH$_3$

4 lines; quartet

3 lines; triplet

$\text{CH}_3$

$\text{CH}_2$
Chemical shift ($\delta$, ppm)

BrCH(CH$_3$)$_2$
15.8 Spectroscopy of Aromatic Compounds

\[ ^1H \text{ NMR:} \]

Aromatic H’s strongly deshielded by ring and absorb between \( \delta 6.5 \) and \( \delta 8.0 \)

- Peak pattern is characteristic of positions of substituents
Ring Currents

- Aromatic ring oriented perpendicular to a strong magnetic field, delocalized $\pi$ electrons producing a small local magnetic field
  - *Opposes* applied field in middle of ring but *reinforces* applied field outside of ring
Spectroscopy of Aromatic Compounds

- UV: Peak near 205 nm and a less intense peak in 255-275 nm range
- $^1$H NMR: Aromatic H’s strongly deshielded by ring and absorb between $\delta$ 6.5 and $\delta$ 8.0
Aryl and Benzylic protons:

Aryl protons, 6.5–8.0 δ

Benzylic protons, 2.3–3.0 δ
$^{13}$C NMR of Aromatic Compounds

- Carbons in aromatic ring absorb at $\delta$ 110 to 140
- Shift is distinct from alkane carbons but in same range as alkene carbons

- Benzene
- Toluene
- Chlorobenzene
- Naphthalene

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# Summary of Spectroscopy

## Table 15.2 Summary of Spectroscopic Information on Aromatic Compounds

<table>
<thead>
<tr>
<th>Kind of spectroscopy</th>
<th>Absorption position</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infrared (cm(^1))</td>
<td>3030</td>
<td>Aryl C–H stretch</td>
</tr>
<tr>
<td></td>
<td>1500 and 1600</td>
<td>Two absorptions due to ring motions</td>
</tr>
<tr>
<td></td>
<td>690–900</td>
<td>Intense C–H out-of-plane bending</td>
</tr>
<tr>
<td>Ultraviolet (nm)</td>
<td>205</td>
<td>Intense absorption</td>
</tr>
<tr>
<td></td>
<td>255–275</td>
<td>Weak absorption</td>
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<tr>
<td>(^1^H) NMR ((\delta))</td>
<td>2.3–3.0</td>
<td>Benzylic protons</td>
</tr>
<tr>
<td></td>
<td>6.5–8.0</td>
<td>Aryl protons</td>
</tr>
<tr>
<td>(^1^3^C) NMR ((\delta))</td>
<td>110–140</td>
<td>Aromatic ring carbons</td>
</tr>
</tbody>
</table>

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