Welcome to CHM 2211
Organic Chemistry II
Chapters 2 (IR), 9, 13-20.

Spectroscopy
(interaction of molecule with electromagnetic radiations)

Chapter 2: Infrared Spectroscopy (IR)
Chapter 9: Nuclear Magnetic Resonance (NMR)
Chapter 9: Mass Spectrometry (MS)
Chapter 13: Ultraviolet-visible Spectroscopy (UV-VIS)

Spectroscopy
Electromagnetic Radiation
• The different forms of electromagnetic radiation make up the electromagnetic spectrum.

Infrared Spectroscopy
Electromagnetic Radiation
• The electromagnetic spectrum is arbitrarily divided into different regions.

• Wavelength (λ) and frequency (ν) are inversely related:

\[ \nu = \frac{c}{\lambda} \quad \text{[C= speed of light]} \]

• The energy (E) of a photon is directly proportional to its frequency and therefore inversely proportional to wavelength:

\[ E = h\nu \quad \text{[h = Planck's constant]} \]
Infrared Spectroscopy

Background

- Infrared (IR) spectroscopy is used to identify the functional groups in a compound. It uses IR radiation as the energy source.
- Frequencies in IR spectroscopy are reported using a unit called wavenumber (\(\tilde{\nu}\)):
  \[
  \tilde{\nu} = \frac{1}{\lambda}
  \]
- Wavenumber is inversely proportional to wavelength and is given in reciprocal centimeters (cm\(^{-1}\)).
- Therefore, frequency (and energy) increases as the wavenumber increases.

Using the wavenumber scale, IR absorptions for all organic compounds (functional groups) occur from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\).

Infrared Spectroscopy

- 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.

Characteristics of an IR Spectrum

- 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.
Infrared Spectroscopy

- Let us now consider the IR spectrum of 1-propanol, CH₃CH₂CH₂OH.
- Always look for the characteristic peak of the functional group present in the molecule.
- Characteristics of an IR Spectrum for 1-Propanol: the specific absorption of the OH group.
- 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.
- Wavenumber, frequency and energy decrease from left to right.
- Where a peak occurs is given in reciprocal centimeters (cm⁻¹).

Infrared Spectroscopy

Characteristics of an Infrared Spectrum

- The IR spectrum is divided into two regions: the functional group region (at ≥ 1500 cm⁻¹), and the fingerprint region (at < 1500 cm⁻¹).
- Please note a characteristic peak for a carbonyl from from ketone and ester at ~1700 cm⁻¹.

Infrared Spectroscopy

- Bonds absorb in four predictable regions of an IR spectrum.

**Summary of the four regions of the IR spectrum**

<table>
<thead>
<tr>
<th>Increasing wavenumber</th>
<th>Increasing energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonds to hydrogen</td>
<td>Triple bonds</td>
</tr>
<tr>
<td>C—H</td>
<td>C=O</td>
</tr>
<tr>
<td>O—H</td>
<td>C=N</td>
</tr>
<tr>
<td>N—H</td>
<td></td>
</tr>
<tr>
<td>lighter atoms</td>
<td>stronger bonds</td>
</tr>
<tr>
<td>higher frequency</td>
<td>higher frequency</td>
</tr>
<tr>
<td>fingerprint region</td>
<td></td>
</tr>
</tbody>
</table>

Infrared Spectroscopy

IR Absorptions in Hydrocarbons - Alkane

Hexane has only C-C single bonds and sp³ hybridized C atoms. Therefore it has only one major absorption at 3000-2850 cm⁻¹.
Infrared Spectroscopy

Even subtle differences that affect bond strength affect the frequency of an IR absorption.

IR Absorptions in Hydrocarbons - Alkenes
1-Hexene has a C=C and Csp3-H, in addition to sp3 hybridized C atoms. Therefore, there are three major absorptions: Csp3-H at 3150-3000 cm⁻¹; Csp3-H at 3000-2850 cm⁻¹; C=C at 1650 cm⁻¹.

IR Absorptions in Hydrocarbons - Alkynes
1-Hexyne has a C≡C and Csp-H, in addition to sp3 hybridized C atoms. Therefore, there are three major absorptions: Csp-H at 3300 cm⁻¹; Csp-H at 3000-2850 cm⁻¹; C≡C at 2250 cm⁻¹.

IR Absorptions in Oxygen Containing Compounds
The C=O groups in the ketones as well as aldehydes and esters show a strong absorption at ~1700 cm⁻¹.
Infrared Spectroscopy

**IR Absorptions in Nitrogen Containing Compounds - Amides**

The amide exhibits absorptions above 1500 cm\(^{-1}\) for both its N—H and C=O groups: N—H (two peaks) at 3200 and 3400 cm\(^{-1}\); C=O at 1660 cm\(^{-1}\).

![Infrared Spectrum of Amide](image)

**Carboxylic Acids and the Acidity of the O—H Bond**

![Infrared Spectrum of Butanoic Acid](image)

Nuclear Magnetic Resonance (NMR) Spectroscopy

- Two common types of NMR spectroscopy are used to characterize organic structure:
  - \(^1\)H NMR is used to determine the type and number of H atoms in a molecule;
  - \(^{13}\)C NMR is used to determine the type of carbon atoms in the molecule.
- The source of energy in NMR is radio waves which have long wavelengths, and thus low energy and frequency.
- When this low-energy radio waves interact with a molecule, they can change the nuclear spins of some elements, including \(^1\)H and \(^{13}\)C.

![NMR Spectra of 1-Bromopropane](image)

**NMR Spectra of 1-Bromopropane**

A typical \(^1\)H NMR spectra of 1-bromopropane is shown here: It has four features:
1. The number of signals in the spectrum tell us how many different set of protons are in the molecule.
2. The position of the signal in the spectrum along x-axis tell us about magnetic environment.
3. The area under the signal tell us how many protons there are in each set being measured.
4. The multiplicity (or splitting pattern) of each signal tell us about the number of protons on atoms adjacent to the one whose signal is being measured.
**NMR Spectroscopy - Chemical Shift Values**

- The position of a signal on the x-axis of an NMR spectrum is called chemical shift.
- It is measured in ppm, according to the following equation:

\[
\text{chemical shift} = \frac{\text{observed chemical shift (in Hz) downfield from TMS}}{\nu \text{ of the NMR spectrometer (in MHz)}}
\]

- Protons in a given environment absorb in a predictable region in an NMR spectrum.
- Most protons absorb between 0-10 ppm.
- The terms “upfield” and “downfield” describe the relative location of peaks. Upfield means to the right, downfield means to the left.
- NMR absorptions are measured relative to the position of a reference peak at 0 ppm on the δ scale due to tetramethylsilane (TMS). TMS is a volatile inert compound that gives a single peak upfield from typical NMR absorptions.

**Nuclear Magnetic Resonance Spectroscopy**

**1H NMR—The Spectrum**

- An NMR spectrum is a plot of the intensity of a peak against its chemical shift, measured in parts per million (ppm).

**1H NMR—Intensity of Signals (Integration)**

- The area under an NMR signal is proportional to the number of absorbing protons.
- An NMR spectrometer automatically integrates the area under the peaks, and prints out a stepped curve (the integral) on the spectrum.
- The height of each step is proportional to the area under the peak, which in turn is proportional to the number of absorbing protons.
**Nuclear Magnetic Resonance Spectroscopy**

**1H NMR—Spin-Spin Splitting**

The signal from a given proton will be split by the effect of magnetic fields associated with protons on neighboring carbons.

**General rule which describes the splitting patterns commonly seen in the 1H NMR spectra of organic compounds is as follow:**

\[
\text{A number of peaks from vicinal coupling in set is equaled } \ n + 1
\]

Where \( n \) is the number of vicinal hydrogens [at nearby (adjacent) carbons] that are nonequivalent to those producing the signal.

Please note that \( H_a \) and \( H_b \) are separated by three \( \sigma \) bonds. They are called vicinal protons because they are on adjacent carbons. Three bond coupling between them is called vicinal coupling.

Splitting is not generally observed between protons separated by more than three \( \sigma \) bonds.

**NMR Spectroscopy - 1H NMR—Spin-Spin Splitting**

Whenever two (or three) different sets of adjacent protons are equivalent to each other, use the \( n + 1 \) rule to determine the splitting pattern.

In general we have to ask only one question and then use \( N + 1 \) rule.

**Question.** How many protons are there on the adjacent carbon or carbons?

**Answer is** \( N = 6 \): Therefore, we should expect 7 lines in the multiplet for \( H \) at CHBr carbon.

**TABLE 15.4: Common Splitting Patterns Observed in 1H NMR**

<table>
<thead>
<tr>
<th>Example</th>
<th>Formula</th>
<th>Multiplet</th>
<th>Multiplet Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>[1]</td>
<td>( \text{CCH}_3 )</td>
<td>( H_a )</td>
<td>two peaks ------ ( n + 1 ) doublet</td>
</tr>
<tr>
<td>[2]</td>
<td>( \text{CHCl}_3 )</td>
<td>( H_a )</td>
<td>three peaks ------- ( n + 1 ) triplet</td>
</tr>
<tr>
<td>[3]</td>
<td>( \text{CH}_2\text{CH}_2\text{Cl}_2 )</td>
<td>( H_a )</td>
<td>three peaks ------- ( n + 1 ) triplet</td>
</tr>
<tr>
<td>[4]</td>
<td>( \text{CH}_2\text{CH}_2\text{Br}_2 )</td>
<td>( H_a )</td>
<td>four peaks ------- ( n + 1 ) quartet</td>
</tr>
<tr>
<td>[5]</td>
<td>( \text{CH}_2\text{CH}_2\text{Cl}_2 )</td>
<td>( H_a )</td>
<td>two peaks ------- ( n + 1 ) doublet</td>
</tr>
<tr>
<td>[6]</td>
<td>( \text{CH}_2\text{CH}_2\text{Br}_2 )</td>
<td>( H_a )</td>
<td>three peaks ------- ( n + 1 ) triplet</td>
</tr>
</tbody>
</table>
Consider the spectrum of alkyl bromides with molecular formula C₃H₇Br.

1. Count the number of signals!
2. Correlate chemical shift with possible structural environments!
3. Determine the relative area of each signal!
4. Interpret the splitting pattern!
5. Join the fragments to make a molecule which structure would be consistent with data!

Nuclear Magnetic Resonance Spectroscopy

Nuclear Spin – The Origin of the Signal
- When a charged particle such as a proton spins on its axis, it creates a magnetic field. Thus, the nucleus can be considered to be a tiny bar magnet.
- Normally, these tiny bar magnets are randomly oriented in space. However, in the presence of a magnetic field B₀, they are oriented with or against this applied field.
- The energy difference between these two states is very small (<0.1 cal).

Nuclear Magnetic Resonance Spectroscopy

- In a magnetic field, there are now two energy states for a proton: a lower energy state with the nucleus aligned in the same direction as B₀; and a higher energy state with the nucleus aligned opposed to B₀.
- When an external energy source (hv) that matches the energy difference (ΔE) between these two states is applied, energy is absorbed, causing the nucleus to “spin flip” from one orientation to another.
- The energy difference between these two nuclear spin states corresponds to the low frequency RF region of the electromagnetic spectrum.

Nuclear Magnetic Resonance Spectroscopy

Schematic of an NMR spectrometer
- Protons (which are the nuclei of hydrogen atoms) that are in different environments absorb at slightly different frequencies, so they are distinguishable by NMR.
- The frequency at which a particular proton absorbs is determined by the strength of the magnetic field generated by the electrons around it.
- NMR spectrometers are referred to as 300 MHz or 500 MHz instruments, and so forth, depending on the frequency of the RF radiation used for resonance.
- These spectrometers use powerful magnets to create a small but measurable energy difference between two possible spin states.
Nuclear Magnetic Resonance Spectroscopy

Shielding and Deshielding of Protons

- In the vicinity of the nucleus, the magnetic field generated by the circulating electron decreases the external magnetic field that the proton "feels".
- Since the electron experiences a lower magnetic field strength, it needs a lower frequency to achieve resonance. Lower frequency is to the right in an NMR spectrum, toward a lower chemical shift, so shielding shifts the absorption upfield.

Shielding and Deshielding of Protons

- The small magnetic field generated by electrons is called an induced field. Since the actual magnetic field sensed by proton is slightly less than the external field, the electrons are said to shield the protons and the signal is shifted upfield since lower energy is needed to achieve resonance.

Position of Signals - Shielding and Deshielding of Protons

Relation to Chemical Shift

- As the electron density around the nucleus increases, the nucleus feels a smaller resultant magnetic field, so a lower frequency is needed to achieve resonance. The absorption shifts upfield.
- As the electron density around the nucleus decreases, the nucleus feels a larger resultant magnetic field, so a higher frequency is needed to achieve resonance. The absorption shifts downfield.
Nuclear Magnetic Resonance Spectroscopy

**Position of Signals - Shielding and Deshielding of Protons**

**Aromatic Compounds**

- In a magnetic field, the six π electrons in benzene circulate around the ring creating a ring current.
- The magnetic field induced by these moving electrons reinforces the applied magnetic field in the vicinity of the protons.
- The protons thus feel a stronger magnetic field and a higher frequency is needed for resonance. Thus they are deshielded and absorb downfield.

**Position of Signals - Shielding and Deshielding of Protons**

**Alkenes**

- In a magnetic field, the loosely held π electrons create a magnetic field that reinforces the applied field in the vicinity of the protons.
- Since the protons now feel a stronger magnetic field, they require a higher frequency for resonance. Thus the protons are deshielded and the absorption is downfield.

**Position of Signals - Shielding and Deshielding of Protons**

**Alkynes**

- In a magnetic field, the π electrons of a carbon-carbon triple bond are induced to circulate, but in this case the induced magnetic field opposes the applied magnetic field (B₀).
- Thus, the proton feels a weaker magnetic field, so a lower frequency is needed for resonance. The nucleus is shielded and the absorption is upfield.

**1H NMR—Position of Signals – Effect of electronegativity**

- Protons near electronegative atoms are deshielded, so they absorb downfield.
- This deshielded nucleus experiences a higher magnetic field strength, so it needs a higher frequency to achieve resonance.
- Higher frequency is to the left in an NMR spectrum, toward higher chemical shift—so deshielding shifts an absorption downfield.
Nuclear Magnetic Resonance Spectroscopy

Summary — Shielding and Chemical Shift Values

<table>
<thead>
<tr>
<th>TABLE 15.2 Effect of π Electrons on Chemical Shift Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton type</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>C=C–H</td>
</tr>
<tr>
<td>H</td>
</tr>
</tbody>
</table>

Aldehyde protons are highly deshielded and resonates at around 9.8 ppm. Why?

Chemical Shift Equivalent and Nonequivalent Protons. Homotopic and Heterotopic Hydrogens

• How do we decide whether two or more protons in a molecule are in identical environment (chemical, magnetic)? - Atom replacement method

Replacing any one of the six hydrogens of ethane by different atoms gives the same compound. All six hydrogens are homotopic and therefore chemical shift equivalent.

Homotopic hydrogens have identical environment and will have the same chemical shift. They are said to be chemical shift equivalent. Heterotopic atoms have different chemical shift and are not chemical shift equivalent.

The number of NMR signals equals the number of different types of protons in a compound.

Protons in different environments give different NMR signals.

Equivalent protons (chemically and magnetically) give the same NMR signal.

However, two H atoms on a ring or double bond protons are equivalent only if they are cis (or trans) to the same groups.

1H NMR — Number of Signals
Nuclear Magnetic Resonance Spectroscopy

\(^1\)H NMR—Enantiotopic and Diastereotopic Protons.

- Enantiotopic hydrogens have the same chemical shift and appear in the same signal.
- When substitution of two H atoms by Z forms enantiomers, the two H atoms are equivalent and give a single NMR signal. These two H atoms are called enantiotopic protons.

\(^1\)H NMR for alkenes:

How can we distinguish between E and Z isomers?

Different magnitude of the coupling constant for the hydrogen in trans and cis relation

The magnitude of the coupling constant \(J\) for trans protons are larger than for the cis protons (the lines in respective doublets are more separated).

\(^1\)H NMR—OH Protons: The Spectra of alcohols.

- Under usual conditions, an OH proton does not split the NMR signal of adjacent protons.
- The signal due to an OH proton is not split by adjacent protons.

\(\text{H}_2\text{O}, \text{H}_3\text{O}^+\)
The frequency difference, measured in Hz between two peaks of the doublet is called the coupling constant, \( J \).

When two adjacent protons \( H_a \) are coupled to \( H_b \), there are four possible combinations of the magnetic moments for the two \( H_a \)s.

- Two of these combinations involve pairings of magnetic moments that cancel each other, causing no net displacement of signal.
- One combination of magnetic moments reinforces and another subtracts from the applied magnetic field.
- \( H_a \) is split into a triplet having a 1:2:1 ratio of signal areas.
When three adjacent protons are coupled to H_a, there are 10 possible combinations of the magnetic moments for the H_b.

Four unique orientations exist and so H_a is split into a quartet with intensities 1:4:4:1.

**NMR Spectroscopy - 13C NMR**

- The two features of a 13C NMR spectrum that provide the most structural information are the number of signals observed and the chemical shifts of those signals.
- The lack of splitting in a 13C spectrum is a consequence of the low natural abundance of 13C.
- Recall that splitting occurs when two NMR active nuclei—like two protons—are close to each other. Because of the low natural abundance of 13C nuclei (1.1%), the chance of two 13C nuclei being bonded to each other is very small (0.01%), and so no carbon-carbon splitting is observed.
- A 13C NMR signal can also be split by nearby protons. This 1H-13C splitting is usually eliminated from the spectrum by using an instrumental technique that decouples the proton-carbon interactions, so that every peak in a 13C NMR spectrum appears as a singlet.

13C NMR Spectroscopy — Number of Signals

- The number of signals in a 13C spectrum gives the number of different types of carbon atoms in a molecule.
- Because 13C NMR signals are not split, the number of signals/lines in the 13C spectrum equals number of nonequivalent carbons.
- In contrast to the 1H NMR situation, peak intensity is not proportional to the number of absorbing carbons, so 13C NMR signals are not integrated.
13C Chemical Shifts

- Just as in 1H NMR spectroscopy, chemical shifts in 13C NMR depend on the electron density around the carbon nucleus.
  - Decreased electron density causes the signal to move downfield (deshielding)
  - Increased electron density causes the signal to move upfield (shielding)

Because of the wide range of chemical shifts, it is rare to have two 13C peaks coincidentally overlap.

A group of 3 peaks at δ 77 comes from the common NMR solvent deuteriochloroform and can be ignored.