INFRARED SPECTROSCOPY

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Hardoi
“Seeing The non-seeable”

“Using electromagnetic radiation as a probe to obtain information about atoms and molecules that are too small to see”
What is Spectroscopy?

- Atoms and molecules interact with electromagnetic radiation (EMR) in a wide variety of ways.
- Atoms and molecules may absorb and/or emit EMR.
- Absorption of EMR stimulates different types of motion in atoms and/or molecules.
- The patterns of absorption (wavelengths absorbed and to what extent) and/or emission (wavelengths emitted and their respective intensities) are called ‘spectra’.
- **Spectroscopy** is the interaction of EMR with matters to get *spectra*, which gives information like, bond length, bond angle, geometry and molecular structure.
Electromagnetic radiation displays the properties of both particles and waves. The particle component is called a photon. The term “photon” is implied to mean a small, massless particle that contains a small wave-packet of EM radiation/light.

The energy (E) component of a photon is proportional to the frequency. Where h is Planck’s constant and ν is the frequency in Hertz (cycles per second).

\[ E = h \nu \]

\( h \) = distance of one wave
\( \nu \) = frequency: waves per unit time (sec\(^{-1}\), Hz)
\( c \) = speed of light (3.0 \( \times \) 10\(^8\) m \( \times \) sec\(^{-1}\))
\( h \) = Planck’s constant (6.63 \( \times \) 10\(^{-34}\) J \( \times \) sec)
Because the speed of light, \( c \), is constant, the frequency, \( n \), (number of cycles of the wave per second) can complete in the same time, must be inversely proportional to how long the oscillation is, or wavelength:

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

\( c = 3 \times 10^{10} \text{ cm/s} \)

Because the atomic particles in matter also exhibit wave and particle properties, EM radiation can interact with matter in two ways:

- **Collision** – particle-to-particle – energy is lost as heat and movement.
- **Coupling** – the wave property of the radiation matches the wave property of the particle and “couple” to the next higher quantum mechanical energy level
Electromagnetic Spectrum

Frequency, $\nu$ in Hz

Energy (kcal/mol)

Wavelength, $\lambda$

- $\gamma$-rays: nuclear excitation (PET)
- X-rays: core electron excitation (X-ray cryst.)
- UV: electronic excitation ($\pi$ to $\pi^*$)
- IR: molecular vibration
- Microwave: molecular rotation
- Radio: Nuclear Magnetic Resonance (NMR)

Visible light
Principles of molecular spectroscopy

**UV-Visible:** valence electron transitions
- gives information about p-bonds and conjugated systems

**Infrared:** molecular vibrations (stretches, bends)
- identify functional groups

**Radiowaves:** nuclear spin in a magnetic field (NMR)
- gives a map of the H and C framework
1. **Nuclear Magnetic Resonance (NMR)** – Excitation of the nucleus of atoms through radiofrequency irradiation. Provides extensive information about molecular structure and atom connectivity.

2. **Infrared Spectroscopy (IR)** – Triggering molecular vibrations through irradiation with infrared light. Provides mostly information about the presence or absence of certain functional groups.

3. **Mass spectrometry** – Bombardment of the sample with electrons and detection of resulting molecular fragments. Provides information about molecular mass and atom connectivity.

4. **Ultraviolet spectroscopy (UV)** – Promotion of electrons to higher energy levels through irradiation of the molecule with ultraviolet light. Provides mostly information about the presence of conjugated p systems and the presence of double and triple bonds.
Infrared (IR) Spectroscopy

- IR deals with the interaction of infrared radiation with matter. The IR spectrum of a compound can provide important information about its chemical nature and molecular structure.

- Most commonly, the spectrum is obtained by measuring the absorption of IR radiation, although infrared emission and reflection are also used.

- Widely applied in the analysis of organic materials, also useful for polyatomic inorganic molecules and for organometallic compounds.
Infrared spectrometry is applied to the **qualitative and quantitative** determination of molecular species of all types.

The most widely used region is the mid-infrared that extends from about **400 to 4000 cm\(^{-1}\)** (2.5 to 25 \(\mu m\)). (Absorption, reflection and emission spectra are employed)

The near-infrared region from **4000 to 14,000 cm\(^{-1}\)** (0.75 to 2.5 \(\mu m\)) also finds considerable use for the routine quantitative determination. (**water, CO\(_2\), low conc. Hydrocarbons, amine nitrogen, many other compounds**)

The far-infrared region has been for the **determination of the structures of inorganic and metal-organic species**.
# Range of IR Radiation

<table>
<thead>
<tr>
<th>Region</th>
<th>Energy (kJ/mol)</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Wavelength (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near IR</td>
<td>150-50</td>
<td>12,800-4000</td>
<td>0.78-2.5</td>
</tr>
<tr>
<td>Mid IR</td>
<td>50-2.5</td>
<td>4000-200</td>
<td>2.5-50</td>
</tr>
<tr>
<td>Far IR</td>
<td>2.5-0.1</td>
<td>200-10</td>
<td>50-1000</td>
</tr>
<tr>
<td>Spectral Regions</td>
<td>Measurement Type</td>
<td>Kind of Analysis</td>
<td>Applicable Samples</td>
</tr>
<tr>
<td>------------------</td>
<td>----------------------</td>
<td>------------------</td>
<td>--------------------------------------------------------</td>
</tr>
<tr>
<td>Near-IR</td>
<td>Diffuse reflectance</td>
<td>Quantitative</td>
<td>Solid or liquid commercial materials</td>
</tr>
<tr>
<td></td>
<td>Absorption</td>
<td>Quantitative</td>
<td>Gaseous mixtures</td>
</tr>
<tr>
<td>Mid-IR</td>
<td>Absorption</td>
<td>Qualitative</td>
<td>Pure solid, liquid, or gases</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Quantitative</td>
<td>Complex liquid, solid, or gaseous mixtures</td>
</tr>
<tr>
<td></td>
<td>Reflectance</td>
<td>Qualitative</td>
<td>Complex liquid, solid, or gaseous mixtures</td>
</tr>
<tr>
<td></td>
<td>Emission</td>
<td>Quantitative</td>
<td>Pure solids or liquids</td>
</tr>
<tr>
<td>Far-IR</td>
<td>Absorption</td>
<td>Qualitative</td>
<td>Atmospheric samples</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pure inorganic or organometallic species</td>
</tr>
</tbody>
</table>
Conditions For IR Activity

- Energy of IR photon insufficient to cause electronic excitation but can cause *vibrational* or *rotational* excitation.
- Molecule electric field (dipole moment) interacts with IR photon electric field (*both dynamic*).
- Magnitude of dipole moment determined by:
  (i) *charge*
  (ii) *separation of charge*
- Molecule must have change in dipole moment due to vibration or rotation to absorb IR radiation.
- Absorption causes increase in vibration amplitude/rotation frequency.
**DIPOLE MOMENT ($\mu$)**

\[ \mu = Q \times r \]

- $Q =$ charge and $r =$ distance between charges
- Asymmetrical distribution of electrons in a bond renders the bond polar
- A result of electro negativity difference
- $\mu$ changes upon vibration due to changes in $r$
- Change in $\mu$ with time is necessary for a molecule to absorb IR radiation
The repetitive changes in $\mu$ makes it possible for polar molecules to absorb IR radiation.

Symmetrical molecules do not absorb IR radiation since they do not have dipole moment ($O_2$, $F_2$, $H_2$, $Cl_2$).

Diatomric molecules with dipole moment are IR-active ($HCl$, $HF$, $CO$, $HI$).

Molecules with more than two atoms may or may not be IR active depending on whether they have permanent net dipole moment.
A bond or molecule must have a permanent dipole moment. If not, then, some of its vibration must produce an induced dipole moment in order to have an absorbance in the IR spectrum.

\[ \text{Case I: } \mu \neq 0 \text{ and } \frac{d\mu}{dx} \neq 0; \text{ IR Active} \]

\[ \text{Case II: } \mu = 0 \text{ and } \frac{d\mu}{dx} \neq 0; \text{ IR Active} \]

\[ \text{Case III: } \mu = 0 \text{ and } \frac{d\mu}{dx} = 0; \text{ IR Inactive} \]

The frequency of vibration of a particular bond must be equal to the frequency of IR radiation.
Molecules with permanent dipole moments (μ) are IR active!

HCl, H₂O, NO
IR active

Atoms, O₂, H₂, Cl₂
IR inactive
Some linear molecules may be IR active

\[ \text{CO}_2 \quad \text{O=O=O} \]

\[ \delta^- \quad 2\delta^+ \quad \delta^- \quad \text{No net dipole moment change} \]
$\delta^-$ $2\delta^+$ $\delta^-$

$\nu_s$ not IR active $\nu_{as}$, bend IR active

Net dipole moment change
IR ABSORPTION BY MOLECULES

- Molecules with covalent bonds may absorb IR radiation
- Absorption is quantized
- Molecules move to a higher energy state
- IR radiation is sufficient enough to cause rotation and vibration. The IR scans a range of frequencies (in the infrared part of the electromagnetic spectrum). Any frequency which matches the characteristic frequency of a bond will be absorbed
- Radiation between 1 and 100 µm will cause excitation to higher vibrational states
Absorption spectrum is composed of broad vibrational absorption bands.

Molecules absorb radiation when a bond in the molecule vibrates at the same frequency as the incident radiant energy.

Molecules vibrate at higher amplitude after absorption.

A molecule must have a change in dipole moment during vibration in order to absorb IR radiation.
Absorption frequency depends on:

- Masses of atoms in the bonds
- Geometry of the molecule
- Strength of bond
- Other contributing factors
Infrared radiation is largely thermal energy. It induces stronger **molecular vibrations** in covalent bonds, which can be viewed as springs holding together two masses, or atoms.

**Specific bonds respond to (absorb) specific frequencies**

\[ \mu = \frac{m_1 \cdot m_2}{m_1 + m_2}, \text{ reduced mass} \]

\[ K = \text{Force constant} \]
As a covalent bond oscillates – due to the oscillation of the dipole of the molecule – a varying electromagnetic field is produced. The greater the dipole moment change through the vibration, the more intense the EM field that is generated.
When a wave of infrared light encounters this oscillating EM field generated by the oscillating dipole of the same frequency, the two waves couple, and IR light is absorbed. The coupled wave now vibrates with twice the amplitude.
Types of vibrations

**Stretching** – Vibration or oscillation along the line of the bond (change of bond length)
Types of vibrations

**Bending** Vibration or oscillation not along the line of the bond (change of bond angle)

- **scissor**
- **rock**

*in plane*

- **twist**
- **wag**

*out of plane*
Symmetric stretching
Antisymmetric stretching
In-plane bending
Out-of-plane bending
Vibrational Modes

- Covalent bonds can vibrate in several modes, including \textit{stretching}, \textit{bending} (rocking, scissoring, wagging and twisting)
- The most useful bands in an infrared spectrum correspond to \textit{stretching frequencies}, and those will be the ones we’ll focus on.

A molecule containing \textit{n atoms}, has \textbf{3n} degrees of freedom.

\textbf{3n = Translational modes} + \textbf{Rotational modes} + \textbf{Vibrational Modes}

\textbf{Linear Molecule :} \quad \text{TM} = 3, \text{ RM} = 2, \text{ hence }, \quad 3n = 3 + 2 + \text{Vibrational Modes}
\quad \text{Vibrational Modes} = (3n-5); \quad \text{C}_2\text{H}_2, \text{ CO}_2
\quad \text{Strecthing vib} = (n-1)
\quad \text{bending vib} \quad = (2n-4)

\textbf{Non-linear Molecule :} \quad \text{Vibrational Modes} = (3n-6); \quad \text{C}_6\text{H}_6, \text{ CHCl}_3
\quad \text{Strecthing vib} \quad = (n-1)
\quad \text{bending vib.} \quad = (2n-5)
Number of possible modes

**Nonlinear molecule: 3N – 6**

**Linear molecule: 3N – 5**

- 3 degrees of freedom – i.e., 3 coordinates in space
- 3 translations and 3 rotations account for 6 motions of molecule
- Rotation about center bond in linear molecule is indistinguishable
- Remaining degrees of motion represent vibrational motion (i.e., number of vibrations within the molecule)
Factors Influencing the Normal Modes

Four factors tend to produce fewer experimental peaks than would be expected from the theoretical number of normal modes.

(1) the symmetry of the molecules is such that no change in dipole results from a particular vibration

(2) the energies of two or more vibrations are identical or nearly identical

(3) the absorption intensity is so low as to be undetectable by ordinary means

(4) the vibrational energy is in a wavelength region beyond the range of the instrument.
Occasionally more peaks are found than are expected based upon the number of normal modes.

The occurrence of overtone peaks that occur at two or three times the frequency of a fundamental peak. In addition combination bands are sometimes encountered when a photon excites two vibrational modes simultaneously.

The frequency of the combination band is approximately the sum or difference of the two fundamental frequencies.
Vibrational Coupling

The energy of a vibration, and thus the wavelength of its absorption peak, may be influenced by other vibrators in the molecule.

A number of factors influence the extent of such coupling:

1. Strong coupling between stretching vibrations occurs only when there is an atom common to the two vibrations.

2. Interaction between bending vibrations requires a common bond between the vibrating groups.
3. Coupling between a stretching and a bending vibration can occur if the stretching bond forms one side of the angle that varies in the bending vibration.

4. Interaction is greatest when the coupled groups have individual energies that are approximately equal.

5. Little or no interaction is observed between groups separated by two or more bonds.

6. Coupling requires that the vibrations be of the same symmetry species.
CO$_2$ Molecule

If no coupling occurred between the two C=O bonds, an absorption peak would be expected at the same peak for the C=O stretching vibration in an aliphatic ketone (about 1700 cm$^{-1}$). Experimentally, carbon dioxide exhibits **two absorption peaks**, the one at 2350 cm$^{-1}$ and the other at 666 cm$^{-1}$. Carbon dioxide is a linear molecule and thus has $3 \times 3 - 5 = 4$ normal modes. Two stretching vibrations are possible. The symmetric vibration causes no change in dipole. Thus, the symmetric vibration is infrared inactive.

The asymmetric vibration produce a change in dipole moments, so absorption at 2330 cm$^{-1}$ results.

The remaining two vibrational modes of carbon dioxide involve scissoring. The two bending vibrations are the resolved components at 90 deg to one another of the bending motion in all possible planes around the bond axis. The two vibrations are identical in energy and thus produce a single peak at 667 cm$^{-1}$.
Example: CO₂

- Symmetrical stretching: 1340 cm⁻¹
- Asymmetrical stretching: 2350 cm⁻¹
- Scissoring bending: 666 cm⁻¹
H\textsubscript{2}O molecule

Triatomic molecule such as water, sulfur dioxide, or nitrogen dioxide have $3 \times 3 - 6 = 3$ vibrational modes. The central atom is not in line with the other two, a symmetric stretching vibration will produce a change in dipole and will thus be responsible for infrared absorption. Stretching peaks at 3650 and 3760 cm\(^{-1}\) appear in the infrared spectrum for the symmetric and asymmetric vibrations of the water molecule. There is only one component to the scissoring vibration for this nonlinear molecule. For water, the bending vibration cause absorption at 1595 cm\(^{-1}\).
Symmetric stretching

Asymmetric stretching

Scissoring
In an IR Spectrum each stretching and bending vibration occurs with a characteristic frequency as the atoms and charges involved are different for different bonds.

The y-axis on an IR spectrum is in units of % transmittance.

In regions where no oscillating bond is interacting with IR light, transmittance nears 100%.

In regions where the EM field of an oscillating bond interacts with IR light of the same frequency, transmittance is low (light is absorbed).
The x-axis of the IR spectrum is in units of wavenumber, \( n \), which is the number of waves per centimeter in units of \( \text{cm}^{-1} \).

(Remember \( E = h\nu \) or \( E = \frac{hc}{\lambda} \))
Use of unit “wavenumbers”

1. This unit \textit{wavenumbers} is used rather than wavelength (microns) because wavenumbers are directly proportional to the energy of transition being observed – \textit{chemists like this, physicists hate it}

\textit{High frequencies and high wavenumbers equate higher energy is quicker to understand than Short wavelengths equate higher energy}

2. This unit is used rather than frequency as the numbers are more “real” than the exponential units of frequency

3. IR spectra are observed for the mid-infrared: 600-4000 cm\textsuperscript{-1}
I. R. Spectrum

The IR spectrum is basically a plot of transmitted (or absorbed) frequencies vs. intensity of the transmission (or absorption). Frequencies appear in the $x$-axis in units of inverse centimeters (wave numbers), and intensities are plotted on the $y$-axis in percentage units.

The graph 2nd above shows a spectrum in transmission mode. This is the most commonly used representation and the one found in most chemistry and spectroscopy books. Therefore we will use this representation
Infrared Active Bonds

1. Not all covalent bonds display bands in the IR spectrum. Only polar bonds do so. These are referred to as IR active.

2. The intensity of the bands depends on the magnitude of the dipole moment associated with the bond in question:
   - Strongly polar bonds such as carbonyl groups (C=O) produce strong bands.
   - Medium polarity bonds and asymmetric bonds produce medium bands.
   - Weakly polar bond and symmetric bonds produce weak or non observable bands.
Infrared Band Shapes

Two of the most common bands are narrow; thin and pointed, like a dagger and broad bands; wide and smoother.

A typical example of a broad band is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids, as shown below.

![Graph showing broad bands]

100 %

0 %
CLASSIFICATION OF IR BANDS

IR bands can be classified as **strong** (s), **medium** (m), or **weak** (w), depending on their relative intensities in the infrared spectrum. A strong band covers most of the y-axis. A medium band falls to about half of the y-axis, and a weak band falls to about one third or less of the y-axis.

- **Strong** (s) – peak is tall, transmittance is low (0-35 %)
- **Medium** (m) – peak is mid-height (75-35%)
- **Weak** (w) – peak is short, transmittance is high (90-75%)
Information Obtained From Ir Spectra

- IR is most useful in providing information about the presence or absence of specific **functional groups**.

- IR can provide a **molecular fingerprint** that can be used when comparing samples. If two pure samples display the same IR spectrum it can be argued that they are the same compound.

- **IR does not** provide detailed information or proof of molecular formula or structure. It provides information on molecular fragments, specifically functional groups.

- Therefore it is very limited in scope, and must be used in conjunction with other techniques to provide a more complete picture of the molecular structure.
The Fingerprint Region

Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the **600 - 1400 cm\(^{-1}\)** range is called the **fingerprint region**. This is normally a complex area showing many bands, frequently overlapping each other.

Focus your analysis on this region. This is where most stretching frequencies appear.

Fingerprint region: complex and difficult to interpret reliably.
Note that the blue coloured sections above the dashed line refer to stretching vibrations, and the green coloured band below the line encompasses bending vibrations.
Summary of IR Absorptions
Applications of Infrared Spectroscopy

- Infrared spectrometry is applied to the qualitative and quantitative determination of molecular species of all types.

- The most widely used region is the **mid-infrared** that extends from about 400 to 4000 cm\(^{-1}\) (2.5 to 25 \(\mu\)m). (Absorption, reflection and emission spectra are employed)

- The **near-infrared region** from 4000 to 14,000 cm\(^{-1}\) (0.75 to 2.5 \(\mu\)m) also finds considerable use for the routine quantitative determination. (water, CO\(_2\), low conc. Hydrocarbons, amine nitrogen, many other compounds)

- The **far-infrared region** has been for the determination of the structures of inorganic and metal-organic species.
# Functional Groups & IR Frequencies

## Table 13.4 Important IR Stretching Frequencies

<table>
<thead>
<tr>
<th>Type of bond</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C≡N</td>
<td>2260–2220</td>
<td>medium</td>
</tr>
<tr>
<td>C≡C</td>
<td>2260–2100</td>
<td>medium to weak</td>
</tr>
<tr>
<td>C＝C</td>
<td>1680–1600</td>
<td>medium</td>
</tr>
<tr>
<td>C＝N</td>
<td>1650–1550</td>
<td>medium</td>
</tr>
<tr>
<td>C＝C (ring)</td>
<td>~1600 and ~1500–1430</td>
<td>strong to weak</td>
</tr>
<tr>
<td>C＝O</td>
<td>1780–1650</td>
<td>strong</td>
</tr>
<tr>
<td>C－O</td>
<td>1250–1050</td>
<td>strong</td>
</tr>
<tr>
<td>C－N</td>
<td>1230–1020</td>
<td>medium</td>
</tr>
<tr>
<td>O－H (alcohol)</td>
<td>3650–3200</td>
<td>strong, broad</td>
</tr>
<tr>
<td>O－H (carboxylic acid)</td>
<td>3300–2500</td>
<td>strong, very broad</td>
</tr>
<tr>
<td>N－H</td>
<td>3500–3300</td>
<td>medium, broad</td>
</tr>
<tr>
<td>C－H</td>
<td>3300–2700</td>
<td>medium</td>
</tr>
</tbody>
</table>
Factors effecting IR absorption

\[ v = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \]

1. Force constant, \( k \)
2. Reduced mass, \( \mu \)
3. Electronegativity difference, \( N \)
4. Bond dissociation energy, \( D \)
5. Internuclear distance, \( r \)

It also depends upon: **Inductive effect, resonance, H-bonding**

and **steric** effect etc.

Stronger bonds will have higher Force constant \( K \)
Sample problem

The force constant for a typical triple bond is $1.91 \times 10^3$ N/m. Calculate the approximate frequency of the main absorption peak due to vibration of CO.
**Force Constant:**

Stronger bonds will have higher Force constant. \( K \)

**Triple bonds > Double bonds > Single bonds**

- \( \text{C≡C} > \text{C=\ce{C}} > \text{C-\ce{C}} \)
- \( \text{C≡O} > \text{C=\ce{O}} > \text{C-\ce{O}} \)
- \( \text{C≡N} > \text{C=\ce{N}} > \text{C-\ce{N}} \)
PREDICTING STRUCTURE OF UNKNOWN

- Identify the major functional groups from the strong absorption peaks

- Identify the compound as aromatic or aliphatic

- Subtract the FW of all functional groups identified from the given molecular weight of the compound

- Look for C≡C and C=C stretching bands

- Look for other unique CH bands (e.g. aldehyde)

- Use the difference obtained to deduce the structure
INTERPRETATION OF IR SPECTRA

Functional Group Region
Strong absorptions due to stretching from hydroxyl, amine, carbonyl, CH\textsubscript{x}

4000 – 1300 cm\textsuperscript{-1}

Fingerprint Region
Result of interactions between vibrations

1300 – 910 cm\textsuperscript{-1}
Conjugation

By resonance, conjugation lowers the energy of a double or triple bond. The effect of this is readily observed in the IR spectrum:

Conjugation will lower the observed IR band for a carbonyl from 20-40 cm\(^{-1}\) provided conjugation gives a strong resonance contributor

Inductive effects are usually small, unless coupled with a resonance contributor (note –CH\(_3\) and –Cl above)
Steric Effects

Usually not important in IR spectroscopy, unless they reduce the strength of a bond (usually p) by interfering with proper orbital overlap:

Here the methyl group in the structure at the right causes the carbonyl group to be slightly out of plane, interfering with resonance

**Strain effects** – Changes in bond angle forced by the constraints of a ring will cause a slight change in hybridization, and therefore, bond strength

As bond angle decreases, carbon becomes more electronegative, as well as less sp$^2$ hybridized (bond angle $< 120^\circ$)
Hydrogen bonding

- Hydrogen bonding causes a broadening in the band due to the creation of a continuum of bond energies associated with it.

- In the solution phase these effects are readily apparent; in the gas phase where these effects disappear or in lieu of steric effects, the band appears as sharp as all other IR bands:

- H-bonding can interact with other functional groups to lower frequencies

\[ \text{C}=\text{O}; 1701 \text{ cm}^{-1} \]
1-hexanol  \( \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH} \)

- **Gas phase**
  - 3670 cm\(^{-1}\): free O-H stretching
  - 2875 cm\(^{-1}\)
  - 2950 cm\(^{-1}\)

- **CCl\(_4\) solution (0.25 M)**
  - 3510 cm\(^{-1}\): terminal hydrogen bond
  - 3638 cm\(^{-1}\): free O-H stretching
  - 3340 cm\(^{-1}\)
  - 2874 cm\(^{-1}\)
  - 2861 cm\(^{-1}\)
  - 2959 cm\(^{-1}\)
  - 2932 cm\(^{-1}\)
  - 324 cm\(^{-1}\)

- **Liquid film**
  - 3324 cm\(^{-1}\)
  - 2958 cm\(^{-1}\)
  - 2933 cm\(^{-1}\)
Steric hindrance to H-bonding in a di-tert-butylphenol
Gas phase spectrum of 1-butanol
Single Bond Region

\[
\begin{align*}
\text{O-H} & \quad \nu = 3400-3600 \text{ cm}^{-1} \\
\text{N-H} & \quad \nu = 3200-3400 \text{ cm}^{-1} \\
\text{C-H} & \quad \nu = 2900-3100 \text{ cm}^{-1}
\end{align*}
\]

Greater the dipole moment, the more intense the absorption. But, actually it is not so. There are other factors which affect the absorption in IR region.
Infrared Absorption Frequencies of C-H

Depend upon the state of hybridization of C-atom attached.

<table>
<thead>
<tr>
<th>Structural unit</th>
<th>Frequency, cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$sp$ C—H</td>
<td>3310-3320</td>
</tr>
<tr>
<td>$sp^2$ C—H</td>
<td>3000-3100</td>
</tr>
<tr>
<td>$sp^3$ C—H</td>
<td>2850-2950</td>
</tr>
</tbody>
</table>
Alkanes – combination of C-C and C-H bonds

- C-C stretches and bends 1360-1470 cm\(^{-1}\)
- CH\(_2\)-CH\(_2\) bond 1450-1470 cm\(^{-1}\)
- CH\(_2\)-CH\(_3\) bond 1360-1390 cm\(^{-1}\)
- sp\(^3\) C-H between 2800-3000 cm\(^{-1}\)
Octane

H–C–H

(w – s) (m)
CH₃(CH₂)₄CH₃
(a) n-hexane

C—H stretch
C—H bending
**n-pentane**

C$_5$H$_{12}$

2850-2960 cm$^{-1}$

3000 cm$^{-1}$ sat’d C-H

1470 & 1375 cm$^{-1}$

CH$_3$CH$_2$CH$_2$CH$_2$CH$_3$
$n$-hexane

$C_6H_{14}$

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$
2-methylbutane (isopentane)

C\textsubscript{5}H\textsubscript{12}
2,3-dimethylbutane

$C_6H_{14}$

- 3176 86
- 2959 4
- 2955 13
- 2876 9
- 2722 84
- 2614 86
- 2591 86
- 2591 77
- 2531 77
- 2504 74
- 2504 74
- 2504 49
- 1651 77
- 1621 72
- 1613 74
- 1607 74
- 1564 24
- 1381 33
- 1371 39
- 1360 79
- 1323 77
- 1280 81
- 1223 64
- 1218 62
- 1209 60
- 1153 77
- 1128 62
- 1095 60
- 991 79
- 966 81
- 960 64
- 870 84
- 823 56
- 814 79

\[
\text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_3 \\
\text{CH}_3 \quad \text{CH}_3
\]
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<tr>
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<tr>
<td>2599</td>
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</table>

`Cyclohexane` is not observed at 1375 cm\(^{-1}\) and does not contain an \(-\text{CH}_3\) group.
Toluene

\[
\text{C} - \text{H} \quad \text{sp}^2 \quad \text{sp}^3 \\
\text{C} - \text{H} 
\]

aromatic

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

aromatic oops
isopropylbenzene

C₉H₁₂

isopropyl split 1370 + 1385
**PHENYLACETYLENE**

\[
C_8H_6
\]

\[
C_8H_6 - C_6H_5 = C_2H
\]

**C-H**

unsat’d 1500, 1600 benzene

3300 **≡C-H**

mono

---

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<tr>
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<td>66</td>
<td>883</td>
<td>84</td>
<td>614</td>
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</tbody>
</table>
**C₄H₈**

- **Unst’d**

- **1640-1680 cm⁻¹**

- **880-900 cm⁻¹**

- **C=CH₂**

- **R₂C=CH₂**

**Isobutylene**

- **CH₃C=CH₂**

**Sadler 8514 K**

**Frequency, cm⁻¹**

**Absorbance**

**Wavelength, μ**
\[ \text{C}_9\text{H}_{12} \]

**C-H unsat’d & sat’d**

**1500 & 1600 benzene**

**C}_9\text{H}_{12} - \text{C}_6\text{H}_5 = -\text{C}_3\text{H}_7**

*isopropylbenzene*

*propylbenzene?*
$n$-propylbenzene

$C_9H_{12}$

\[
\text{3108 77  2873 20  1466 41  1111 77  619  74}
\text{3085 52  1941 79  1453 18  1095 62  743  9}
\text{3064 43  1801 81  1379 55  1076 81  696  4}
\text{3028 22  1604 49  1341 70  1060 74  587  70}
\text{3002 62  1584 74  1258 84  1031 66  565  62}
\text{2960 8  1538 64  1203 84  989 74  490  57}
\text{2931 10  1498 18  1178 81  888 77  481  66}
\]
Alkenes — addition of the C=C and vinyl C-H bonds

- C=C stretch at 1620-1680 cm\(^{-1}\) weaker as substitution increases
- Vinyl C-H stretch occurs at 3000-3100 cm\(^{-1}\)
- The difference between alkane, alkene or alkyne C-H is important! If the band is slightly above 3000 it is vinyl sp\(^2\) C-H or alkyl sp C-H, if it is below it is alkyl sp\(^3\) C-H
1-Octene

(w – m)

(w – m)

84
IR frequencies of ALKENES

=\text{C—H bond, “unsaturated” vinyl}
(sp^2) \quad 3020-3080 \text{ cm}^{-1}
+ \quad 675-1000

R\text{CH=CH}_2 \quad + \quad 910-920 \& 990-1000

R_2\text{C=CH}_2 \quad + \quad 880-900

cis-R\text{CH=CHR} \quad + \quad 675-730 \text{ (v)}

trans-R\text{CH=CHR} \quad + \quad 965-975

C=\text{C bond} \quad 1640-1680 \text{ cm}^{-1} \text{ (v)}
(b) 1-hexene

3080 \( \equiv \text{C} - \text{H} \) stretch

1642 \( \equiv \text{C} - \text{C} \) stretch

\( \text{CH}_3(\text{CH}_2)_3\text{CH} \equiv \text{CH}_2 \)
1-Hexene

\[
\text{CH}_2=\text{CH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3
\]
1-decene

$C_{10}H_{20}$

unsat’d C-H

3020-3080 cm$^{-1}$

C=C 1640-1680

910-920 & 990-1000 RCH=CH$_2$

CH$_2$=CH$-(CH_2)_7$-CH$_3$
4-methyl-1-pentene

$C_6H_{12}$

910-920 & 990-1000
RCH=CH$_2$
2-methyl-1-butene

$\text{C}_5\text{H}_{10}$

880-900 cm$^{-1}$

$R_2\text{C} = \text{CH}_2$

\[
\begin{align*}
\text{CH}_2 & \equiv \text{C} & \text{CH}_2 & \equiv \text{CH}_3 \\
& \quad | & & \quad \downarrow \text{CH}_3 \\
& & & \text{CH}_3
\end{align*}
\]
2,3-dimethyl-1-butene

\[ \text{C}_6\text{H}_{12} \]

880-900

\[ \text{R}_2\text{C}=\text{CH}_2 \]
Non Terminal Alkene

This spectrum shows that the band appearing around \(3080 \text{ cm}^{-1}\) can be obscured by the broader bands appearing around \(3000 \text{ cm}^{-1}\).

( lower )
Alkynes

- C≡C stretch 2100-2260 cm\(^{-1}\); strength depends on asymmetry of bond,
- strongest for terminal alkynes, weakest for symmetrical internal alkynes
- C-H for terminal alkynes (sharp & weak) occurs at 3200-3300 cm\(^{-1}\)
- Internal alkynes ( R-C≡C-R ) would not have this band!
I.R. Spectrum of Alkynes

- **H–C≡C(CH₂)₅CH₃**
  - (a) 1-octyne
  - 2119 cm⁻¹ C≡C stretch
  - 3313 cm⁻¹ C–H stretch

- **CH₃(CH₂)₂–C≡C(CH₂)₂CH₃**
  - (b) 4-octyne
  - No C≡C stretch visible
  - Alkane C–H stretch

Wavenumber (cm⁻¹)
Aromatics

Due to the delocalization of e- in the ring, C-C bond order is 1.5, the stretching frequency for these bonds is slightly lower in energy than normal C=C.

These show up as a pair of sharp bands, 1500 & 1600 cm⁻¹.

C-H bonds of the ring show up similar to vinyl C-H at 3000-3100 cm⁻¹.

Ethyl benzene (w–m)
IR spectra BENZENEs

=\text{C—H bond, “unsaturated” “aryl”}

(sp^2) \quad 3000-3100 \text{ cm}^{-1} \\
\quad + \quad 690-840

\text{mono-substituted} \quad + \quad 690-710, 730-770

\text{ortho-disubstituted} \quad + \quad 735-770

\text{meta-disubstituted} \quad + \quad 690-710, 750-810 (m)

\text{para-disubstituted} \quad + \quad 810-840 (m)

\text{C=C bond} \quad 1500, 1600 \text{ cm}^{-1}
ethylbenzene

C₆H₁₀

3000-3100 cm⁻¹

Unsaturated C-H

1500 & 1600

Benzene ring

690-710, 730-770

mono-

3468 84  2933 21  1802 79  1178 81  904 68
3108 70  2898 44  1744 84  1110 81  788 57
3087 52  2675 32  1606 42  1090 70  772 42
3065 39  1956 84  1496 13  1084 70  746 20
3028 21  1942 77  1453 13  1037 57  697  4
3003 57  1881 84  1376 86  1030 46  556 46
2967 10  1866 79  1329 79  966 72  486 63
o-xylene

$C_6H_{10}$

**735-770**

ortho
p-xylene

$C_8H_{10}$

810-840 (m) para
$m$-xylene

$C_9H_{10}$

 meta

690-710, 750-810 (m)
styrene

C₆H₅

no sat’d C-H

1640
C=C

910-920 &
990-1000

RCH=CH₂

mono

<table>
<thead>
<tr>
<th>3299</th>
<th>74</th>
<th>1946</th>
<th>74</th>
<th>1496</th>
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<td>442</td>
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</tr>
</tbody>
</table>
2-phenylpropene

C₉H₁₀

Sat'd C-H

880-900

R₂C=CH₂

mono
p-methylstyrene

C₉H₁₀

H₃C

para

<table>
<thead>
<tr>
<th>Wavenumber</th>
<th>Intensity</th>
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<td>3087</td>
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<td>2980</td>
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<tr>
<td>2946</td>
<td>60</td>
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</table>
Nitriles (the cyano- or –C≡N group)

• Principle group is the **carbon nitrogen triple** bond at 2100-2280 cm\(^{-1}\)

• This band has a **sharp, pointed** shape just like the alkyne C-C triple bond, but because the CN triple bond is more polar, this band is stronger than alkynes.
propionitrile

(s)
Ir Spectrum of Nitrile

[Diagram showing the spectrum of an nitrile compound with peaks at specific wavenumbers.]

- C≡N stretch at 2249 cm⁻¹
- butyronitrile (CH₃CH₂CH₂C≡N)
Ethers

- Addition of the C-O-C asymmetric band and vinyl C-H bonds
- Show a strong band for the antisymmetric C-O-C stretch at 1050-1150 cm$^{-1}$
methyl \textit{n}-propyl ether

\[ C_4H_{10}O \]

no O--H

C-O ether

\[ \text{CH}_3 - (\text{CH}_2)_2 - O - \text{CH}_3 \]
Diisopropyl ether
<table>
<thead>
<tr>
<th>Structural unit</th>
<th>Frequency, cm(^{-1})</th>
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</thead>
<tbody>
<tr>
<td>Stretching vibrations (single bonds)</td>
<td></td>
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<tr>
<td>O—H (alcohols &amp; phenols)</td>
<td>3200-3600</td>
</tr>
<tr>
<td>O—H (carboxylic acids)</td>
<td>3000-3100</td>
</tr>
</tbody>
</table>

First examine the absorption bands in the vicinity of 4000-3000 cm\(^{-1}\)
Alcohols

• Strong, broad O-H stretch from 3200-3400 cm\(^{-1}\)
• Like ethers, C-O stretch from 1050-1260 cm\(^{-1}\)
• Band position changes depending on the alcohols substitution:
  • 1° 1075-1000;
  • 2° 1075-1150;
  • 3° 1100-1200;
• phenol 1180-1260

OH band in neat aliphatic alcohols is a broad band centered at ~ 3200 cm\(^{-1}\) due to hydrogen bonding (3200 – 3400 cm\(^{-1}\))

- OH band in dilute solutions of aliphatic alcohols is a sharp peak ~ 3400 cm\(^{-1}\)
1-butanol

\[ \begin{array}{c}
\text{H} - \text{O} \\
\text{C}_3\text{H}_7
\end{array} \]

(m – s) br

(s)
1-butanol

$C_4H_{10}O$

3200-3640 (b) $\text{o-H}$

C-O $1^\circ$

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-OH}$
2-butanol

$\text{C}_4\text{H}_{10}\text{O}$

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

\[ \text{OH} \]

\[ \text{C-O}^{\circ} \]

\[ \text{O-H} \]

Wavenumbers (cm$^{-1}$):

- 3363 10
- 2968 4
- 2832 12
- 2880 16
- 2734 70
- 1457 25
- 1416 44

Transmittance (%):

| 666 | 60 |
| 651 | 60 |
| 501 | 72 |

Frequency Table:

| 3363 | 10 |
| 2968 | 4  |
| 2832 | 12 |
| 2880 | 16 |
| 2734 | 70 |
| 1457 | 25 |
| 1416 | 44 |
tert-butyl alcohol

C₄H₁₀O

O-H

C-O 3°
Cyclohexanol

- O-H stretch
- bending
- C-O stretch
- sp\(^3\) C-H stretch
Phenol

CO→H stretch is broad band

C→H stretch ~ 3050 cm⁻¹

C–C→O band ~ 1225 cm⁻¹

C–O–H bend ~ 1350 cm⁻¹

Aromatic ring C stretching between 1450 – 1600 cm⁻¹

Mono substituted bands ~ 745 – 895 cm⁻¹ and 1650 – 2000 cm⁻¹
Carboxylic Acids

- Consist of both, C=O and O-H groups.
- C=O band occurs between 1700-1725 cm\(^{-1}\)
- The highly dissociated O-H bond has a broad band from 2400-3500 cm\(^{-1}\) covering up to half the IR spectrum in some cases
4-phenylbutyric acid

(w - m) br  (s)  (s)
IR Spectrum of A Carboxylic Acid

![IR Spectrum of A Carboxylic Acid](image)

- O-H stretch
- C-H stretch
- C=O stretch

CH$_3$(CH$_2$)$_4$COOH
hexanoic acid
Propionic Acid
IR Spectrum of Carbonyl Compounds

- Carbonyl compounds are those that **contain the C=O functional group**

- **Aldehydes and ketones** show a strong, prominent, band around 1710 - 1720 cm\(^{-1}\) (right in the middle of the spectrum). This band is due to the **highly polar** C=O bond.

- Because aldehydes also contain a C-H bond to the \(sp^2\) carbon of the C=O bond, they also show a pair of medium strength bands positioned about \(2700\) and \(2800\) cm\(^{-1}\).

- These bands are missing in the spectrum of a ketone because the \(sp^2\) carbon of the ketone lacks the C-H bond.
### Infrared Absorption Frequencies of C=O

<table>
<thead>
<tr>
<th>Structural unit</th>
<th>Frequency, cm⁻¹</th>
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<tr>
<td>Stretching vibrations (carbonyl groups)</td>
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<tr>
<td>1. Aldehydes and ketones</td>
<td>1710-1750</td>
</tr>
<tr>
<td>2. Carboxylic acids</td>
<td>1700-1725</td>
</tr>
<tr>
<td>3. Acid anhydrides</td>
<td>1800-1850 and 1740-1790</td>
</tr>
<tr>
<td>4. Esters</td>
<td>1730-1750</td>
</tr>
<tr>
<td>5. Amides</td>
<td>1680-1700</td>
</tr>
<tr>
<td>6. Acid Chloride</td>
<td>1800</td>
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</tbody>
</table>

\[ \text{ν C=O Decreasing order} \]

\[ \text{RCO}_2\text{O > RCOX > RCOOR’ > RCHO > RCOR > RCOOH > RCONH}_2 \]
**ν C=O of Aldehydes And Ketones**

Both aldehyde and ketone have a common functional group, called as carbonyl, C=O.

**Strong, sharp C=O peak 1670 - 1780 cm⁻¹**
How does Adsorption differ in Aldehydes & Ketones?

1. CH₂O , EDG-CHO , EWG-CHO  
   (CH₃-CHO) , (Cl₃C- CHO)

2. CH₃-CHO , CH₃-CO-CH₃

3. Ph –CHO, CH₃-CHO

4. Ph –CO-CH₃, CH₃-CO-CH₃
Aldehydes

- C=O (carbonyl) stretch from 1720-1740 cm\(^{-1}\)
- Band is sensitive to conjugation, as are all carbonyls (upcoming slide)
- A highly unique \(sp^2\) C-H stretch appears as a doublet, 2720 & 2820 cm\(^{-1}\) called a “Fermi doublet”
(b) butyraldehyde

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

- **C–H stretch**
- **C=O stretch**

- Saturated C–H stretch
- 2720
- 2820
- 1720
- Wavenumber (cm\(^{-1}\))

(References to specific peaks and their assignments are indicated on the spectrum.)
Mono-substituted aromatic aldehyde
3540
O-H stretch

vanillin
(CCl₄ solution)

H-C=O
stretch

hydrogen
bond

1695
C=O stretch

1268

1034
C-O stretching bands
Ketones

- Simplest of the carbonyl compounds as far as IR spectrum – carbonyl only

- $\text{C}=\text{O}$ stretch occurs at 1705-1725 cm$^{-1}$
IR: Ketones

Cyclohexanone liquid film
2-butanone

C₄H₈O

~1700 (s)
4-Methyl-2-pentanone

C-H < 3000, C=O 1715 cm$^{-1}$
Cyclic aliphatic ketone

cyclohexanone
Mono substituted aromatic methyl ketone

acetophenone

aromatic C=C

C=O

Wavenumber

%Transmittance
Mono substituted aromatic ketone

![Benzophenone structure](image)

Wavenumber

% Transmittance

90 92 94 96 98 100

900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900 2000 2100 2200 2300 2400 2500 2600 2700 2800 2900 3000 3100 3200 3300 3400
**Effect Of Conjugation on $\nu$ C=O**

Conjugation with a double bond or benzene ring lowers the stretching frequency by 30 to 40 cm\(^{-1}\). Ketones are sensitive to conjugation

1660-1700 cm\(^{-1}\) rotational isomers cause doubling. *S*-trans 1674, *S*-cis 1699

1650-1700 cm\(^{-1}\)

1580-1640 cm\(^{-1}\) for enol
1715 cm\(^{-1}\) for the keto bond

Along with br. OH str.
Effects of Conjugation

Aldehydes

CH₃CH₂CH₂

CH₃CH=CHCH

1715 cm⁻¹

1750 cm⁻¹

1705 cm⁻¹

1705 cm⁻¹

Ketones

CH₃CCH₃

CH₃CH=CHCCH₃

1716 cm⁻¹

1685 cm⁻¹

1617 (C=C)

1716 cm⁻¹

1683 cm⁻¹

1678 cm⁻¹

1627 (C=C)
Strain on C=O of Ketones

Ring strain increases frequency
- Incorporation of the carbonyl group in a small ring (5, 4 or 3-membered), raises the stretching frequency.

30 cm\(^{-1}\) higher for every C atom removed

α-diketones, str-str for open chain, IR inactive; in ring, 1720, 1740

α-haloketones--can see second band from rotamer populations (1720, 1745)
Esters and Lactones:

- C=O stretch at 1735-1750 cm\(^{-1}\)
- Strong band for C-O at a higher frequency than ethers or alcohols at 1150-1250 cm\(^{-1}\)
- Lactones absorb at higher frequency than esters
Aliphatic ester I

![Graph showing the IR spectrum of an aliphatic ester with peak wavenumbers at 2985, 1740, 1447, 1098, 938, and 847 cm⁻¹. The molecule structure shown is ethyl acetate.]
Aliphatic ester II

![Graph showing infrared spectra with wavenumber values: 2875, 2962, 1741, 1466, 1366, 1241, 1031, 950.]

-butyl acetate-
Aliphatic ester III

[Graph showing infrared spectrum with labeled wavenumbers and a chemical structure labeled "isobutyl acetate"]
Mono substituted aromatic ester
Mono substituted aromatic conjugated ester

![Graph of methyl cinnamate with wavenumber values: 1638, 1495, 1454, 1282, 1174, 1014, 986, 937, 870, and 2948.](image)
Effects of conjugation

IR: C=O: Esters

- 1735 cm$^{-1}$ in saturated esters
  - Electron donating O increased the frequency
- 1715 cm$^{-1}$ in esters next to aromatic ring or a double bond
  - Conjugation decreases the frequency

![Esters structures]

- CH$_3$COCH$_3$: 1735 cm$^{-1}$
- CH$_3$CH=CHCOCH$_3$: 1715 cm$^{-1}$
- Phenyl ester: 1715 cm$^{-1}$
Effects of conjugation

Lowers to 1715 cm\(^{-1}\)

Similar, to 1715 cm\(^{-1}\)

Raises to 1770 cm\(^{-1}\)

Weakens DB character

Strengthens DB character (inductive over resonance)
Mono substituted aromatic conjugated ester

methyl cinnamate
Lactones, similar effects

\begin{align*}
\text{1735 cm}^{-1} & \\
\text{1765 cm}^{-1} & \\
\text{1770 cm}^{-1} & \\
\text{1715 cm}^{-1} & 
\end{align*}
INTERPRETATION OF IR SPECTRA

Nitrogen-Containing Compounds

- 1° amines (NH₂) have scissoring mode and low frequency wagging mode

- 2° amines (NH) only have wagging mode (cannot scissor)

- 3° amines have no NH band and are characterized by C–N stretching modes ~ 1000 – 1200 cm⁻¹ and 700 – 900 cm⁻¹

- 1°, 2°, 3° amides are similar to their amine counterparts but have additional C=O stretching band
INTERPRETATION OF IR SPECTRA

Nitrogen-Containing Compounds

- C=O stretching called amide I in 1o and 2o amides and amide II in 3o amides

- N−H stretch doublet ~ 3370 – 3291 cm⁻¹ for 1o amines

- 1o N−H bend at ~ 1610 cm⁻¹ and 800 cm⁻¹

- Single N−H stretch ~ 3293 cm⁻¹ for 2o but absent in 3o amine

- C−N stretch weak band ~ 1100 cm⁻¹
INTERPRETATION OF IR SPECTRA

Amino Acids [RCH(NH$_2$)COOH]

- IR spectrum is related to salts of amines and salts of acids

- Broad CH bands that overlap with each other

- Broad band ~ 2100 cm$^{-1}$

- NH band ~ 1500 cm$^{-1}$

- Carboxylate ion stretch ~ 1600 cm$^{-1}$
**Amides**

- Display features of amines and carbonyl compounds
- C=O stretch at 1640-1680 cm\(^{-1}\)
- If the amide is **primary** (-NH\(_2\)) the N-H stretch occurs from 3200-3500 cm\(^{-1}\) as a doublet
- If the amide is **secondary** (-NHR) the N-H stretch occurs at 3200-3500 cm\(^{-1}\) as a sharp singlet
pivalamide

\[
\begin{align*}
\text{NH}_2 \\
\end{align*}
\]
The graph shows an infrared spectrum with various peaks labeled. The peaks at around 3300 cm\(^{-1}\) are labeled as N–H stretch. The peaks at 2900–3000 cm\(^{-1}\) are labeled as C–H stretch. The peak at 1630–1660 cm\(^{-1}\) is labeled as C–O stretch.

The structure (a) is shown with the chemical formula CH\(_3\)CH\(_2\)CH\(_2\)C–NH\(_2\).
Acid anhydrides

• Coupling of the anhydride though the ether oxygen splits the carbonyl band into two with a separation of 70 cm\(^{-1}\)
• Bands are at 1740-1770 cm\(^{-1}\) and 1810-1840 cm\(^{-1}\)
• Mixed mode C-O stretch at 1000-1100 cm\(^{-1}\)
Propionic anhydride

\[
\begin{align*}
\text{Propionic anhydride} & : \overset{\text{C}}{\text{C}} \overset{\text{O}}{\text{O}} \\
& \overset{\text{C}}{\text{C}} \overset{\text{O}}{\text{O}} \\
& \overset{\text{C}}{\text{C}} \overset{\text{O}}{\text{O}}
\end{align*}
\]
Amines - Primary

• Shows the –N-H stretch for NH$_2$ as a *doublet* between 3200-3500 cm$^{-1}$ (symmetric and anti-symmetric modes)
• -NH$_2$ has deformation band from 1590-1650 cm$^{-1}$
• Additionally there is a “wag” band at 780-820 cm$^{-1}$ that is not diagnostic
2-aminopentane
1-Butanamine

\[ \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2 \]

**N-H stretch doublet**

**sp\(^3\) C-H stretch**

**N-H bend**

**CH\(_2\)**

**CH\(_3\)**

**bend**

Wavenumbers

161
Amines – Secondary

• N-H band for $R_2N-H$ occurs at 3200-3500 cm$^{-1}$ as a single sharp peak weaker than –O-H

• Tertiary amines ($R_3N$) have no N-H bond and will not have a band in this region
pyrrolidine

(w - m)

163
dipropylamine
(CH₃CH₂CH₂)₂NH

- N–H stretch
- spike
- saturated C–H stretch
INTERPRETATION OF IR SPECTRA

Halogenated Compounds

- C→X strong absorption bands in the fingerprint and aromatic regions

- More halogens on the same C results in an increase in intensity and a shift to higher wavenumbers

- Absorption due to C–Cl and C–Br occurs below 800 cm⁻¹
**PAUSE AND REVIEW**

- Inspect the bonds to H region (2700 – 4000 cm\(^{-1}\))
- Peaks from 2850-3000 are simply \(\text{sp}^3\) C-H in most organic molecules
- Above 3000 cm\(^{-1}\) **Learn shapes, not wavenumbers!**:
  - **Broad U-shape peak** - O-H bond
  - **V-shape peak** - N-H bond for 2° amine (\(\text{R}_2\text{N}-\text{H}\))
  - **W-shape peak** - N-H bond for 1° amine (\(\text{RNH}_2\))
  - **Sharp spike** - C≡C—H bond
  - Small peak shouldered just above 3000 cm\(^{-1}\) C=C—H or Ph—H
Study of metal complexes

The metal-heteroatom bond stretching vibration can be studied with the help of far IR spectroscopy

Examples:

1. \( \text{H}_3\text{C} \text{S} \text{CH}_3 \) \( \text{v C}=\text{O} \) and \( \text{v C-S} \)

2. \( \text{H}_2\text{N}-\text{C}=\text{O}-\text{NH}_2 \)

\text{urea}
Q. Which of the following will absorb at higher $\nu \text{C} = \text{O}$/ $\nu \text{C}-\text{O}$ in IR?

1. Acetophenone
2. Benzophenone
3. Acetone

1. Diphenylether
2. Anisole
3. Dimethyl ether

1. 1
2. 2
3. 3
Ques. Predict the approximate positions of all of the important absorptions in the IR spectrum of this compound.

\[
\text{CH}_3\text{CH}_2\text{CH} = \text{CHCOOH}
\]

Ques. Explain how IR spectroscopy could be used to distinguish between these two compounds. Be as specific as possible.

\[
\begin{align*}
\text{CH}_2\text{COCH}_3 \\
\text{CCH}_2\text{CH}_3
\end{align*}
\]
Explain which functional group is present in the compound with the following IR spectrum. Show a possible structure for the compound.

- The peak at 3300 cm\(^{-1}\) indicates the presence of an spC-H bond.
- The peaks at 3000 - 2850 cm\(^{-1}\) indicate the presence of sp\(^3\)C-H bonds.
- The peak at 2150 cm\(^{-1}\) indicates the presence of a carbon-carbon triple bond.

So the compound is a 1-alkyne. A possible structure is

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}≡\text{C}−\text{H}
\]
Identify the compound from the IR.

A) benzyl alcohol
B) 2,4,6-cycloheptahptatrien-1-one
C) acetophenone
D) benzaldehyde
E) phenylacetic acid
A) 2,4,5-trimethylbenzaldehyde
B) p-allylanisole
C) 2-allyl-4-methylphenol
D) 1-phenyl-2-butanone
A) cyclopropanone
B) propynol
C) acrylaldehyde
D) propenoic acid
A) methylbenzoate
B) o-hydroxyacetophenone
C) o-toluic acid
D) p-anisaldehyde (p-methoxybenzaldehyde)
A) benzylformate
B) o-hydroxyacetophenone
C) 2-methoxytropone
D) o-anisaldehyde (p-methoxybenzaldehyde)
E) p-toluic acid
The following IR spectrum is one of the four compounds shown below. Circle the correct compound.
Which compound is this?

a) 2-pentanone
b) 1-pentanol
c) 1-bromopentane
d) 2-methylpentane

1-pentanol
What is the compound?

a) 1-bromopentane
b) 1-pentanol
c) 2-pentanone
d) 2-methylpentane

2-pentanone
A. biphenyl  
B. o-xylene  
C. allylbenzene  
D. n-pentane  
E. 1,2-diphenylethane  
F. n-butylbenzene
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<th>Intensity</th>
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<td>3082 37</td>
<td>1946 81</td>
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<td>3064 34</td>
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<tr>
<td>3029 26</td>
<td>1639 34</td>
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<tr>
<td>3005 50</td>
<td>1603 44</td>
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<tr>
<td>2979 49</td>
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<td>2904 50</td>
<td>1485 17</td>
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<tr>
<td>2833 70</td>
<td>1476 77</td>
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HIT-NO=1355  SCORE=  SDBS-NO=1182  IR-NIDA-60114 : KBR DISC

5

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<tr>
<th>Wavenumber (cm⁻¹)</th>
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<td>466</td>
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4000  | 3000  | 2000  | 1000  | 500   |

0     | 50    | 100   | 150   | 200   | 250   | 300   | 350   | 400   | 450   | 500   |
Strengths and Limitations

- IR alone cannot determine a structure
- Some signals may be ambiguous
- The functional group is usually indicated
- The *absence* of a signal is definite proof that the functional group is absent
- Correspondence with a known sample’s IR spectrum confirms the identity of the compound
THANK YOU FOR PATIENCE