Infrared Spectroscopy

- General Theory of IR Spectroscopy
- Overview of the IR spectrometer
- Signal Intensity in an IR Spectrum
- Location of Peaks in an IR Spectrum
- Guide to Analyzing an IR Spectrum

General Theory of IR Spectroscopy

• Covalent bonds are not static.

General Theory of IR Spectroscopy

Sample IR Spectrum:



General Theory of IR Spectroscopy

- Nearly any compound possessing covalent bonds will absorb certain frequencies of electromagnetic radiation from the infrared region of the electromagnetic spectrum.
- IR absorption is quantized. This means only select energies are absorbed by a particular molecule.
- Since different molecules absorb different sets of energies, different molecules have different (distinguishable) IR spectra.



General Theory of IR Spectroscopy



General Theory of IR Spectroscopy

• Absorption of IR energy causes excitations in the vibrational motions of molecules.

$$E = hv = rac{hc}{\lambda}$$



General Theory of IR Spectroscopy

General Theory of IR Spectroscopy



Overview of the IR spectrometer

Fourier Transform infrared (FT-IR) spectrometer:



Overview of the IR spectrometer

Our IR spectrometer contains an Attenuated Total Reflectance (ATR) accessory.



Signal Intensity in an IR Spectrum

For a bond to absorb in IR, there must be a change in the dipole moment during the vibration.

If a bond is non-polar due to symmetry, IR light will not be absorbed and the vibration is said to be IR inactive.

symmetry



 $H_3C \longrightarrow CH_3$

CEC is IR active

CEC is IR inactive

Signal Intensity in an IR Spectrum

A more polar bond will have a stronger absorption than a less polar bond.



Signal Intensity in an IR Spectrum

relative bond polarities relative intensities of IR absorption



Signal Intensity in an IR Spectrum

An alkene C=C stretch generally appears ~ 1650 cm⁻¹.



Location of Peaks in an IR Spectrum

Two General Regions in an IR Spectrum:



Hydroxyl Group, OH

Generally broad and intense ~3300 cm⁻¹



Location of Peaks in an IR Spectrum

Some factors affecting peak location:

1. Mass of the atoms: The stretching frequency of a bond connected to a lighter atom will be greater than the same bond connected to a heavier atom.

H – CI vs H – Br

2. Bond Strength: A stronger bond will have a higher stretching frequency than a weaker bond.

 $C \equiv C > C = C > C - C$

Location of Peaks in an IR Spectrum

Carboxylic Acid OH Group

A Carboxylic Acid O–H stretch is generally lower in frequency and even more broad than an alcohol OH. Often ${\sim}3000~{\rm cm}^{-1}$



Amine Group, NH and NH₂

Generally less broad and less intense than the OH stretch. Generally appear between 3300 and 3500 $\rm cm^{-1}$

Primary amines R-NH₂ exhibit two N-H stretching bands.



Location of Peaks in an IR Spectrum

Carbon-Hydrogen, CH

All C-H stretches occur between 2700 and 3300 cm⁻¹. They are relatively intense and typically quite narrow.

Csp³–H (-CH₂–H) appear just below3000 cm⁻¹



Location of Peaks in an IR Spectrum

Amine Group, NH and NH₂

Generally less broad and less intense than the OH stretch. Generally appear between 3300 and 3500 $\rm cm^{-1}$

Secondary amines R₂NH exhibit one N-H stretching band.



Location of Peaks in an IR Spectrum

Carbon-Hydrogen, CH

All C-H stretches occur between 2700 and 3300 cm⁻¹. They are relatively intense and typically quite narrow.

Csp²–H (C=C–H) appear just above 3000 cm⁻¹



Carbonyl Group, C=O

The C=O stretch is very strong and generally appears between 1650-1850 cm⁻¹

CI — O	1750-1850
RO ————————————————————————————————————	1700-1750
⊢	1720-1740
>⊨o	1680-1750
H ₂ N >=0	1650-1700

Location of Peaks in an IR Spectrum

Carbonyl Group, C=O

The C=O stretch is very strong and generally appears between 1650-1850 cm⁻¹



Location of Peaks in an IR Spectrum

Carbonyl Group, C=O



When the C=O is in conjugation to a C=C or a C≡C, the frequency is lowered 20-40 cm⁻¹

Location of Peaks in an IR Spectrum

Carbonyl Group: Aldehyde

In addition to the C=O stretch, the aldehyde C–H stretch appears as two bands. One will be at ~2720 and the other at ~2820 cm⁻¹.



Alkyne (C \equiv C) and Nitrile (C \equiv N) Groups

Both $C \equiv C$ and $C \equiv N$ bonds appear as a sharp peak between 2100 and 2260 cm⁻¹. Internal alkynes and nitriles are generally difficult to distinguish.



Location of Peaks in an IR Spectrum

Carbon-Carbon Double Bond (C=C)

C=C stretches are one of the more difficult functional groups to identify in an IR spectrum. Alkene stretches occur between 1620 and 1680 cm⁻¹. They are sharper and less intense than C=O signals.



Location of Peaks in an IR Spectrum

Alkyne (C \equiv C) and Nitrile (C \equiv N) Groups

Terminal alkynes are much easier to identify. In addition to the C \equiv C stretch, a sharp C–H stretch at ~3300 cm⁻¹ will also be observed.



Location of Peaks in an IR Spectrum

Aromatic Carbon-Carbon Double Bond (C=C)

C=C stretches corresponding to an aromatic ring generally occur between 1450 and 1600 cm⁻¹. There can be up to three signals: One at ~1600, One at ~1500, and one slightly <1500 cm⁻¹.



Carbon Oxygen Single Bond Stretch (C-O)

Csp³-0 1000-1100 cm⁻¹ Csp²-0 1200-1300 cm⁻¹

CH ₃ CH ₂ —OH an alcohol	CH ₃ CH ₂ —O—CH ₂ CH ₃ an ether	сн₃ ^С ⋛ён←	→ CH ₃ C U	сн₃ ^с ∼ё <mark>ё</mark> −сн₃	$\rightarrow CH_{3} CH_{3} CH_{3} CH_{3}$
~1050 cm ⁻¹ ~1050 cm ⁻¹	a carboxylic acid ~1250 cm ⁻¹		an ester ~1250 cm ⁻¹ and ~1050 cm ⁻¹		

The carbon—oxygen bond in an alcohol is a pure single bond.

The carbon—oxygen bond in an ether is a pure single bond.

The carbon—oxygen single bond in a carboxylic acid has partial double bond character.

One carbon—oxygen single bond in an ester is a pure single bond and one has partial double bond character.

Location of Peaks in an IR Spectrum

Carbon Oxygen Single Bond Stretch (C-O)

Csp³-0 1000-1100 cm⁻¹



Location of Peaks in an IR Spectrum

Carbon Oxygen Single Bond Stretch (C-O)

 $\begin{array}{c} \text{Csp}^3 \text{--} 0 \hspace{0.2cm} 1000\text{--}1100 \hspace{0.2cm} \text{cm}^{\text{-}1} \\ \text{Csp}^2 \text{--} 0 \hspace{0.2cm} 1200\text{--}1300 \hspace{0.2cm} \text{cm}^{\text{-}1} \end{array}$



Location of Peaks in an IR Spectrum

Carbon-Hydrogen (C-H) Bending Vibrations

Bending vibrations are generally less pronounced than stretching. Additionally, because the bending vibrations are generally found in the fingerprint region, they are often hard to identify.

-CH₃ bending just below 1400 cm⁻¹

R₂CH₂ and R₃CH bending just above 1400 cm⁻¹



Guide to Analyzing an IR Spectrum

The first thing to keep in mind is that it is nearly impossible to deduce a structure based solely on a compounds IR spectrum.

The IR spectrum should be used to identify key functional groups that are present in a molecule.



Guide to Analyzing an IR Spectrum

2-methyl-1-pentene



Guide to Analyzing an IR Spectrum

2-propyn-1-ol



Guide to Analyzing an IR Spectrum

acrylamide



Guide to Analyzing an IR Spectrum

ethyl benzyl ketone



Guide to Analyzing an IR Spectrum

How could you use IR to differentiate $C_4H_8O_2$ isomers?



Guide to Analyzing an IR Spectrum

How could you use IR to differentiate $C_4H_8O_2$ isomers?



Guide to Analyzing an IR Spectrum

How could you use IR to differentiate $C_4H_8O_2$ isomers?



