Infrared Spectroscopy

Characteristics

- Sensitive to polar groups and antisymmetric modes
- Small amounts of samples needed (mg, as low as ng)
- Signal detection is simple
- Special sample preparation is often needed (thin films, KBr pellets....)
Raman Spectroscopy

Characteristics

Sensitive to nonpolar groups and symmetric modes
Inefficient detection scheme (1 photon out of a million)
Special site-specific techniques available
  resonance Raman spectroscopy
  surface enhanced Raman spectroscopy
Sampling method is often simple
Highly focused laser beam
Characteristics

Solution NMR

Signal intensity can be directly and quantitatively related to chemical group concentration.

Sensitive to molecular mobility.

Sensitive to surrounding electronic environment.

Sensitivity depends on the nucleus of interest (natural abundance and magnetogyric ratio).

Some nuclei show little signal overlap.
NMR Spectroscopy

Characteristics

Solid-state NMR

In addition to the characteristics in solution-state NMR,…

Can study frozen solid state conformation

Ability to determine the position of proton

Ability to determine the correlation among nuclei
Mass Spectrometry

Characteristics

Very sensitive (amount of detectable sample, pg and fg)

Ability to determine precise mass of a molecular fragment or mother molecule (MALDI)

Needs to be vaporized and ionized (fragmentation)

Various sampling and ionization techniques
IR SPECTROSCOPY
Interaction of light with matter
White light

- Light sources are most of the time “white”
- Newton proved that white light is a mixture of different types of light
- Light of different colors are “basic” types of light
- Newton proved this in the 1660’s by using two prisms to decompose white light
White light
Light

• Light is an electromagnetic wave (Electric and Magnetic fields oscillation and propagating)

• Visible light is only a particular type, with a particular of oscillation

• The complete spectrum of electromagnetic radiation is referred to as Electromagnetic Spectrum.
Visible

Radio Microwaves Infrared Ultraviolet X-ray Gamma Ray

Low Frequency

Long Wavelength

High Frequency

Short Wavelength

Violet
Indigo
Blue
Aqua
Green
Yellow
Orange
Red
Dark Red

4,000 Å
400 nm

4,250 Å
425 nm

4,700 Å
470 nm

4,900 Å
490 nm

5,500 Å
550 nm

6,000 Å
800 nm

6,300 Å
850 nm

6,650 Å
965 nm

7,000 Å
700 nm
Characteristics of waves

- Waves transfer energy without transporting any of the oscillating “stuff”
- Example: String oscillating
Characteristics of waves

- Amplitude

Maximum height of the oscillating stuff
Characteristics of waves

- Wavelength: Distance between adjacent
Characteristics of waves

- The SHAPE moves, the oscillating stuff stays (the wave propagates, carries energy)
- Frequency: number of crests passing a point each second. Units = Hertz (Hz) = cycles/s
Characteristics of waves

- Velocity of propagation: determined by frequency and wavelength of the wave
Characteristics of waves

\[ \text{frequency} \times \text{wavelength} \]

How often do peaks arrive

How far apart the peaks are
Characteristics of waves

frequency × wavelength = speed of propagation

For light, this is $c = 300,000 \text{ km/s} = 3 \times 10^8 \text{ m/s}$

$f \times \lambda = c$
Characteristics of waves

\[ f \times \lambda = c \]

Since \( c \) is constant, each type of light is characterized by its wavelength (or frequency) only.
Characteristics of waves

- Wavelength = 1 cm, frequency = 30 GHz
- Wavelength = \frac{1}{2} cm, frequency = 2 \times 30 GHz = 60 GHz
- Wavelength = \frac{1}{4} cm, frequency = 4 \times 30 GHz = 120 GHz

Half \lambda
Double f
Different types of “light”
Quantum Mechanics and Light

- Experiments (1902) show that light behaves both as a wave and as a particle.
- Particles (*quantum*) of light are called *photons* (Einstein 1905).

Each photon has a wavelength and a frequency.

The energy of a photon depends on its frequency.
Quantum Mechanics and Light

- $E = hf$ = energy of each photon
- $h = 6.626 \times 10^{-34}$ joules × s

Planck’s constant
Quantum Mechanics and Light

\[ E = h \times f \]

The energy of each photon is big in light of high frequency, but low in light of small frequency.
Light and Matter

- The interactions between light and matter determine the appearance of everything we see.
Light and Matter

- Refraction, reflection or scattering
- Transmission:
  - Transparent objects transmit light.
  - Opaque objects block (absorb) light.
- Emission
- Absorption
So...what is light?

- Light is a form of energy.
- *Visible* light comes in many colors that combine to form white light.
- It is an electromagnetic wave that also comes in individual “pieces” called photons. Each photon has a precise wavelength, frequency, and energy.
- Radio waves, microwaves, infrared, visible light, ultraviolet, X rays, and gamma rays.
Absorption and emission of light from matter

\[ E_2 - E_1 = h\nu \]

must satisfy Bohr relation

emission could be induced or spontaneous
The Beer-Lambert Law

Most absorbing materials satisfy the Beer-Lambert Law.

If

- $I_0 =$ incident light intensity at frequency $\nu$
- $I =$ intensity of transmitted light at same frequency
- $C =$ concentration of absorbers
- $\varepsilon =$ molar extinction coefficient
- $l =$ length of light path through the absorbers

then

$$\log_{10} \frac{I_0}{I} = \varepsilon l C$$

Quantity $\log_{10} \frac{I_0}{I} = A$ is called the absorbance or sometimes optical density (OD).
E (Molecules or Atoms) = Transition + Electronic + Vibration + Rotation

- Quantized Energy levels
- Uv-Visb frequencies (200-400 nm)
- IR frequencies (2.5 - 15 μm, 400 – 4000 cm⁻¹)
- Microwave frequencies (1 – 10⁻³ m)
Electronic and Vibration energy levels
Substances exposed to radiation from frequency range $10^{14}$ Hz to $10^{13}$ Hz (wavelengths 2.5μm - 15μm)

Causing *vibrational* energy changes in the molecule

These absorb infrared radiation of *specific* frequencies.

Point is to identify *functional groups* in the molecule
Vibrations in Molecules and Bond Deformations
SIMPLE diatomic molecules can only vibrate **one way**, by *stretching*.

For these molecules there is only **one** vibrational infrared absorption.
More complex molecules have more possible deformations

\[ \text{symmetric stretch} \]
BOND DEFORMATION

asymmetric stretch
BOND DEFORMATION

O C O
BOND DEFORMATION
BOND DEFORMATION
BOND DEFORMATION
BOND DEFORMATION

O CO O
BOND DEFORMATION
BOND DEFORMATION

bending
from this equation we can get the reciprocal of the wavelength \((1/\lambda)\) this is a direct measure of the frequency
the reciprocal is described as the **wavenumber**. It is the wavenumber, measured in cm\(^{-1}\), that is recorded on an infrared spectrum.
Important...
When an ir spectrum is obtained we do not try to explain the whole thing, simply look for one or two signals that are characteristic of different bonds.
O–H bond stretch

C–H bond stretch

C–O bond stretch

ETHANOL
C–H bond stretch 3010 – 2850 cm\(^{-1}\)

C–O bond stretch 1050 cm\(^{-1}\)

O–H bond stretch 3670 cm\(^{-1}\)
Below 1500 cm$^{-1}$ the IR spectrum can be quite complex.

This region is characteristic of a particular molecule.

Hence known as ‘fingerprint region’.

<table>
<thead>
<tr>
<th>Absorption range / cm$^{-1}$</th>
<th>Bonds responsible</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000-2500</td>
<td>Single bonds to H</td>
<td>O-H, C-H, N-H</td>
</tr>
<tr>
<td>2500-2000</td>
<td>Triple bonds</td>
<td>C≡C, C≡N</td>
</tr>
<tr>
<td>2000-1500</td>
<td>Double bonds</td>
<td>C=C, C=O</td>
</tr>
<tr>
<td>Below 1500</td>
<td>various</td>
<td>C-O, C-X</td>
</tr>
</tbody>
</table>
INFRARED SPECTROSCOPY

Principles and practice
SUMMARY
The infrared region of the electromagnetic spectrum.

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

\[ \lambda = 2.5 \times 10^{-3} \text{ cm} = 25 \mu \text{m} \]
\[ \tilde{\nu} = 400 \text{ cm}^{-1} \]
In the infrared region of the spectrum photons do not excite electrons but may induce vibrational excitation of covalently bonded atoms and groups.

Molecules experience a wide variety of vibrational motion.

Virtually all organic compound will absorb radiation that corresponds to these vibrations.
Common sampling methods

- **KBr pellet**
  - Good for powders; a few milligrams of the sample power and an excess of KBr are finely ground and pressed under high pressure into a pellet. This is a useful and very general method for solids.

- **Salt cells:**
  - Good for organic liquids; the liquid is placed into a reservoir milled in alkali salt windows.

- **Nujol mull:**
  - The material of interest is suspended in oil, such as mineral oil, and the resulting paste is spread thinly on a salt window to form a film. This is a good technique for oils and waxy solids that do not press well into pellets.
Infrared spectra may be obtained from samples in all phases (liquid, solid and gaseous). Liquids are usually examined as a thin film sandwiched between two polished salt plates (note that glass absorbs infrared radiation, whereas NaCl is transparent).
If solvents are used to dissolve solids, care must be taken to avoid *obscur**ing* important spectral regions by solvent absorption. Perchlorinated solvents such as carbon tetrachloride, chloroform and tetrachloroethene are commonly used.

Alternatively, solids may either be incorporated in a thin KBr disk, prepared under high pressure, or mixed with a little non-volatile liquid and ground to a paste (or mull) that is smeared between salt plates.
Water has a dipole moment and absorbs light in the infrared very strongly.

It is difficult to measure the infrared spectrum of biological materials in water due to the spectrum of water obscuring the information.

A combination of H$_2$O and D$_2$O is often used to overcome this problem.
A sample of IR Spectra
Infrared spectrum of vanillin

Note inverted peaks
Top: 100% transmission
Bottom: No transmission

Frequency cm\(^{-1}\) = Hz/c

Wavelength \( \mu = 10^{-6} \) meter
A molecule composed of \( n \)-atoms has \( 3n \) degrees of freedom, six of which are translations and rotations of the molecule itself.

This leaves \( 3n-6 \) degrees of vibrational freedom (\( 3n-5 \) if the molecule is linear).

Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking and twisting.
Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking, waging and twisting.
Infrared spectrum of formaldehyde

- 2785 cm\(^{-1}\): CH\(_2\) sym stretch
- 2850 cm\(^{-1}\): CH\(_2\) asym stretch
- 1485 cm\(^{-1}\): CH\(_2\) scissor
- 1165 cm\(^{-1}\): CH\(_2\) wag
- 1250 cm\(^{-1}\): CH\(_2\) rock
- 1750 cm\(^{-1}\): C=O stretch
The four-atom molecule of formaldehyde, the gas phase spectrum of which is shown, provides an example of these terms.

We expect **six** fundamental vibrations (12 minus 6), and these have been assigned to the spectrum absorptions.
The exact frequency at which a given vibration occurs is determined by the strengths of the bonds involved and the mass of the component atoms.

In practice, infrared spectra do not normally display separate absorption signals for each of the $3n-6$ fundamental vibrational modes of a molecule.

The number of observed absorptions may be increased by additive and subtractive interactions leading to combination tones and overtones of the fundamental vibrations, in much the same way that sound vibrations from a musical instrument interact.
The number of observed absorptions may be decreased by molecular symmetry, spectrometer limitations, and spectroscopic selection rules.

One selection rule that influences the intensity of infrared absorptions, is that a change in dipole moment should occur for a vibration to absorb infrared energy.

Absorption bands associated with C=O bond stretching are usually very strong because a large change in the dipole takes place in that mode.
Stretching frequencies are higher than corresponding bending frequencies. (It is easier to bend a bond than to stretch or compress it.)

Bonds to hydrogen have higher stretching frequencies than those to heavier atoms.

Triple bonds have higher stretching frequencies than corresponding double bonds, which in turn have higher frequencies than single bonds. (Except for bonds to hydrogen).
General regions of an infrared spectrum

- O-H, N-H
- C-H
- C=O
- C=N
- C-C, C=O, C-N

Frequency (cm⁻¹)

Wavelength (microns)
Features of infrared spectroscopy

- It is rarely, if ever, possible to identify an unknown compound by using IR spectroscopy alone.

- The principal strengths are:
  - It is a quick and relatively cheap spectroscopic technique,
  - It is useful for identifying certain functional groups in molecules and
  - An IR spectrum of a given compound is unique and can therefore serve as a fingerprint for this compound.
Infrared spectroscopy group frequencies

3700 – 2500 cm\(^{-1}\) **Single bonds to hydrogen**

2300 – 2000 cm\(^{-1}\) **Triple bonds**

1900 - 1500 cm\(^{-1}\) **Double bonds**

1400 - 650 cm\(^{-1}\) **Single bonds (other than hydrogen)**
Infrared group frequencies
<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>$\text{C} \equiv \text{H}$</td>
<td>2850–2960</td>
<td>Medium to strong</td>
</tr>
<tr>
<td>$\text{C} \equiv \text{C}$</td>
<td>3020–3100</td>
<td>Medium</td>
</tr>
<tr>
<td>Alkenes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\equiv\text{C} \equiv \text{H}$</td>
<td>1640–1680</td>
<td>Medium</td>
</tr>
<tr>
<td>$\equiv\text{C} \equiv \text{C}$</td>
<td>3300</td>
<td>Strong</td>
</tr>
<tr>
<td>Alkynes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\equiv\text{C} \equiv \text{H}$</td>
<td>2100–2260</td>
<td>Medium</td>
</tr>
<tr>
<td>Alkyl halides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C} \equiv \text{Cl}$</td>
<td>600–800</td>
<td>Strong</td>
</tr>
<tr>
<td>$\text{C} \equiv \text{Br}$</td>
<td>500–600</td>
<td>Strong</td>
</tr>
<tr>
<td>$\text{C} \equiv \text{I}$</td>
<td>500</td>
<td>Strong</td>
</tr>
<tr>
<td>Alcohols</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{O} \equiv \text{H}$</td>
<td>3400–3650</td>
<td>Strong, broad</td>
</tr>
<tr>
<td>$\text{C} \equiv \text{O}$</td>
<td>1050–1150</td>
<td>Strong</td>
</tr>
<tr>
<td>Aromatics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\equiv\text{C} \equiv \text{H}$</td>
<td>3030</td>
<td>Weak</td>
</tr>
<tr>
<td>$\equiv\text{C} \equiv \equiv \text{C}$</td>
<td>1660–2000</td>
<td>Weak</td>
</tr>
<tr>
<td>$\equiv\text{C} \equiv \equiv \text{C}$</td>
<td>1450–1600</td>
<td>Medium</td>
</tr>
<tr>
<td>Amines</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{N} \equiv \text{H}$</td>
<td>3300–3500</td>
<td>Medium</td>
</tr>
<tr>
<td>$\text{C} \equiv \text{N}$</td>
<td>1030–1230</td>
<td>Medium</td>
</tr>
<tr>
<td>Carbonyl compounds*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C} \equiv \text{O}$</td>
<td>1670–1780</td>
<td>Strong</td>
</tr>
<tr>
<td>Carboxylic acids</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{O} \equiv \text{H}$</td>
<td>2500–3100</td>
<td>Strong, very broad</td>
</tr>
<tr>
<td>Nitriles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C} \equiv \equiv \text{N}$</td>
<td>2210–2260</td>
<td>Medium</td>
</tr>
<tr>
<td>Nitro compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{NO}_2$</td>
<td>1540</td>
<td>Strong</td>
</tr>
</tbody>
</table>

*Carboxylic acids, esters, aldehydes, and ketones.
**Infrared group frequencies**

- **Alcohols and amines** display strong broad O-H and N-H stretching bands in the region 3400-3100 cm$^{-1}$. The bands are **broadened** due to **hydrogen bonding** and a sharp 'non-bonded' peak can often be seen at around 3400 cm$^{-1}$.

- **Alkene and alkyne** C-H bonds display sharp stretching absorptions in the region 3100-3000 cm$^{-1}$. The bands are of **medium** intensity and are often obscured by other absorbances in the region (i.e., OH).
Triple bond stretching absorptions occur in the region 2400-2200 cm$^{-1}$. Absorptions from nitriles are generally of medium intensity and are clearly defined. Alkynes absorb weakly in this region unless they are highly asymmetric; symmetrical alkynes do not show absorption bands.
Carbonyl stretching bands occur in the region 1800-1700 cm\(^{-1}\). The bands are generally very strong and broad. Carbonyl compounds which are more reactive in nucleophilic addition reactions (acyl halides, esters) are generally at higher wave number than simple ketones and aldehydes, and amides are the lowest, absorbing in the region 1700-1650 cm\(^{-1}\).
Carbon-carbon double bond stretching occurs in the region around 1650-1600 cm\(^{-1}\). The bands are generally \textbf{sharp} and of medium intensity. Aromatic compounds will typically display a series of sharp bands in this region.

Carbon-oxygen single bonds display stretching bands in the region 1200-1100 cm\(^{-1}\). The bands are generally strong and broad. You should note that \textbf{many other functional groups} have bands in this region which appear similar.
Infrared spectrum of vanillin

[Diagram showing the infrared spectrum of vanillin with labeled wavelengths and notes on inverted peaks and conversion factor.]
Examples of infrared spectra

[Graph showing infrared spectra with labeled peaks for O-H, Saturated C-H, Unsaturated C-H, CH Stretch, and Wave Number cm⁻¹ on the x-axis and Wavelength, microns on the y-axis.]
Examples of infrared spectra

- The infrared spectrum of benzyl alcohol displays a broad, hydrogen-bonded -OH stretching band in the region ~3400 cm\(^{-1}\), a sharp unsaturated (sp2) CH stretch at about 3010 cm\(^{-1}\) and a saturated (sp3) CH stretch at about 2900 cm\(^{-1}\); these bands are typical for alcohols and for aromatic compounds containing some saturated carbon.

- Acetylene (ethyne) displays a typical terminal alkyne C-H stretch.
Examples of infrared spectra
Saturated and unsaturated CH bands are shown clearly in the spectrum of vinyl acetate (ethenyl ethanoate). This compound also shows a typical ester carbonyl at \( 1700 \text{ cm}^{-1} \) and an example of a carbon-carbon double bond stretch at about \( 1500 \text{ cm}^{-1} \). Both of these bands are shifted to slightly lower wave numbers than are typically observed (by about 50 cm\(^{-1}\)) by conjugation involving the vinyl ester group.
Example spectra (1)

1-Buthanol
Example spectra

- **n-Butanol CH₃CH₂CH₂CH₂OH**
  - O-H Stretch 3330 cm⁻¹
  - C-O Stretch 1070 cm⁻¹
  - Hydrogen Bonded
Example spectra (2)

(Ethanoic acid)
Example spectra

- **Ethanoic Acid CH$_3$COOH**
  - O-H Stretch 3050 cm$^{-1}$
  - C=O stretch 1715 cm$^{-1}$
  - C-O Stretch 1295 cm$^{-1}$
  - Hydrogen Bonded
Example spectra (3)

(2-butaneone)
Example spectra

- 2-Butanone \( \text{CH}_3\text{COCH}_2\text{CH}_3 \)
  - \( \text{C}=\text{O} \) Stretch 1715 cm\(^{-1} \)
Example spectra

(ethyl ethanoate)
**Example spectra**

- **Ethyl Ethanoate** $\text{CH}_3\text{COOC}_2\text{H}_5$
  - C=O Stretch 1710 cm$^{-1}$
  - C-O Stretch 1240 cm$^{-1}$
  - C-O Stretch 1050 cm$^{-1}$
Infrared Spectrum of Silicone (polydimethylsiloxane)

- CH\textsubscript{3} stretching of CH\textsubscript{3}
- CH\textsubscript{3} symmetric deformation of Si-CH\textsubscript{3}
- CH\textsubscript{3} asymmetric deformation of Si-CH\textsubscript{3}
- Si-O-Si stretching vibrations
- Si-C stretching and CH\textsubscript{3} rocking
Step 1

- Look first for the carbonyl C=O band.
- Look for a strong band at 1820-1660 cm$^{-1}$. This band is usually the most intense absorption band in a spectrum. It will have a medium width. If you see the carbonyl band, look for other bands associated with functional groups that contain the carbonyl by going to step 2.
- If no C=O band is present, check for alcohols and go to step 3.
Infrared interpretation

**Step 2**

- If a C=O is present you want to determine if it is part of an acid, an ester, or an aldehyde or ketone. At this time you may not be able to distinguish aldehyde from ketone.
Infrared interpretation

- **ACID**
  - Look for indications that an O-H is also present. It has a broad absorption near 3300-2500 cm\(^{-1}\). This actually will overlap the C-H stretch. There will also be a C-O single bond band near 1100-1300 cm\(^{-1}\). Look for the carbonyl band near 1725-1700 cm\(^{-1}\).

- **ESTER**
  - Look for C-O absorption of medium intensity near 1300-1000 cm\(^{-1}\). There will be no O-H band.
**Infrared interpretation**

- **ALDEHYDE**
  - Look for aldehyde type C-H absorption bands. These are two weak absorptions to the right of the C-H stretch near 2850 cm\(^{-1}\) and 2750 cm\(^{-1}\) and are caused by the C-H bond that is part of the CHO aldehyde functional group. Look for the carbonyl band around 1740-1720 cm\(^{-1}\).

- **KETONE**
  - The weak aldehyde CH absorption bands will be absent. Look for the carbonyl CO band around 1725-1705 cm\(^{-1}\).
Step 3

If no carbonyl band appears in the spectrum, look for an alcohol O-H band.

ALCOHOL

Look for the broad OH band near 3600-3300 cm\(^{-1}\) and a C-O absorption band near 1300-1000 cm\(^{-1}\).
**Step 4**
- If no carbonyl bands and no O-H bands are in the spectrum, check for double bonds, C=C, from an aromatic or an alkene.

**ALKENE**
- Look for weak absorption near 1650 cm\(^{-1}\) for a double bond. There will be a CH stretch band near 3000 cm\(^{-1}\).

**AROMATIC**
- Look for the benzene, C=C, double bonds which appear as medium to strong absorptions in the region 1650-1450 cm\(^{-1}\). The CH stretch band is much weaker than in alkenes.
Step 5

- If none of the previous groups can be identified, you may have an alkane.

ALKANE

- The main absorption will be the C-H stretch near 3000 cm\(^{-1}\). The spectrum will be simple with another band near 1450 cm\(^{-1}\).
Step 6

- If the spectrum still cannot be assigned you may have an alkyl halide.

ALKYL BROMIDE

- Look for the C-H stretch and a relatively simple spectrum with an absorption to the right of 667 cm⁻¹.