Molecular Vibrations

IR & Raman Spectroscopies

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OUTLINE

• Introduction
• IR spectroscopy: fundamentals
• Characteristic vibration zones
• Main functional groups and characteristic frequencies
• IR spectra of organic compounds
• Factors controlling frequency groups. Hydrogen bonding
• IR spectra of inorganic compounds
• Raman spectroscopy
• Comparison of IR and Raman spectroscopies
INTRODUCTION:
TECHNIQUES FOR STRUCTURAL DETERMINATION

1. **Nuclear Magnetic Resonance (NMR)** – Excitation of nucleus of atoms by radiofrequency irradiation → molecular structure & atom connectivity.

2. **Infrared Spectroscopy (IR)** – Trigger molecular vibrations with IR light → the presence of certain functional groups.

3. **Raman Spectroscopy** – Irradiation of sample with laser beam → the presence of certain functional groups.

4. **Mass spectrometry** – Bombardment the sample with e- and detection of resulting molecular fragments → molecular mass & atom connectivity.

5. **Ultraviolet absorption spectroscopy (UV)** – Promotion of e- to higher energy levels by irradiation with UV light. → conjugated π systems & double or triple bonds.
I. Introduction

**Spectroscopy** study the interaction of matter with the electromagnetic spectrum

1. Electromagnetic radiation properties of both particles and waves

2. The particle component is called a *photon*

3. The energy \((E)\) of a photon is proportional to the frequency \(\nu\) of the electromagnetic wave, where \(h\) is Planck’s constant

\[
h = 6.62 \times 10^{-34} \text{ J x s}
\]

**PLANCK RELATION:**

\[
E = h \nu = \frac{hc}{\lambda} = hc\tilde{\nu}
\]

- \(c\) (speed of light) = \(3 \times 10^{10}\) cm/s
- \(\lambda\): wavelength; \(\tilde{\nu}\): wavenumber
Infrared Spectroscopy (IR)

Measures the bond vibration frequencies in a molecule

Information about the functional groups

\[ \lambda \quad \nu \quad 12.500 \text{ cm}^{-1} \]

\[ \Delta \nu = 1 \]

Harmonic vibrations

Fundamental vibrations & rotational structure

Rotational spectroscopy

\[ \Delta \nu = 2 \]

Overtone/harmonic vibrations
When a sample is exposed to **IR LIGHT**, it can **absorb** some frequencies and **transmit** the rest. Some light can be reflected back to the source.

- **Incident light** $P_o$
- **Chemical sample**
- **Transmitted light** $P$
- **Detector**

**Beer–Lambert law**

$$T = \left(\frac{P}{P_o}\right) \times 100$$

$$A = -\log T$$

- **Transmittance** $T$
- **Absorbance** $A$

**How strongly light was absorbed?**

- **100%** $T$
- **No absorption**

**Y-axis:** Intensity of the absorption or transmission in %

**X-axis:** Frequencies in wavenumbers

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**Graphs:**

- **Absorption**
  - ~3600 (cm$^{-1}$)
  - Frequency in wavenumbers (cm$^{-1}$)
  - 100 %
  - 0 %

- **Transmission**
  - ~3600 (cm$^{-1}$)
  - Frequency in wavenumbers (cm$^{-1}$)
  - 100 %
  - 0 %
Inert solid electrically heated to 1500-2000 K. The heated material emit IR radiation:

The signal originates from the potential difference caused by heating a junction with the IR beam.

Contains a crystal that exhibits an internal electrical field. Effect depends on the rate of temperature change.
Infrared Spectroscopy (IR): fundamentals

Consider the atoms of a diatomic molecule as point masses connected by springs (bonds).

Hooke’s Law

\[ F = -kx \]

- \( F \) = force, restoring back to equilibrium position
- \( k \) = force or spring constant
- \( x \) = displacement from the equilibrium position

Directly on the bonding strength (\( \uparrow k \sim \uparrow \nu \))

Inversely on the reduced mass (\( \downarrow m_r \sim \uparrow \nu \))

For a X-H bond, \( m_r \) is \( \sim 1 \)
For a C-C bond, \( m_r \) is \( \sim 6 \)

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m_r}} \]

\( \nu \) = frequency
\( k \) = constant (bond strength)
\( m_r \) = reduced mass (\( \sim \) mass of smallest atom)

- C-C \( \nu \sim 1000 \text{ cm}^{-1} \)
- C-H \( \nu \sim 3000 \text{ cm}^{-1} \)
Stretching frequencies and correlations with bond strengths (bond order)

<table>
<thead>
<tr>
<th>Bond strength (kJ/mol)</th>
<th>Bond order</th>
<th>$\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>350</td>
<td>1000 cm$^{-1}$</td>
</tr>
<tr>
<td>C=C</td>
<td>600</td>
<td>1600 cm$^{-1}$</td>
</tr>
<tr>
<td>C≡C</td>
<td>840</td>
<td>2200 cm$^{-1}$</td>
</tr>
</tbody>
</table>

For same reduced mass!

$I$ depends on how fast the energy of frequency $\nu$ can be transferred to the atoms involved in the vibration: the $\text{change}$ in dipole moment, $I$.

$O_2$, $N_2$ and $H_2$ DO NOT ABSORB IR LIGHT!

Dipole Moment Must Change for a vibration to be “IR active”!
Vibrations of $\text{O}=\text{C}=\text{O}$ which change the dipole moment $\rightarrow$ absorb IR light

- **Symmetric stretch** $1340 \text{ cm}^{-1}$
  - C is fixed.
  - O moves in and out
  - O together in same direction
  - C moves in opposite

- **Asymmetric stretch** $2350 \text{ cm}^{-1}$

**Strongly polar bonds** $\rightarrow$ strong bands.
**Medium polarity bonds and asymmetric bonds** $\rightarrow$ medium bands.
**Weakly polar bonds and symmetric bonds** $\rightarrow$ weak or non observable bands.

**Transmission**

- **Strong** (w)
- **Medium** (m)
- **Weak** (s)
- **Not observable**
Degrees of vibrational freedom: 3N-6 (3N-5 for linear molecules)  

Two types of molecular vibrations:

- **Stretching** – Distance between atoms increases or decreases. Bond length changes. Atoms remain in same axis  
  → High frequency

- **Bending** – Bond angle changes. Bond length changes. Atoms remain in different axes  
  → Lower frequency.

- **Scissoring** (δs): Une atom approaches while other departs from the central atom. 
- **Rocking** (δas): Une atom approaches while other departs from the central atom. 
- **Wagging** (γs): Une atom approaches while other departs from the central atom. 
- **Twisting** (γas): Une atom approaches while other departs from the central atom.

https://www.youtube.com/watch?v=1PQqDfJKXvA
**Characteristic vibration zones**

Functional groups: 4000-1400 cm\(^{-1}\) stretching vibrations of diatomic units

Fingerprint: 1400-900 cm\(^{-1}\) the peaks are unique to each molecule → data from an unknown sample can be compared to standards for identification

Aromatic: 910-650 cm\(^{-1}\) (out-of-plane bending bands)

Inorganic bonds: 650-200 cm\(^{-1}\)

![IR and Raman Spectroscopy Diagram](image-url)
The area of a IR band is not proportional to the concentration of the functional group. The greater the difference in electronegativity, the larger the peak. The greater the change in stretching > bending.
**Main functional groups and characteristic frequencies**

### 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></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></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>
1. **Alkanes** – combination of C-C and C-H bonds
   - C-C stretching at 1030 cm\(^{-1}\) (too weak to be detected)
   - C-H bending (scissoring) in CH\(_2\)-CH\(_2\): 1450-1470 cm\(^{-1}\)
     - CH\(_2\)-CH\(_3\): 1360-1390 cm\(^{-1}\)
   - sp\(^3\) C-H between 2800-3000 cm\(^{-1}\) (\(\nu_{\text{as}} > \nu_{s}\))
Alkyl Halides

Halogen: C-F stretching 1400-1100 cm\(^{-1}\)
C-Cl stretching 785-540 cm\(^{-1}\)
2. **Alkenes** – C=C and vinyl C-H bonds
   - C=C stretch at 1620-1680 cm\(^{-1}\) as substitution
   - vinyl C-H stretch at 3000-3100 cm\(^{-1}\)
   - Difference between alkane, alkene or alkyne: νC-H

>3100 cm\(^{-1}\) → alkynyl sp C-H; 3000-3100 cm\(^{-1}\) → vinyl sp\(^2\) C-H; <3000 cm\(^{-1}\) → alkyl sp\(^3\) C-H
3. Aromatics

- C-C bond order is 1.5 \( \nu_S < \text{C} = \text{C} \)
- Pair or three sharp bands (depending on molecule and conjugation) 1600-1585 and 1500-1400 cm\(^{-1}\) (lower frequency band is stronger)
- Aromatic C-H stretching similar to vinyl C-H at 3000-3100 cm\(^{-1}\)
- 1250-1000 cm\(^{-1}\) C–H in-plane bending; 690-900 cm\(^{-1}\) C-H out of plane bending
3. Aromatics

- Region between 1667-2000 cm\(^{-1}\) Weak peaks for aromatic systems
- Analysis of this overtones of bending region substitution pattern

- 1,2 disubstituted \((ortho\) or \(o\)-)
- 1,2 disubstituted \((meta\) or \(m\)-)
- 1,4 disubstituted \((para\) or \(p\)-)
4. Unsaturated Systems – substitution patterns

- The substitution of aromatics and alkenes → out-of-plane bending vibration

<table>
<thead>
<tr>
<th>Substitution</th>
<th>IR cm⁻¹</th>
<th>Raman cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>R C=CH₂</td>
<td>985-997</td>
<td>730-770</td>
</tr>
<tr>
<td></td>
<td>905-915</td>
<td>690-710</td>
</tr>
<tr>
<td>R C=C H</td>
<td>960-980</td>
<td>735-770</td>
</tr>
<tr>
<td>H R</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TRANS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R C=C H R</td>
<td>665-730</td>
<td>860-900</td>
</tr>
<tr>
<td>CIS</td>
<td></td>
<td>750-810</td>
</tr>
<tr>
<td></td>
<td></td>
<td>680-725</td>
</tr>
<tr>
<td>R C=CH₂ R</td>
<td>885-895</td>
<td>800-860</td>
</tr>
<tr>
<td>R R</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R C=C H R</td>
<td>790-840</td>
<td>800-860</td>
</tr>
<tr>
<td>CIS</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
note that the aromatic C–H stretches are to the left of 3000, and the alkyl C–H stretches are to the right of 3000.
5. Alcohols

- Strong, broad O-H stretch $\rightarrow$ 3200-3400 cm$^{-1}$
  Shape depends on H-bonds (the stronger H bonding, the broader and more intense, frequency)
  O-H bending: in plane at 1350 and out of plane at 650 cm$^{-1}$
- C-O stretch $\rightarrow$ 970-1260 cm$^{-1}$
- Band position changes depending on the substitution:
  1° 1075-970; 2° 1075-1150; 3° 1100-1200; phenol 1180-1260
  $-$CH$_2$OH  $-$CHROH  $-$CR$_2$OH  C$_6$H$_5$OH

![IR Spectrogram of 1-butanol](image)
6. Amines –

- Primary: N-H stretch as a **doublet** 3200-3500 cm\(^{-1}\) (\(\nu_S\) and \(\nu_{AS}\)). Weaker and sharper than alcohol
- Secondary (\(R_2NH\)): single weak band 3300-3000 cm\(^{-1}\)
- Tertiary \(R_3N\): No band
- -NH\(_2\) bending band (scissoring) 1590-1650 cm\(^{-1}\)
- C–N stretch (aliphatic amines) from 1250–1020 cm\(^{-1}\)
- “waging” band at 780-820 cm\(^{-1}\)
7. Ketones

- C=O stretch occurs at 1705-1725 cm\(^{-1}\)
- C-C-C stretching and bending at 1100 cm\(^{-1}\)
8. Carboxylic Acids:
- C=O band 1700-1725 cm\(^{-1}\)
- C-O band 1320-1210 cm\(^{-1}\) (as a doublet due to coupling between O-H in plane bending and C-O)

- The O-H bond has a broad band from 2400-3500 cm\(^{-1}\)
9. Amides

C=O stretch at 1640-1680 cm$^{-1}$

- Primary amine $\rightarrow$ N-H stretch 3200-3500 cm$^{-1}$ as a doublet
- Secondary amine $\rightarrow$ (-NHR) N-H stretch at 3200-3500 cm$^{-1}$ as sharp singlet
- C–N stretch :1250–1020 cm$^{-1}$

![Infrared Spectroscopy](image)
Factors controlling frequency groups

1. **Coupled vibrations**: mechanical coupling interaction between oscillators.
   It appears when:
   i) Two bond oscillators share a common atom
   ii) Their oscillation frequencies are quite similar
   i.e. O=C=O  Asymmetrical stretching: The two C=O bonds stretch out of phase: one stretches as the other contracts.  $v_{as}$ at 2350 cm$^{-1}$ higher frequency than a single C=O in aliphatic ketones (1750-1650 cm$^{-1}$) strong mechanical coupling between the 2 C=O

2. **Fermi Resonance**: Interaction between fundamental vibrations and overtones
   e.g. $v_s$ of O=C=O in Raman at 1337 cm$^{-1}$.
   - Two equivalent bending vibrations at 667.3 cm$^{-1}$.
   The first overtone is $2 \times 667.3 = 1334.6$ cm$^{-1}$
   The mixing of 1337 and 1334 cm$^{-1}$ gives 2 bands at 1285 and 1388 cm$^{-1}$ with I ratio 1:0.9

3. **Hydrogen bonding**: Electrostatic attraction between two polar groups that occurs when a H atom covalently bound to a electronegative atom (N, O or F) experiences the electrostatic field of another electronegative atom nearby
IR & Raman Spectroscopy

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Occurs in systems with H donors and H acceptors.

The stronger the H-bond, the longer the X-H bond, the frequency broader and more intense band.

N-H stretching of amines
O-H stretching of alcohols

\[ \nu O-H \text{ (free)}: 3580-3650 \text{ cm}^{-1} \]
\[ \nu O-H \text{ (H-bonded)}: 3200-3550 \text{ cm}^{-1} \]

2 atoms of 2 different molecules
**Intermolecular** H-bonds ➔ broad bands
Intensity ↓ after dilution (bonds broken)

2 atoms of same molecule
**Intramolecular** H-bonds ➔ sharp bands
Unaffected after dilution

Strength of H-bonding depends:
- Molecular geometry
- Acidity of donor and acceptor groups.
4. **Electronic effects**
Change in $\nu$ when the substituents in the neighbourhood of the group are changed

- **Inductive effect**: transmission of charge through a chain of atoms resulting in a permanent dipole in a bond

High electronegative atoms (halogens, NO$_2$) leave the positive charge onto carbon atoms chain: electron-withdrawing effect -I effect. $\nu \uparrow$

$\text{CH}_2\text{Cl}_2$  $\nu$ C-H at 3030 cm$^{-1}$

Low electronegative groups (alkyl) tend to give electrons: electron-releasing effect +I effect: weakening of the bond $\nu \downarrow$

$\text{HCHO}$  1750 cm$^{-1}$  $\text{CH}_3\text{CHO}$  1745 cm$^{-1}$  $\text{CH}_3\text{COCH}_3$  1715 cm$^{-1}$

- **Mesomeric (resonance) effect**: resonance stabilization of the molecule due to delocalization of charge.

*Conjugation causes weakening and lengthening of a double or triple bond $\nu \downarrow$*

1684 cm$^{-1}$  C=O  1715 cm$^{-1}$  C=O
5. Field effect
In ortho-substituted compounds, the lone pair of e- on two atoms influence each other by interactions and change the vibrational frequencies of both groups.

Acetophenone C=O at 1700 cm\(^{-1}\)
Ortohalo acetophenone C=O at 1680 cm\(^{-1}\)
6. Steric effects – usually not important in IR spectroscopy, unless they reduce the strength of a bond (usually \( \pi \)) by interfering with proper orbital overlap:

\[
\begin{align*}
\text{C}=\text{O} & : 1686 \text{ cm}^{-1} \\
\text{C}=\text{O} & : 1693 \text{ cm}^{-1}
\end{align*}
\]

The methyl group causes the CO to be out of the plane

Difficult the stabilization by resonance

\( v \) increases

7. Strain effects – changes in bond angle forced by the constraints of a ring

- change in hybridization
- bond strength

As the size of the ring increases, bond angle decreases, C is more electronegative, difference with O decreases, bond order decreases, and \( v \) decreases.

\[
\begin{align*}
\text{sp}^2 & : 1815 \text{ cm}^{-1} \\
\text{sp}^2 & : 1775 \text{ cm}^{-1} \\
\text{sp}^2 & : 1750 \text{ cm}^{-1} \\
\text{sp}^3 & : 1715 \text{ cm}^{-1} \\
\text{sp}^3 & : 1705 \text{ cm}^{-1}
\end{align*}
\]

(120°) (109°)
SPECTRA OF INORGANIC COMPOUNDS

1. Boron compounds
   OH stretching $3208 \text{ cm}^{-1}$
   B-N stretching $1413 \text{ cm}^{-1}$
   B-O stretching at $1181 \text{ cm}^{-1}$
   B-N bending at $715 \text{ cm}^{-1}$
2. Carbonate compounds  
  bond order: $1.3 < \text{C}=\text{O}$
  - $1455 \text{ cm}^{-1}$ asymmetric C-O stretching
  - $1082 \text{ cm}^{-1}$ symmetric C-O stretching
  - $857 \text{ cm}^{-1}$ out of plane bending
  - $703 \text{ cm}^{-1}$ symmetric in plane bending

Spectrum of CaCO$_3$ (a) and modified clam shell (b)
3. Phosphorous compounds

**Phosphines:** \( R\text{-PH}_2 \) \( \text{R}_2\text{PH} \)

- \( \nu \) \( \text{P—H} \): Sharp 2320 – 2270 cm\(^{-1}\)
- \( \delta_{ip} \) \( \text{PH}_2 \) bending: 1090 – 1075 and 840 - 810 cm\(^{-1}\)
- \( \delta_{oop} \) \( \text{PH} \) bending: 990 - 886 cm\(^{-1}\)

**Phosphine Oxide:** \( \text{R}_3\text{P}=\text{O} \)

- \( \nu \) \( \text{P}=\text{O} \) very strong: 1210 - 1140 cm\(^{-1}\)

**Phosphate Esters:** \((\text{OR})_3\text{P}=\text{O}\)

- \( \nu \) \( \text{P}=\text{O} \) very strong: 1300 - 1240 cm\(^{-1}\)
- \( \nu \) \( \text{P-O} \) very strong: 1088 – 920 cm\(^{-1}\)
- \( \delta_{ip} \) \( \text{P-O} \): 845 - 725 cm\(^{-1}\)
Phosphorous compounds

$\nu$ O-H

$\nu$ C-H

$\nu$ C=O

$\nu$ P=O

$\delta_{ip}$ P–O

$\nu$ C–N
## IR & Raman Spectroscopy

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<table>
<thead>
<tr>
<th>Functional Groups</th>
<th>Region (cm(^{-1}))</th>
<th>Intensity</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PN vibrations:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P–N</td>
<td>1110–930, 750–680</td>
<td>m–s</td>
<td>Possibly due to P–S–M group</td>
</tr>
<tr>
<td>P–N–CH(_3)</td>
<td>1320–1260, 1205–1155, 1080–1050</td>
<td>m–m, w–m</td>
<td></td>
</tr>
<tr>
<td>P–N(_\text{III})N</td>
<td>1010–790</td>
<td>m–s</td>
<td></td>
</tr>
<tr>
<td>P–N(C(_2)H(_3))(_2)</td>
<td>1225–1190, 1190–1155, 1110–1085, 1075–1055, 1050–1015, 975–930, 930–915</td>
<td>m–s, w–m, m</td>
<td></td>
</tr>
<tr>
<td>P–NH(_2)</td>
<td>3330–3100, 1600–1535, 1110–920, 840–660</td>
<td>m, m–w, w</td>
<td>NH(_2) str, NH(_2) def vib</td>
</tr>
<tr>
<td>P–NH</td>
<td>3200–2900, 1145–1075, 1110–930</td>
<td>m–s, m, w</td>
<td>P–N–C asym str, NH str</td>
</tr>
<tr>
<td>P=N (cyclic compounds)</td>
<td>1440–1100</td>
<td>m–s</td>
<td>P=N str, see ref. 15. Trimer 1300–1155 cm(^{-1}), tetramer 1420–1180 cm(^{-1}).</td>
</tr>
<tr>
<td>P=N (acyclic compounds)</td>
<td>1500–1230, 1385–1325</td>
<td>s</td>
<td>P=N str, P=N str</td>
</tr>
<tr>
<td>(RO(_3))(_2)P=N–Ar</td>
<td></td>
<td>s</td>
<td></td>
</tr>
<tr>
<td>R–NH–P(O)Cl(_2)</td>
<td>~560</td>
<td>~7.86</td>
<td></td>
</tr>
<tr>
<td>N–P(S)Cl(_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4. Silicon Compounds

IR SPECTRA OF SILICA

When the 4 vertices of the SiO$_4^-$ tetrahedron are shared is the silica (SiO$_2$)

- Si-H: $2200 \text{ cm}^{-1}$ (Stretch)
  - $950 - 800 \text{ cm}^{-1}$ (bend)

- Si-O-H:
  - OH: $3700 - 3200 \text{ cm}^{-1}$ (Stretch)
  - Si-O: $830 - 1110 \text{ cm}^{-1}$

- $\nu$ O-H
- $\delta$O-H
- $\nu_s$ Si-O
- $\delta$O-Si-O
- $\nu_{AS}$ Si-O

Relative transmittance

Wave number / cm$^{-1}$

IR SPECTRA OF SILICA
5. Sulfate Compounds

S=O stretching 1350-1060 cm\(^{-1}\)
S-O stretching 900-700 cm\(^{-1}\)
Raman Spectroscopy

Studies the dispersed light instead of the absorbed light. Visible light (laser) interacts with molecule and goes to a virtual state. When it relaxes, it can return to the ground vibrational state (no change in $E$, Raman scattering) or to the first vibrational state ($E\downarrow$) or from the first vibrational state to the ground state ($E\uparrow$). The shift in energy gives information about the vibrational modes in the molecule.

Scattering: radiation interacts with particles, changes the direction and can change the energy.
Elastic Scattering (without change in energy: Rayleigh)

Inelastic Scattering (with loss or gain in energy: stokes and antistokes)

Energy exchange between the photon and molecule leads to inelastic scatter.

The strongest scattering is Rayleigh scatter.

In Raman Scattering the scattered photon has different energy (frequency, wavelength) than the incident photon:

Stokes lines are those in which the photon has lost energy:

\[ v_0 - v_t \]

Anti-Stokes lines are those in which the photon has gained energy:

\[ v_0 + v_t \]

Since molecular energy levels are quantized this produces discrete lines from which we can gain info on the molecule itself.
IR & Raman Spectroscopy

- Laser are used as photon sources due to their highly monochromatic nature, and high beam fluxes.
- The helium-neon laser, which emits highly monochromatic light at 632.8 nm,

Detector: Photomultiplier tube with excellent sensitivity and low noise
**Raman spectroscopy:** complementary to IR spectroscopy

- Radiation is scattered by the molecule with *shifts* in the wavelength of the incident beam.
- Frequency shifts are related to vibrational changes in the molecule → associated with IR
- Raman suitable for aqueous solutions, IR only in solid state (H₂O strongly absorbs in IR)
- IR range 4000-400 cm⁻¹. Raman range 4000-50 cm⁻¹; shifts can be small (100-10 cm⁻¹)

Raman *frequency shift* and IR absorption *peak frequency* are identical

**Comparison of Raman & IR:**

<table>
<thead>
<tr>
<th>IR</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. vibrational modes; strong bands</td>
<td>vibrational modes; weak bands</td>
</tr>
<tr>
<td>ii. change in dipole moment</td>
<td>change in polarizability of the molecule</td>
</tr>
<tr>
<td>iii. excitation of molecule to excited vibrational state</td>
<td>momentary distortion of the e- distributed around the bond.</td>
</tr>
<tr>
<td>iv. asymmetric vibrations (active)</td>
<td>symmetric vibrations (active)</td>
</tr>
</tbody>
</table>

\[ \delta^- \ 2\delta^+ \ \delta^- \]

*Intensity of Raman lines are 0.001% intensity of the source*
ETHANOL \( CH_3CH_2OH \)

- C=O and C-O stretching (polar bonds) → more intense in IR
- O-H stretching (polar bond) → more intense in IR
- C=C stretching (non-polar bond) → more intense in Raman
- C-H stretching (low polar) → more intense in Raman
IR & Raman Spectroscopy

Infrared and Raman Spectra of Polyamide (Nylon 66)

- $\nu$ N-H
- $\nu$ C-H
- $\delta$ C-H
- $\nu$ C-N
- $\delta$ N-H
- $\nu$ C-C

$400 \text{ cm}^{-1}$
RAMAN SPECTRA OF CARBON NANOTUBES

- Heating
- G' Band (D overtone)
- Tangential G Band
- D Band Disorder-induced
- Radial Breathing Modes

(vibration of sp² carbon atoms)
(expansion & contraction, Diameter & agglomeration)
Thank you for your attention!