Raman and circular dichroism (CD) spectroscopy

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What is Raman scattering?

In 1928, an Indian physicist, named C.V. Raman, observed that wavelength of some scattering light had changed when light transverse \( \text{CCl}_4 \) solvent. This amazing phenomenon was called Raman scattering or Raman effect.

Nobel Laureate in Physics in 1930

First Raman Spectrometer in the world invented by C.V. Raman
Rayleigh scattering
Elastic scattering
\[ E_{\text{in}} = E_{\text{out}} \]

Raman scattering
Inelastic scattering
\[ E_{\text{in}} \neq E_{\text{out}} \]

Difference between IR and Raman

**Figure 4.** Interaction of the radiation with the matter for IR spectroscopy (A) and for Raman spectroscopy (B).
Stokes & Anti-stokes Raman scattering
Raman spectrum

Relative Raman Shift = \frac{c}{\lambda_{em}} - \frac{c}{\lambda_{ex}}

Relative wavenumber
Mechanism of Raman effect

• The Raman effect can be described by the polarizability of molecule. When an incident light transverse a molecule, the induced dipole moment $\mu$ can be written as below.

$$\mu = \alpha \cdot E$$

Where, $\alpha$ is the polarizability of molecule; $E$ is the applied field.

• Selection rules for Raman effect
  
  – The change of quantum number is limited to $\pm 1$.
  
  $$\Delta \nu = \pm 1$$

  – Polarizability should change. In general, the electron cloud in apolar bond is stronger polarizable than that of polar bond.
Figure 4.7 The changes in the polarizability ellipsoid of carbon dioxide during its vibrations, and a graph showing the variation of the polarizability, $\alpha$, with the displacement coordinate, $\xi$, during each vibration.
## Difference between IR and Raman

<table>
<thead>
<tr>
<th>Infrared</th>
<th>Raman</th>
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<tbody>
<tr>
<td>The change in dipole moment is essential.</td>
<td>The change in polarizability is essential.</td>
</tr>
<tr>
<td>Absorption spectroscopy (requires a lamp covering the whole IR radiation range)</td>
<td>Scattering spectroscopy (requires ONLY one excitation light)</td>
</tr>
<tr>
<td>Water (O-H bond) has a significant influence on the IR spectrum.</td>
<td>Water (O-H bond) has a minor influence on the spectrum.</td>
</tr>
<tr>
<td>Sample preparation is elaborate.</td>
<td>Easy to prepare sample</td>
</tr>
<tr>
<td>IR instrument is relatively cheap.</td>
<td>Raman device costs a lot.</td>
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</table>
Mutual exclusion rule

- If a molecule possesses a center of symmetry, its vibrational modes are either IR-active or Raman-active. No modes can be both IR-active and Raman-active.
Mutual exclusion rule

• In case of noncentrosymmetric molecule, a vibrational mode can be both Raman-active and IR-active.

- Symmetric Stretch
  3657 cm\(^{-1}\)
  Raman-active (strong), IR-active (strong)

- Bend
  1595 cm\(^{-1}\)
  Raman-active (weak), IR-active (strong)

- Asymmetric Stretch
  3756 cm\(^{-1}\)
  Raman-active (weak), IR-active (strong)
Instrumentation of Raman spectroscopy
Circular Dichroism (CD)

- Linearly polarized light
- Circularly polarized light
How to generate circularly polarized light?

• Linear polarized light is actually composed of two waves, which have the same amplitude and phase. And the oscillation direction of their electric fields are c to each other.

• Circularly polarized light is also composed of two orthogonal waves which have the same amplitude. But they differ in phase by one quarter.
CD spectroscopy

- CD spectroscopy utilizes circularly polarized light, and commonly exploits differences in the interactions of chiral molecules with left- and right-circularly polarized light (CPL).

\[ \Delta A = A_{\text{Left CPL}} - A_{\text{Right CPL}} \]
Chiral Molecules

- Normally, when a tetrahedral atom has four different substituents it is chiral. There exist two molecules which are mirror images like our left and right hand.
CD spectroscopy

- CD is only useful in the absorption band of molecules. Usually, it covers from UV to visible range.

\[ \text{CD Signal} = A_L - A_R \]

- Monochromatic light
- Alternating left and right CPL
- Optically active sample
- PMT detector
• When circularly polarized light (CPL) passes through a sample without chirality, the decreases in amplitude of both left CPL and right CPL are equal. Therefore, the resultant wave is also linear polarized light.

• When circularly polarized light (CPL) passes through a sample which possesses chirality, the decreases in amplitude of left CPL and right CPL are different. This leads to the resultant wave oscillates elliptically.
• $\phi$ is the angle between the initial plane of polarization and the major axis of the ellipse of the resultant transmitted light.

• $\theta$ is defined such that $\tan \theta$ is the ratio of the minor axis to the major axis of the ellipse of the transmitted light.

\[
\theta \left( \text{rad cm}^{-1} \right) = \frac{2.303(A_L - A_R)}{4l}
\]

$\theta$ Ellipticity  
$l$ Path length through the sample  
$A$ Absorption

The molar ellipticity $[\theta]$ is given by

\[
[\theta] = 3298 \times (\varepsilon_L - \varepsilon_R)
\]
CD spectroscopy is especially useful in protein science because of the chiral nature of the structural features of proteins.

Protein is a kind of biopolymers whose building block is amino acid. Amino acids are intrinsically asymmetric. It exhibits circular dichroism.

Due to the asymmetrical arrangement of the backbone of protein molecule, its secondary structure of protein also possesses the property of circular dichroism.

The term of mean residue ellipticity is used to describe the molar circular dichroism for individual protein residues instead of whole protein molecules.
Instrumentation of CD

High intensity light source → Monochromator and linear polarizer → PEM → CD active medium → Detector
Problems

1. Ethyne is a linear molecule. Please point out the type of each vibrational mode shown below. Is it Raman-active or IR-active or both?

   ![Diagram of vibrational modes](image)

   - $v_1$
   - $v_2$
   - $v_3$
   - $v_4$
   - $v_5$

2. If the excitation wavelength is set to 350 nm, Raman band of water appears at 398 nm. What will be the position of the Raman band of water if the excitation wavelength becomes 450 nm?