IV Semester M Sc PHYSICS:  
CHAPTER-3  
Microwave spectroscopy

Resmi. K. R  
Asst. Professor  
Dept. Of Physics  
MESKC
• Spectroscopy: the study of interaction of electromagnetic radiation with matter

• Two types:
  • Atomic and molecular spectroscopy
• Spectrometer: producing, observing and measuring spectral lines

• Spectrograph: Taking photograph of spectral lines
<table>
<thead>
<tr>
<th>Change of spin</th>
<th>Change of orientation</th>
<th>Change of configuration</th>
<th>Change of electron distribution</th>
<th>Change of nuclear configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>N.m.r.</td>
<td>E.s.r.</td>
<td>Microwave</td>
<td>Infra-red</td>
<td>Visible and ultra-violet</td>
</tr>
<tr>
<td><img src="image1" alt="Diagram" /></td>
<td><img src="image2" alt="Diagram" /></td>
<td><img src="image3" alt="Diagram" /></td>
<td><img src="image4" alt="Diagram" /></td>
<td><img src="image5" alt="Diagram" /></td>
</tr>
</tbody>
</table>

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td></td>
<td>$10^{-2}$</td>
<td>1</td>
<td>100</td>
<td>$10^4$ cm$^{-1}$</td>
<td>$10^9$ Wavenumber</td>
<td>$10^8$</td>
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<tr>
<td></td>
<td>10 m</td>
<td>100 cm</td>
<td>1 cm</td>
<td>100 μm</td>
<td>1 μm</td>
<td>10 nm Wavelength</td>
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<tr>
<td></td>
<td>$3 \times 10^6$</td>
<td>$3 \times 10^8$</td>
<td>$3 \times 10^{10}$</td>
<td>$3 \times 10^{12}$</td>
<td>$3 \times 10^{14}$ Hz</td>
<td>$3 \times 10^{16}$ Frequency</td>
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<tr>
<td></td>
<td>$10^{-3}$</td>
<td>$10^{-1}$</td>
<td>10</td>
<td>$10^3$</td>
<td>$10^4$ joules/mole</td>
<td>$10^7$ Energy</td>
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</table>
Microwave spectroscopy
Rigid diatomic molecule
\[ E_J = \frac{\hbar^2}{8\pi^2 I} J(J+1) \text{ joules} \quad \text{where } J = 0, 1, 2, \ldots \]

\[ \varepsilon_J = \frac{E_J}{\hbar c} = \frac{\hbar}{8\pi^2 Ic} J(J+1) \text{ cm}^{-1} \quad (J = 0, 1, 2, \ldots) \]

\[ \varepsilon_J = BJ(J+1) \text{ cm}^{-1} \quad (J = 0, 1, 2, \ldots) \]

\[ B = \frac{\hbar}{8\pi^2 I_B c} \text{ cm}^{-1} \]
The allowed rotational energies of a rigid diatomic molecule.
Selection rule: $\Delta J = \pm 1$
Non-rigid rotator

<table>
<thead>
<tr>
<th>$i$</th>
<th>$v_{\text{obs}, \dagger}$ (cm$^{-1}$)</th>
<th>$v_{\text{calc}, \ddagger}$ (cm$^{-1}$)</th>
<th>$\Delta v_{\text{obs}}$ (cm$^{-1}$)</th>
<th>$B$ (=$\frac{1}{2} \Delta \bar{v}$)</th>
<th>$r$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41.08</td>
<td>41.11</td>
<td>41.11</td>
<td>20.56</td>
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<td>163.94</td>
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<td>204.55</td>
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<td>324.61</td>
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<tr>
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<td>402.70</td>
<td>38.31</td>
<td>19.16</td>
<td>0.0963</td>
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<tr>
<td>11</td>
<td>441.13</td>
<td>441.00</td>
<td>37.81</td>
<td>18.91</td>
<td>0.0969</td>
</tr>
</tbody>
</table>

Rotation spectrum of hydrogen fluoride
• Bonds are considered as elastic
• Two consequences are:
• 1) molecule may have vibrational energy with force constant: \[ k = 4\pi^2 \omega^2 c^2 \mu \]
• 2) the quantities ‘r’ and ‘B’ vary during vibration

• The increase in ‘J’ reflects the fact that more quickly a diatomic molecule rotates greater is the centrifugal force tending to move the atoms apart
The Spectrum of a Non-rigid Rotator

Solving Schrödinger eq. for non rigid molecules, the rotational energy levels are:

\[ E_J = \frac{\hbar^2}{8\pi^2 I} J(J + 1) - \frac{\hbar^4}{32\pi^4 I^2 r^2 k} J^2(J + 1)^2 \]

\[ \varepsilon_J = BJ(J + 1) - DJ^2(J + 1)^2 \text{ cm}^{-1}, \quad J = 0, 1, 2, \ldots \]

\[ D = \frac{\hbar^3}{32\pi^4 I^2 r^2 kc} \text{ cm}^{-1} \]

For anharmonic force field:

\[ \varepsilon_J = BJ(J + 1) - DJ^2(J + 1)^2 + HJ^3(J + 1)^3 + KJ^4(J + 1)^4 \ldots \text{ cm}^{-1} \]
selection rule \[ \Delta J = \pm 1. \]

\[
\varepsilon_{J+1} - \varepsilon_J = \bar{v}_J = B[(J + 1)(J + 2) - J(J + 1)] \\
- D[(J + 1)^2(J + 2)^2 - J^2(J + 1)^2] \\
= 2B(J + 1) - 4D(J + 1)^3 \text{ cm}^{-1}
\]

The relation between B and D is:

\[
D = \frac{16B^3 \pi^2 \mu c^2}{k} = \frac{4B^3}{\omega^2}
\]
For HF molecule:

$$\bar{\omega}^2 = \frac{4B^3}{D} = 16.33 \times 10^6 \text{ (cm}^{-1})^2$$

$$\bar{\omega} \approx 4050 \text{ cm}^{-1}.$$

The force constant follows directly:

$$k = 4\pi^2 c^2 \bar{\omega}^2 \mu = 960 \text{ N m}^{-1}$$

which indicates, as expected, that H—F is a relatively strong bond.
Spectrum of symmetric top molecule

\[ I_B = I_C \neq I_A \quad I_A \neq 0 \]

There are two directions of rotations in which molecule absorb or emit energy
1) Main symmetry axis
2) Perpendicular to the symmetry axis

\[ J \text{ can be } 0, 1, 2, \ldots, \infty \]

\[ K = J, J - 1, J - 2, \ldots, 0, \ldots, -(J - 1), -J \]
\[ \varepsilon_{J,K} = \frac{E_{J,K}}{hc} = BJ(J + 1) + (A - B)K^2 \quad \text{cm}^{-1} \]

\[ B = \frac{h}{8\pi^2 I_{Bc}} \quad \text{and} \quad A = \frac{h}{8\pi^2 I_{Ac}} \]
Spectrum

\[ \Delta J = \pm 1 \text{ (as before)} \quad \text{and} \quad \Delta K = 0 \]

\[ \epsilon_{J+1,K} - \epsilon_{J,K} = \bar{\nu}_{J,K} = B(J+1)(J+2) + (A - B)K^2 \]
\[ - [BJ(J+1) + (A - B)K^2] \]
\[ = 2B(J + 1) \text{ cm}^{-1} \]
\[ \varepsilon_{j,k} = B_j (J + 1) + (A - B)K^2 - D_j \cdot J^2(J + 1)^2 - D_{jk} \cdot J(J + 1)K^2 - D_{jk}K^4 \text{ cm}^{-1} \]

\[ \overline{V}_{j,k} = 2B_j (J + 1) - 4D_j (J + 1)^3 - 2D_{jk} (J + 1)K^2 \text{ cm}^{-1} \]

\[ \overline{V}_{j,k} = 2[B - 2D_j (J + 1)^2 - D_{jk} K^2] (J + 1) \text{ cm}^{-1} \]
VIBRATIONAL EXCITATION EFFECT

\[ B_v = \frac{\hbar}{8\pi^2 I_v c} \]

\[ B_v = B_e - \alpha_e \left( v + \frac{1}{2} \right); \quad \alpha_e \approx \frac{12 B_e^2}{V} \]
LINEAR POLYATOMIC MOLECULES

$$\bar{v}_J = 2B(J + 1) - 4\tilde{D}(J + 1)^3 \text{ cm}^{-1}, \quad J = 0, 1, 2, \ldots$$
\[ m_x (r_{xy} + r) + m_y r = m(r_{xy} - r) \]

\[ M = m_x + m_y + m_z \]

\[ I = m (r_{xy} + r)^2 + m (r_{x}^2 + m_z (r_{xy} - r)^2) \]

\[ I = m_x^2 + m_y^2 + m_z^2 - M \]
\[ I = \frac{m_x m_y r_{xy}^2 + m_y m_z r_{yz}^2 + m_x m_z (r_{xy} + r_{yz})^2}{m_x + m_y + m_z} \]
STARK EFFECT

Stark effect is the splitting of a spectral line in the presence of an electric field.

It is the splitting of a rotational absorption line into various $m_f$ components.

The total Hamiltonian

$$H = H_{\text{rot}} - \mu \cdot X$$

The Stark term $-\mu \cdot X$ is generally small and can be treated as a small perturbation.
For symmetric tops

\[ E_{J K m_J} = BhcJ(J + 1) + (A - B)hcK^2 - \frac{\mu K m_J X}{J(J + 1)} \]

\[ J = 0, 1, 2, ..., K = 0, \pm 1, \pm 2, ..., \pm J \quad m_J = 0, \pm 1, \pm 2, ..., \pm J \]

The selection rule \( \Delta J = +1, \Delta K = 0 \) and \( \Delta m_J = 0 \)

\[ \Delta E^{(1)} = \frac{2\mu X K m_J}{J(J + 1)(J + 2)} \]

\[ \Delta v^{(1)} = \frac{\Delta E^{(1)}}{h} = 0.5035 \mu X \frac{2K m_J}{J(J + 1)(J + 2)} \text{ MHz} \]
First order Stark effect of a symmetric top molecule for the $J = 1, K = 1 \rightarrow J = 2, K = 1$ transition.
For linear molecules

\[ E_{Jm}^{(2)} = \frac{\mu^2 X^2}{2 \hbar B} \frac{J(J+1) - 3m_J^2}{J(J+1)(2J-1)(2J+3)} \]

Stark effect of the \( J = 0 \rightarrow J = 1 \) transition of a linear molecule.
Microwave spectrometer
• Source: Klystron

• Frequency measuring device: Cavity wavemeters

• Guidance of radiation to the cell: Wave guides

• Sample cell: Eg; stark cell employing stark modulation techniques

• Detector:
Stark modulation

• In stark cell a flat metal strip is mounted half way between the faces of waveguide with a dielectric insulating plate from the wave guide
• By injecting a 0-2000V square wave potential between metallic plate and waveguide the resonance frequencies of the molecule can be modulated via stark effect
• This is followed by a phase lock detector, which will respond only to molecular resonance
• Hence the cell background characteristics can be eliminated in stark modulation spectrographs
INFORMATION DERIVED FROM ROTATIONAL SPECTRA

Molecular structure

\[ A = \frac{\hbar}{8 \pi^2 I_{ac}} \text{cm}^{-1}, \quad B = \frac{\hbar}{8 \pi^2 I_{bc}} \text{cm}^{-1}, \quad C = \frac{\hbar}{8 \pi^2 I_{cc}} \text{cm}^{-1} \]

\[ I = \mu r^2, \quad r = \left[ I \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \right]^{1/2} \]

\[ \bar{V}^2 = \frac{4B^3}{D}, \quad \bar{V} = \frac{1}{2 \pi c} \sqrt{\frac{k}{\mu}} \]

\[ k = \frac{16 \pi^2 c^2 \mu B^3}{D} \]
Dipole moment:

Atomic mass:

\[ B = \frac{h}{8\pi^2 Ic}, \quad B' = \frac{h}{8\pi^2 I'c} \]

\[ \frac{B}{B'} = \frac{I'}{I} = \frac{\mu'}{\mu} \]

Nuclear quadrupole moment: