Lecture 4: Polyatomic Spectra

1. From diatomic to polyatomic
2. Classification of polyatomic molecules
3. Rotational spectra of polyatomic molecules
4. Vibrational bands, vibrational spectra
1. From diatomic to polyatomic

Rotation – Diatomics

Recall: For diatomic molecules

**Energy:** \( F(J), \text{cm}^{-1} = BJ(J+1) - DJ^2(J+1)^2 \)  
**Rotational constant:** \( B, \text{cm}^{-1} = \frac{\hbar}{8\pi^2 I_c} \)

**Selection Rule:** \( J' = J'' + 1 \rightarrow \Delta J = +1 \)

**Line position:** \( \nu_{J''+1 \leftrightarrow J''} = 2B(J''+1) - 4D(J''+1)^3 \)

**Notes:**

1. \( D_v \) is small, i.e., \( \frac{D}{B} = 4\left(\frac{B}{\nu_{vib}}\right)^2 \ll 1 \)

2. E.g., for NO, \( \left(\frac{D}{B}\right)_{NO} = 4\left(\frac{B}{\omega_o}\right)^2 \approx 4\left(\frac{1.7}{1900}\right)^2 \approx 3 \times 10^{-6} \)

\( \rightarrow \) Even @ J=60, \( \frac{D}{B} \cdot J^2 \approx 0.01 \)

*What about polyatomics (≥3 atoms)?*
1. From diatomic to polyatomic

- 3D-body rotation

- 3 principal axes (orthogonal): A, B, C
- 3 principal moments of inertia: \( I_A, I_B, I_C \)
- Molecules are classified in terms of the relative values of \( I_A, I_B, I_C \)

- Convention: A-axis is the “unique” or “figure” axis, along which lies the molecule’s defining symmetry
2. Classification of polyatomic molecules

Types of molecules

<table>
<thead>
<tr>
<th>Type</th>
<th>Linear Molecules</th>
<th>Symmetric Tops</th>
<th>Spherical Tops</th>
<th>Asymmetric Rotors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative magnitudes of $I_{A,B,C}$</td>
<td>$I_B=I_C; I_A\approx 0^*$</td>
<td>$I_B=I_C\neq I_A$</td>
<td>$I_A=I_B=I_C$</td>
<td>$I_A\neq I_B\neq I_C$</td>
</tr>
</tbody>
</table>

**Examples**

- CO$_2$
- C$_2$H$_2$
- OCS
- CO$_2$
- NH$_3$
- CH$_3$F
- CH$_4$
- BCl$_3$
- H$_2$O
- NO$_2$

- Relatively simple
- No dipole moment
- Not microwave active
- Largest category
- Most complex

*Actually finite, but quantized momentum means it is in lowest state of rotation
2. Classification of polyatomic molecules

- Linear molecules

E.g., Carbon oxy-sulfide (OCS)

Center of mass

\[ r_{CO} = 1.165\text{Å} \]
\[ r_{CS} = 1.558\text{Å} \]

\[ I_B = I_C; I_A \approx 0 \]

\[ B, \text{cm}^{-1} = \frac{h}{8\pi^2 I_{BC}} \]
2. Classification of polyatomic molecules

- Symmetric tops

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

- **Prolate**
  \[ I_A < I_B = I_C, \ A > B = C \]
  E.g., CH$_3$F

\[
A, \text{cm}^{-1} = \frac{h}{8\pi^2 I_A c}
\]
\[
B, \text{cm}^{-1} = \frac{h}{8\pi^2 I_B c}
\]
\[
C, \text{cm}^{-1} = \frac{h}{8\pi^2 I_C c}
\]

Tripod-like (tetrahedral bonding)
2. Classification of polyatomic molecules

- Symmetric tops

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

\[ A, \text{cm}^{-1} = \frac{\hbar}{8\pi^2 I_A c} \]

\[ B, \text{cm}^{-1} = \frac{\hbar}{8\pi^2 I_B c} \]

\[ C, \text{cm}^{-1} = \frac{\hbar}{8\pi^2 I_C c} \]

**Oblate**

\( I_A > I_B = I_C, \ A < B = C \)

E.g., \( \text{BCl}_3 \) (Planar)

\( \nabla \text{No elec. dipole mom.} \rightarrow \text{no QM selection rule} \)

Planar view
2. Classification of polyatomic molecules

- Spherical tops
  \[ I_A = I_B = I_C \]
  E.g., \( \text{CH}_4 \) (methane)
  Cube w/ C at center and H at diagonal corners
  Symmetric, but No dipole moment
  No rotational spectrum

- Asymmetric rotors
  \[ I_A \neq I_B \neq I_C \]
  E.g., \( \text{H}_2\text{O} \)
  Complex and not addressed here
3. Rotational spectra of polyatomic molecules

- Linear molecules ($I_B=I_C; I_A \approx 0$)
  - Examples
    - OCS
    - HCN
    - CO$_2$
    - C$_2$H$_2$
    - HC$_2$Cl
  - Symmetric, no dipole moment
  - Must be asymmetric to have electric dipole moment (isotopic substitution doesn’t change this as bond lengths remain fixed)

- Energies and line positions
  - Can treat like diatomic (1 value of $I$) → same spectrum
  - $F(J) = BJ(J + 1) - D(J + 1)^2$
  - $\overline{\nu}(J) = 2B(J + 1) - 4D(J + 1)^3$
  - Note: Larger $I$, smaller $B$ (& line spacing) than diatomics
  - (“is suppressed, i.e. J=J”)
3. Rotational spectra of polyatomic molecules

- Linear molecules ($I_B = I_C; I_A \approx 0$)
  - Bond lengths
    
    N atoms → N-1 bond lengths to be found

- Abs./Emis. spectra → $B$ → 1 value of $I_B$
- Use N-1 isotopes → N-1 values of $I_B$

Example: OCS (carbon oxy-sulfide)

Use 2 isotopes for 2 equations:

\[
I_{16}^{12}C^{32}S = F(masses, r_{CO}, r_{CS})
\]
\[
I_{18}^{12}C^{32}S = F(masses, r_{CO}, r_{CS})
\]

Solve for $r_{CO}, r_{CS}$
3. Rotational spectra of polyatomic molecules

- Symmetric tops ($I_B = I_C \neq I_A; I_A \neq 0$)
  - 2 main directions of rotation \( \rightarrow \) 2 quantum numbers
  - \( J \) (total angular momentum): 0, 1, 2, …
  - \( K \) (angular momentum about A): \( J, J-1, \ldots, 1, 0, -1, \ldots -J \)
  - + & - allowed, w/o change in energy
    \[ 2J+1 \text{ possibilities of } K \text{ for each } J \]

- Quantized angular momentum
  - As before: \( I_A \omega_A^2 + I_B \omega_B^2 + I_C \omega_C^2 = J(J+1)\hbar^2 \)
  - Plus new: \( I_A \omega_A^2 = K^2 \hbar^2 \)

- Energy levels
  \[ E_{J,K} = \frac{1}{2} \sum_i I_i \omega_i^2 \]

\[ F(J, K) = BJ(J+1) + (A - B)K^2 \]

\(^\dagger\) Note degeneracy, i.e., independent of sign of \( K \)
3. Rotational spectra of polyatomic molecules

- Symmetric tops ($I_B = I_C \neq I_A; I_A \neq 0$)
  - Q.M. Selection rules
    - $\Delta J = +1$ Remember that $\Delta J = J' - J''$
    - $\Delta K = 0$
      - No dipole moment for rotation about A-axis
      - No change in K will occur with abs./emis.
  - Line positions
    \[
    \tilde{\nu}_{J,K} = F(J + 1, K) - F(J, K) = 2BJ(J + 1) \quad [cm^{-1}]
    \]

- Note: Independent of K for a rigid rotor
  - Same as rigid diatomic!
  - K-dependence introduced for non-rigid rotation
3. Rotational spectra of polyatomic molecules

- Symmetric tops ($I_B = I_C \neq I_A; I_A \neq 0$)
  - Non-rigid rotation

Effect of extending bond lengths (w/ changes in $K$)

Change energies of rotation

Centrifugal distortion const. $D_J, D_K, D_{JK}$

$$F(J,K) = BJ(J+1) + (A-B)K^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4$$

$$\tilde{v}_{J,K} = 2(J+1)[B - 2D_J (J+1)^2 - D_{JK} K^2] \quad [cm^{-1}]$$

Note: Each $J$ has $2J+1$ components, but only $J+1$ frequencies

E.g., CH$_3$F, Methyl Fluoride

$$B = 0.851 \text{ cm}^{-1}$$
$$D_J = 2 \times 10^{-6} \text{ cm}^{-1}$$
$$D_{JK} = 1.47 \times 10^{-5} \text{ cm}^{-1}$$

If $J \approx 20$, $J^2 \approx 400$, $2D_{JK} \approx 1.6 \times 10^{-3}$, $2D_J^2/B \approx 0.2\%$
3. Rotational spectra of polyatomic molecules

- Symmetric tops \( (I_B = I_C \neq I_A; I_A \neq 0) \rightarrow \text{gets complex fast!} \)

**Prolate**

\[
I_A < I_B = I_C, \ A > B = C
\]

\[
F(J, K) = BJ(J + 1) + (A - B)K^2
\]

\[
A - B = \frac{h}{8\pi^2c} \left( \frac{1}{I_A} - \frac{1}{I_B} \right) > 0
\]

**Oblate**

\[
I_A > I_B = I_C, \ A < B = C
\]

\[
F(J, K) = BJ(J + 1) + (A - B)K^2
\]

\[
A - B = \frac{h}{8\pi^2c} \left( \frac{1}{I_A} - \frac{1}{I_B} \right) < 0
\]

Example energy levels
3. Rotational spectra of polyatomic molecules

- Rotational partition function

<table>
<thead>
<tr>
<th>Linear</th>
<th>Symmetric top</th>
<th>Spherical top</th>
<th>Asymmetric rotor</th>
</tr>
</thead>
<tbody>
<tr>
<td>B=C; I_A≈0</td>
<td>B=C≠A; I_A≠0</td>
<td>A=B=C</td>
<td>A≠B≠C</td>
</tr>
</tbody>
</table>

\[ Q_{rot} = \frac{kT}{\sigma \hbar c B} \]
\[ Q_{rot} = \frac{1}{\sigma} \sqrt{\frac{\pi}{AB^2}} \left( \frac{kT}{\hbar c} \right)^3 \]
\[ Q_{rot} = \frac{1}{\sigma} \sqrt{\frac{\pi}{B^3}} \left( \frac{kT}{\hbar c} \right)^3 \]
\[ Q_{rot} = \frac{1}{\sigma} \sqrt{\frac{\pi}{ABC}} \left( \frac{kT}{\hbar c} \right)^3 \]

\( \sigma \) – molecule-dependent symmetry factor

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \sigma )</th>
<th>Molecule Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO_2</td>
<td>2</td>
<td>Linear</td>
</tr>
<tr>
<td>NH_3</td>
<td>3</td>
<td>Symmetric Top</td>
</tr>
<tr>
<td>CH_4</td>
<td>12</td>
<td>Spherical Top</td>
</tr>
<tr>
<td>H_2O</td>
<td>2</td>
<td>Asymmetric Rotor</td>
</tr>
</tbody>
</table>
3. Rotational spectra of polyatomic molecules: Summary

- Linear (diatomic & polyatomic) and symmetric top molecules give similar (equal spacing) spectra at rigid rotor level
- High resolution needed to detect corrections / splittings
- Spectra $\rightarrow$ microscopic parameters ($r_e$, angles)
- Isotopes useful for spectral studies
4. Vibrational Bands, Rovibrational Spectra

1. Number of vibrational modes
2. Types of bands
   - Parallel and perpendicular
   - Fundamental, overtones, combination and difference bands
3. Relative strengths
4. Rovibrational spectra of polyatomic molecules
   - Linear molecules
   - Symmetric tops

Spectrum of bending mode of HCN
### 4.1. Number of vibrational modes

**N-atom molecule**

- **3N dynamical coordinates needed to specify instantaneous location and orientation**

<table>
<thead>
<tr>
<th></th>
<th>Linear molecules</th>
<th>Nonlinear molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Center of Mass:</strong></td>
<td>3 coordinates (3 translational modes)</td>
<td></td>
</tr>
<tr>
<td><strong>Rotation:</strong></td>
<td>2 angular coordinates (rot. modes)</td>
<td>3 angular coordinates (rot. modes)</td>
</tr>
<tr>
<td><strong>Vibration:</strong></td>
<td>3N-5 vibrational coordinates (vib. modes)</td>
<td>3N-6 angular coordinates (vib. modes)</td>
</tr>
</tbody>
</table>

**Total:** 3N
4.2. Types of bands

- Numbering (identification) convention of vibrational modes
  - Symmetry
  - Decreasing energy

\[ \nu_1, \nu_2, \ldots, \nu_i, \nu_{i+1}, \nu_{i+2}, \ldots \] [cm\(^{-1}\)]

Symmetric Declining frequency

- \( \nu_1 \) Highest-frequency symmetric vibrational mode
- \( \nu_2 \) 2\textsuperscript{nd} highest symmetric mode
- \( \ldots \) \( \ldots \)
- \( \nu_i \) Lowest-frequency symmetric mode

Asymmetric Declining frequency

- \( \nu_{i+1} \) Highest-frequency asymmetric vibrational mode
- \( \nu_{i+2} \) 2\textsuperscript{nd} highest symmetric mode
- \( \ldots \) \( \ldots \)

*Exception: the perpendicular vibration for linear \( XY_2 \) and \( XYZ \) molecules is always called \( \nu_2 \)*
# 4.2. Types of bands

- **Parallel and perpendicular modes**

## Examples:

|                  | Parallel (||)                                                      | Perpendicular (⊥)                                               |
|------------------|-------------------------------------------------------------------|-----------------------------------------------------------------|
|                  | Dipole changes are || to the main axis of symmetry                | Dipole changes are ⊥ to the main axis of symmetry                |
| **H₂O**          | ![Symmetric stretch](image1) ν₁=3652cm⁻¹                            | ![Asymmetric stretch](image2) ν₃=3756cm⁻¹                         |
| (3x3-6=3 vib. modes) | ![Symmetric bending](image3) ν₂=1595cm⁻¹                          | ![Not IR-active!](image4)                                        |
|                  | ![Symmetric stretch](image5) ν₁=1330cm⁻¹                           | ![Symmetric bending (2 degenerate)](image6) ν₂=667cm⁻¹          |
| **CO₂**          | No dipole moment                                                  | Asymmetric stretch ν₃=2349cm⁻¹                                  |
| (3x3-5=4 vib. modes) | ![Not IR-active!](image7)                                        | ![Symmetric bending (2 degenerate)](image8) ν₂=667cm⁻¹          |
4.2. Types of bands

Parallel and perpendicular modes

Symmetric molecules: vibrational modes are either IR-active or Raman-active (Chapter 6)

Vibrational modes of CO₂

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency [cm⁻¹]</th>
<th>Type</th>
<th>Description</th>
<th>IR</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₁</td>
<td>1388</td>
<td>--</td>
<td>Symmetric stretch</td>
<td>Not active</td>
<td>Active</td>
</tr>
<tr>
<td>ν₂</td>
<td>667</td>
<td>⊥</td>
<td>Symmetric bend (Degenerate)</td>
<td>Strong</td>
<td>Not active</td>
</tr>
<tr>
<td>ν₃</td>
<td>2349</td>
<td></td>
<td></td>
<td></td>
<td>Asymmetric stretch</td>
</tr>
</tbody>
</table>

Vibrational modes of HCN

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency [cm⁻¹]</th>
<th>Type</th>
<th>Description</th>
<th>IR</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₁</td>
<td>3310</td>
<td></td>
<td></td>
<td></td>
<td>Symmetric stretch</td>
</tr>
<tr>
<td>ν₂</td>
<td>715</td>
<td>⊥</td>
<td>Symmetric bend (Degenerate)</td>
<td>Very strong</td>
<td>Weak</td>
</tr>
<tr>
<td>ν₃</td>
<td>2097</td>
<td></td>
<td></td>
<td></td>
<td>Asymmetric stretch</td>
</tr>
</tbody>
</table>
4.2. Types of bands

- Terminology for different types of vibrational bands

**Fundamental Bands:** \( \nu_i \), the \( i \)th vibrational mode; \( \Delta \nu = \nu' - \nu'' = 1 \) for the \( i \)th mode

**1st Overtone:** \( 2\nu_i \); \( \Delta \nu = \nu' - \nu'' = 2 \) for the \( i \)th mode

**2nd Overtone:** \( 3\nu_i \); \( \Delta \nu = \nu' - \nu'' = 3 \) for the \( i \)th mode

**Combination bands:** Changes in multiple quantum numbers, e.g.,

\( \nu_1 + \nu_2 \); \( \Delta \nu_1 = \Delta \nu_2 = 1 \), i.e., \( \nu_1 \) and \( \nu_2 \) both increase by 1 for absorption or decrease by 1 for emission

\( 2\nu_1 + \nu_2 \); \( \Delta \nu_1 = 2 \) and \( \Delta \nu_2 = 1 \)

**Difference bands:** Quantum number changes with mixed sign

\( \nu_1 - \nu_2 \); \( \nu_{1,\text{final}} - \nu_{1,\text{initial}} = \pm 1 \) and \( \nu_{2,\text{final}} - \nu_{2,\text{initial}} = \mp 1 \), i.e., a unit increase in \( \nu_1 \) is accompanied by a unit decrease in \( \nu_2 \), and vice-versa.
4.2. Types of bands

- Vibrational partition function

\[ Q_{\text{vib}} = \prod_{i}^{\text{modes}} \left[ 1 - \exp \left( - \frac{\hbar c \omega_{e,i}}{kT} \right) \right]^{-g_{i}} \]

E.g., NH$_3$: 3N-6 = 6 vib. modes

\[ Q_{\text{vib}} = \left[ 1 - \exp \left( - \frac{\hbar c \omega_{e,1}}{kT} \right) \right]^{-1} \left[ 1 - \exp \left( - \frac{\hbar c \omega_{e,2}}{kT} \right) \right]^{-1} \left[ 1 - \exp \left( - \frac{\hbar c \omega_{e,3}}{kT} \right) \right]^{-2} \left[ 1 - \exp \left( - \frac{\hbar c \omega_{e,4}}{kT} \right) \right]^{-2} \]

<table>
<thead>
<tr>
<th>Vibration</th>
<th>Frequency [cm$^{-1}$]</th>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>3337</td>
<td>$\parallel$</td>
<td>Symmetric stretch</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>950</td>
<td>$\parallel$</td>
<td>Symmetric bend</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>3444</td>
<td>$\perp$</td>
<td>Asymmetric stretch (Degenerate)</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>1627</td>
<td>$\perp$</td>
<td>Asymmetric bend (Degenerate)</td>
</tr>
</tbody>
</table>
4.3. Relative strength

In general

- Fundamental bands are much stronger than combination, difference, and overtone bands

- Fairly harmonic molecules
  - E.g., CO
  - Relative strength between fundamental and overtones \( \sim 10^2 \)
  - Closely SHO, overtone bands are nearly forbidden (low transition probabilities)

- Highly anharmonic molecules
  - E.g., NH\(_3\)
  - Relative strength between fundamental and overtones \( \leq 10 \)
  - Overtone bands are less forbidden

Exception – Fermi resonance:
Accidental degeneracies (i.e., near resonances) can strengthen weak processes. Two vib. Modes strongly coupled by radiative and collisional exchanges.
E.g., \( 2\nu_2 \text{CO}_2 \,(\text{at } 1334\text{cm}^{-1}) \approx \nu_1,\text{CO}_2 \)
4.4. Rovibrational spectra of polyatomic molecules

- Linear polyatomic molecules
  (limit consideration to fundamental transitions)

  **Energy:** \( T(v_i, J) = G(v_i) + F(J) \)

- Case I: Parallel bands (*symmetric* and *asymmetric* stretch)

  **Selection Rule:**
  \[
  \Delta v_i = 1 \\
  \Delta J = \pm 1 \\
  \text{ (R and P branches)} \\
  \Delta v_j = 0, j \neq i
  \]

  **Absorption Spectrum:** P & R branches only

  **Example:** HCN\((v_1, v_3)\)

  **Note:** No \( v_1 \) parallel band for CO\(_2\)
4.4. Rovibrational spectra of polyatomic molecules

Linear polyatomic molecules

- Case I: Parallel band

Example-2: A parallel band of the linear molecule CO\textsubscript{2}
4.4. Rovibrational spectra of polyatomic molecules

- Linear polyatomic molecules
  (limit consideration to fundamental transitions)
  \[ T(v_i, J) = G(v_i) + F(J) \]

- Case II: Perpendicular bands

**Selection Rule:**
- \( \Delta v_i = 1 \)
- \( \Delta J = \pm 1, 0 \)
  - (R, P and Q branches)
- \( \Delta v_j = 0, j \neq i \)

1. If \( B' = B'' \), all Q branch lines occur at the same frequency
2. If \( B' \neq B'' \), \( Q(J'') = \omega_0 + (B' - B'') J'' (J''+1) \)
   Q branch “degrades” to lower frequencies (i.e., to the “red” in wavelength)
4.4. Rovibrational spectra of polyatomic molecules

- Linear polyatomic molecules
  - Case II: Perpendicular bands

Example:
Spectrum of the bending mode of HCN, showing the PQR structure

![Graph showing the spectrum of the bending mode of HCN, with labeled peaks and an impurity mark.](image)
4.4. Rovibrational spectra of polyatomic molecules

Symmetric top molecules (e.g., CH$_3$F, BCl$_3$)

Recall: K – quantum number for angular momentum around axis A

Energy: \( T(v_i, J, K) = G(v_i) + F(J, K) \)

\[
= (v_i + 1/2) \omega_e^i - \omega_e^i x_e^i (v_i + 1/2)^2 + BJ(J+1) + (A-B)K^2
\]

Case I: Parallel bands

**Selection Rule:**

\( \Delta v_i = 1 \)

\( \Delta J = \pm 1, 0 \) (\( P, Q, R \) branches)

\( \Delta K = 0 \)

1. \( 2J+1 \) values of \( K \) (\( K=J, J-1, \ldots, 0, \ldots, -J \))
2. Intensity of Q branch is a function of \( (I_A/I_B) \)
3. As \( (I_A/I_B) \to 0 \)
   - symmetric top \( \to \) linear molecule
   - strength of Q branch \( \to 0 \)
4.4. Rovibrational spectra of polyatomic molecules

Symmetric top molecules (e.g., CH₃F, BCl₃)

- Case I: Parallel bands

![Diagram of resolved components of a parallel band showing contributions from each of the K levels of the v=0 state](image)

Note:

1. Splitting in P and R branch due to a difference in (A-B) in upper and lower vib. levels
2. Splitting in Q branch due to difference in B in upper and lower vib. levels
3. For K=0, spectrum reduces to that of linear molecules, no Q branch
4. K cannot exceed J
4.4. Rovibrational spectra of polyatomic molecules

Symmetric top molecules

- Case I: Parallel bands

**Example-1:** A parallel absorption band of the symmetric top molecule CH₃Br. The P branch is partly resolved, while only the contours of the R and Q branches is obtained.
4.4. Rovibrational spectra of polyatomic molecules

- Symmetric top molecules
  - Case I: Parallel bands

Example-2: The parallel stretching vibration, centered at 1251 cm\(^{-1}\), of the symmetric top molecule CH\(_3\)I, showing the typical PQR contour.
4.4. Rovibrational spectra of polyatomic molecules

Symmetric top molecules (e.g., CH$_3$F, BCl$_3$)

Case II: Perpendicular bands

**Selection Rule:**
\[ \Delta v_i = 1 \]
\[ \Delta J = \pm 1, 0 \text{ (} P, Q, R \text{ branches)} \]
\[ \Delta K = \pm 1 \]

**R Branch:**
\[ \Delta J = +1, \Delta K = \pm 1 \]
\[ \bar{v}_R = \omega_o + 2B(J+1) + (A-B)(1 \pm 2K) \]

**P Branch:**
\[ \Delta J = -1, \Delta K = \pm 1 \]
\[ \bar{v}_P = \omega_o - 2BJ + (A-B)(1 \pm 2K) \]

**Q Branch:**
\[ \Delta J = 0, \Delta K = \pm 1 \]
\[ \bar{v}_Q = \omega_o + (A-B)(1 \pm 2K) \]

*Note: Two sets of R, P and Q branches for each lower state value of K*
4.4. Rovibrational spectra of polyatomic molecules

- Symmetric top molecules (e.g., CH$_3$F, BCl$_3$)
  - Case II: Perpendicular bands

Energy levels of a symmetric top molecule showing transitions that are allowed for a perpendicular band

Resulting spectrum, components of a perpendicular band showing the contributions from each K levels of the v=0 state
4.4. Rovibrational spectra of polyatomic molecules

Symmetric top molecules

- Case II: Perpendicular bands

Example: The Q-branch of a perpendicular band, for the symmetric top molecule CH$_3$Cl

Note: Spacing of the Q branch lines in a perpendicular band can be identified with 2(A-B), and hence are observable if A-B is large enough.
Next: Quantitative Emission/Absorption

- Spectral Absorptivity
- Eqn. of Radiative Transfer
- Einstein Coefficients/Theory
- Radiative Lifetime, Line Strength