Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

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: \[ \bar{\nu}_{J''+1 \leftrightarrow J''} = 2B(J''+1) - 4D(J''+1)^3 \]

Notes:

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

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

\[ \rightarrow \text{Even @ J}=60, \quad D/B \cdot J^2 \approx 0.01 \]

What about polyatomics (\( \geq 3 \) 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>$I_B = I_C \neq I_A; I_A \neq 0$</td>
<td>$I_A = I_B = I_C$</td>
<td>$I_A \neq I_B \neq I_C$</td>
</tr>
</tbody>
</table>

### Examples

- **CO$_2$**
- **NH$_3$**
- **CH$_4$**
- **H$_2$O**
- **C$_2$H$_2$** (Acetylene)
- **CH$_3$F**
- **BCl$_3$** (Boron trichloride)
- **OCS** (Carbon oxysulfide)
- **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)

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

Center of mass

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

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

- Symmetric tops

**Prolate**

$I_A < I_B = I_C$, $A > B = C$

E.g., $\text{CH}_3\text{F}$

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

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

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

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

- Symmetric tops

Oblate

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

E.g., BCl\(_3\) (Planar)

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

No elec. dipole mom. → no QM selection rule

Planar view
2. Classification of polyatomic molecules

- Spherical tops
  \[ I_A = I_B = I_C \]
  E.g., CH₄ (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., H₂O
  E. g., H₂O
  \[ 95.84\text{pm} \]
  \[ 104.45^\circ \]
  C.M.
  Complex and not addressed here
3. Rotational spectra of polyatomic molecules

- Linear molecules ($I_B=I_C; I_A\approx0$)
  - 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 $I$) $\rightarrow$ same spectrum

  $$F(J) = BJ(J + 1) - DJ^2(J + 1)^2$$
  $$\nu(J) = 2B(J + 1) - 4D(J + 1)^3$$

  Rotational const.  Centrifugal distortion const.

  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 $\rightarrow$ N-1 bond lengths to be found

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

Example: OCS (carbon oxy-sulfide)

Use 2 isotopes for 2 equations:

$$I_{^{16}O^{12}C^{32}S} = F(masses, r_{CO}, r_{CS})$$
$$I_{^{18}O^{12}C^{32}S} = F(masses, r_{CO}, r_{CS})$$

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

- Symmetric tops (I_B=I_C≠I_A; I_A≠0)
  - 2 main directions of rotation → 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
    - \( 2J+1 \) possibilities of \( K \) for each \( J \)

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

- Energy levels
  
  \[
  E_{J,K} = \frac{1}{2} \sum_i I_i \omega_i^2
  \]
  
  \[
  F(J, K) = BJ(J+1) + (A - B)K^2
  \]

  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
  \[
  \bar{v}_{J,K} = F(J+1,K) - F(J,K) = 2B(J+1) \left[ cm^{-1} \right]
  \]

- 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. $D_J$, $D_K$, $D_{JK}$

$$F(J, K) = BJ(J+1) + (A - B)K^2 - D_J J^2 (J+1)^2$$
$$- D_{JK} J(J+1) K^2 - D_K K^4$$
$$\tilde{v}_{J,K} = 2(J+1)\left[ B - 2D_J (J+1)^2 - D_{JK} K^2 \right] \text{[cm}^{-1} \text{]}$$

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 $J \approx 20$, $J^2 \approx 400$, $2DJ^2 \approx 1.6 \times 10^{-3}$, $2DJ^2/B \approx 0.2\%$

$J$ range

3 lines for $J=2$

$K=2,1,0$

$2B \approx 1.7 \text{cm}^{-1}$
3. Rotational spectra of polyatomic molecules

- Symmetric tops ($I_B = I_C \neq I_A; I_A \neq 0$) → gets complex fast!

**Prolate**

$I_A < I_B = I_C, A > B = C$

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

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

**Oblate**

$I_A > I_B = I_C, A < B = C$

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

\[
A - B = \frac{\hbar}{8\pi^2c} \left( \frac{1}{I_A} - \frac{1}{I_B} \right) < 0
\]
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; $I_A \approx 0$</td>
<td>B=C≠A; $I_A \neq 0$</td>
<td>A=B=C</td>
<td>A≠B≠C</td>
</tr>
</tbody>
</table>

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

$\sigma$ – molecule-dependent symmetry factor

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

<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$_2$O</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 → 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
1. Number of vibrational modes

- N-atom molecule

3N dynamical coordinates needed to specify instantaneous location and orientation

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

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

\[ \nu_1 \quad \text{Highest-frequency symmetric vibrational mode} \]
\[ \nu_2 \quad 2^{\text{nd}} \text{highest symmetric mode} \]
\[ \ldots \quad \ldots \]
\[ \nu_i \quad \text{Lowest-frequency symmetric mode} \]
\[ \nu_{i+1} \quad \text{Highest-frequency asymmetric vibrational mode} \]
\[ \nu_{i+2} \quad 2^{\text{nd}} \text{highest symmetric mode} \]
\[ \ldots \quad \ldots \]

\[ [\text{cm}^{-1}] \]

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 (⊥) |
|-----------|---------------|-------------------|
| H$_2$O (3x3-6=3 vib. modes) | Dipole changes are || to the main axis of symmetry | Dipole changes are ⊥ to the main axis of symmetry |
| CO$_2$ (3x3-5=4 vib. modes) | No dipole moment Not IR-active! Symmetric stretch $\nu_1=1330$cm$^{-1}$ | Asymmetric stretch $\nu_3=2349$cm$^{-1}$ |
| | Symmetric stretch $\nu_1=3652$cm$^{-1}$ | Asymmetric stretch $\nu_3=3756$cm$^{-1}$ |
| | Symmetric bending $\nu_2=1595$cm$^{-1}$ | Symmetric bending (2 degenerate) $\nu_2=667$cm$^{-1}$ |

Dipole changes are parallel (||) or perpendicular (⊥) to the main axis of symmetry.
4.2. Types of bands

- Parallel and perpendicular modes

Symmetric molecules: vibrational modes are either IR-active or Raman-active

Vibrational modes of \( \text{CO}_2 \):

<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>( \nu_1 )</td>
<td>1388</td>
<td>--</td>
<td>Symmetric stretch</td>
<td>Not active</td>
<td>Active</td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>667</td>
<td>( \perp )</td>
<td>Symmetric bend (Degenerate)</td>
<td>Strong</td>
<td>Not active</td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td>2349</td>
<td>( \parallel )</td>
<td>Asymmetric stretch</td>
<td>Very strong</td>
<td>Not active</td>
</tr>
</tbody>
</table>

Vibrational modes of \( \text{HCN} \):

<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>( \nu_1 )</td>
<td>3310</td>
<td>( \parallel )</td>
<td>Symmetric stretch</td>
<td>Strong</td>
<td>Weak</td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>715</td>
<td>( \perp )</td>
<td>Symmetric bend (Degenerate)</td>
<td>Very strong</td>
<td>Weak</td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td>2097</td>
<td>( \parallel )</td>
<td>Asymmetric stretch</td>
<td>Weak</td>
<td>Strong</td>
</tr>
</tbody>
</table>
4.2. Types of bands

- Terminology for different types of vibrational bands

**Fundamental Bands:** $v_i$, the $i^{th}$ vibrational mode; $\Delta v = v'-v"=1$ for the $i^{th}$ mode

**1st Overtone:** $2v_i$; $\Delta v = v'-v"=2$ for the $i^{th}$ mode

**2nd Overtone:** $3v_i$; $\Delta v = v'-v"=3$ for the $i^{th}$ mode

**Combination bands:** Changes in multiple quantum numbers, e.g., $v_1 + v_2$; $\Delta v_1 = \Delta v_2 = 1$, i.e., $v_1$ and $v_2$ both increase by 1 for absorption or decrease by 1 for emission
$2v_1 + v_2$; $\Delta v_1 = 2$ and $\Delta v_2 = 1$

**Difference bands:** Quantum number changes with mixed sign $v_1 - v_2$; $v_{1,\text{final}} - v_{1,\text{initial}} = \pm 1$ and $v_{2,\text{final}} - v_{2,\text{initial}} = \mp 1$, i.e., a unit increase in $v_1$ is accompanied by a unit decrease in $v_2$, 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., \( \text{NH}_3\): \(3N-6 = 6\) 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 vibrational modes strongly coupled by radiative and collisional exchanges.
E.g., $2\nu_2$ CO$_2$ (i.e. $2 \times 667 \text{ cm}^{-1} = 1334 \text{ cm}^{-1}$) $\approx \nu_1$, 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:** \( \Delta v_i = 1 \)
  \( \Delta J = \pm 1 \)
  \( (R \text{ and } P \text{ branches}) \)
  \( \Delta v_j = 0, j \neq i \)

  **Absorption Spectrum:** \( P & R \text{ branches only} \)

  **Example:** \( \text{HCN}(v_1, v_3) \)

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

Linear polyatomic molecules

- Case I: Parallel band

Example-2: A parallel band ($\nu_3$) of the linear molecule 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 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 $\nu_2$ bending mode of HCN, showing the PQR structure
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: $T(v_i, J, K) = G(v_i) + F(J, K)$

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

Case I: Parallel bands

Selection Rule: $\Delta v_i = 1$
$\Delta J = \pm 1, 0 (P, Q, R$ branches$)$
$\Delta K = 0$

1. 2$J+1$ 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 $(I_A/I_B) \rightarrow 0$
   symmetric top $\rightarrow$ linear molecule
   strength of Q branch $\rightarrow 0$
4.4. Rovibrational spectra of polyatomic molecules

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

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

Resolved components of a parallel band showing contributions from each of the K levels of the v=0 state
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 CH$_3$Br. 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., CH₃F, BCl₃)

Case II: Perpendicular bands

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

**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