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:** \( F(J), \text{cm}^{-1} = BJ(J+1) - D(J+1)^2 \)

Centrifugal distortion constant

**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 is small, i.e., \( D / B = 4 \left( B / \bar{\nu}_{vib} \right)^2 \ll 1 \)

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

→ Even @ J=60, \( D / B \cdot J^2 \approx 0.01 \)

**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 $I_A, I_B, I_C$</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>

<table>
<thead>
<tr>
<th>Examples</th>
<th>Relatively simple</th>
<th>No dipole moment</th>
<th>Not microwave active</th>
<th>Largest category</th>
<th>Most complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂H₂</td>
<td>Acetylene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCS</td>
<td>Carbon oxysulfide</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BCl₃</td>
<td></td>
<td></td>
<td>Boron trichloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*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)

![Diagram of OCS molecule with bond lengths and center of mass](image)

- Center of mass:
  
  \[ r_{CO} = 1.165\text{Å} \]
  \[ r_{CS} = 1.558\text{Å} \]

- \[ l_B = l_C; l_A \approx 0 \]

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

- Symmetric tops

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

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

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

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

Prolate

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

E.g., CH₃F

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

- Symmetric tops

### Oblate

- **$I_B = I_C \neq I_A; I_A \neq 0$**

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

- E.g., BCl$_3$ (Planar)

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

- No elec. dipole mom. → no QM selection rule
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
  - 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

  \[
  F(J) = B J (J + 1) - D J^2 (J + 1)^2
  \]

  \[
  \nu(J) = 2B(J + 1) - 4D(J + 1)^3
  \]

  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

  \[ \text{N atoms} \rightarrow \text{N-1 bond lengths to be found} \]

  - 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:

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

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

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 $A$): $J$, $J-1$, ..., 1, 0, -1, ..., -$J$
    - + & - allowed, w/o change in energy
      $\Rightarrow$ 2$J$+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
  $E_{J,K} = \frac{1}{2} \sum_i I_i \omega_i^2$
  $F(J, K) = BJ(J+1) + (A - B)K^2$

$\Rightarrow$ 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
    $$\tilde{v}_{J,K} = F(J+1,K) - F(J,K) = 2BJ(J+1) \left[ cm^{-1} \right]$$

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

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

\[ \bar{\nu}_{J,K} = 2(J+1) \left[ B - 2D_J (J+1)^2 - D_{JK} K^2 \right] \text{ cm}^{-1} \]

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 lines for $J=2$

$K=2,1,0$

2B \approx 1.7 \text{ cm}^{-1}$

$2D_{JK}(J+1)K^2 \approx 4 \times 10^{-4} \text{ cm}^{-1}$

$2D_{JK}(J+1)K^2 \approx 10^{-3} \text{ cm}^{-1}$
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**

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

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

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

**Oblate**

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

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

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

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; $I_A \approx 0$</td>
<td>B=C#A; $I_A \neq 0$</td>
<td>A=B=C</td>
<td>A#B#C</td>
</tr>
</tbody>
</table>

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

$\sigma$ – 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$_2$O</td>
<td>2</td>
<td>Asymmetric Rotor</td>
</tr>
</tbody>
</table>

A, $cm^{-1} = \frac{h}{8\pi^2 I_A c}$  
B, $cm^{-1} = \frac{h}{8\pi^2 I_B c}$  
C, $cm^{-1} = \frac{h}{8\pi^2 I_C c}$
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></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 vibrational coordinates (vib. modes)</td>
</tr>
</tbody>
</table>

**Total:** \(3N\)
4.2. Types of bands

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

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

<table>
<thead>
<tr>
<th>Symmetric Declining frequency</th>
<th>Asymmetric Declining frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_1 ) Highest-frequency symmetric vibrational mode</td>
<td>( \nu_1+1 ) Highest-frequency asymmetric vibrational mode</td>
</tr>
<tr>
<td>( \nu_2 ) 2\text{nd} highest symmetric mode</td>
<td>( \nu_1+2 ) 2\text{nd} highest symmetric mode</td>
</tr>
<tr>
<td>( \ldots ) ( \ldots )</td>
<td>( \ldots ) ( \ldots )</td>
</tr>
<tr>
<td>( \nu_i ) Lowest-frequency symmetric mode</td>
<td></td>
</tr>
</tbody>
</table>

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       |
| \( \text{H}_2\text{O} \) (3x3-6=3 vib. modes) | Symmetric stretch \( \nu_1=3652\text{cm}^{-1} \) | Asymmetric stretch \( \nu_3=3756\text{cm}^{-1} \) |
|                     | Symmetric bending \( \nu_2=1595\text{cm}^{-1} \)   | Symmetric bending (2 degenerate) \( \nu_2=667\text{cm}^{-1} \) |
| \( \text{CO}_2 \) (3x3-5=4 vib. modes)       | No dipole moment Not IR-active! Symmetric stretch \( \nu_1=1330\text{cm}^{-1} \) | Asymmetric stretch \( \nu_3=2349\text{cm}^{-1} \) |
### 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 $[\text{cm}^{-1}]$</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 HCN

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency $[\text{cm}^{-1}]$</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:** \( \nu_i \), 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., \( \text{NH}_3 \): \( 3N-6 = 6 \) 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 vib. Modes strongly coupled by radiative and collisional exchanges.
E.g., \( 2\nu_2 \) CO\(_2\) (@ 1334 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:**
  \[ \Delta v_i = 1 \]
  \[ \Delta J = \pm 1 \]
  \( (R \text{ and } P \text{ branches}) \)
  \[ \Delta v_j = 0, j \neq i \]

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

  **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 $\text{CO}_2$

$\nu = 1$

Anti-symmetric
Stretches
Vibration

$\nu = 0$

Per cent Transmission

$\nu (cm^{-1})$

$\bar{\nu}$
4.4. Rovibrational spectra of polyatomic molecules

- Linear polyatomic molecules
  (limit consideration to fundamental transitions)
  **Energy:** \( T(v, J) = G(v) + F(J) \)

- 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)

![Diagram of rovibrational spectra](image)
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
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: $T(v_i, J, K) = G(v_i) + F(J, K) = (v_i + 1/2)\omega_e^i - \omega_e x_e^i (v_i + 1/2)^2 + BJ(J + 1) + (A - B)K^2$

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 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., CH₃F, BCl₃)

Case II: Perpendicular bands

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

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., CH₃F, BCl₃)
  - 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

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.

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

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