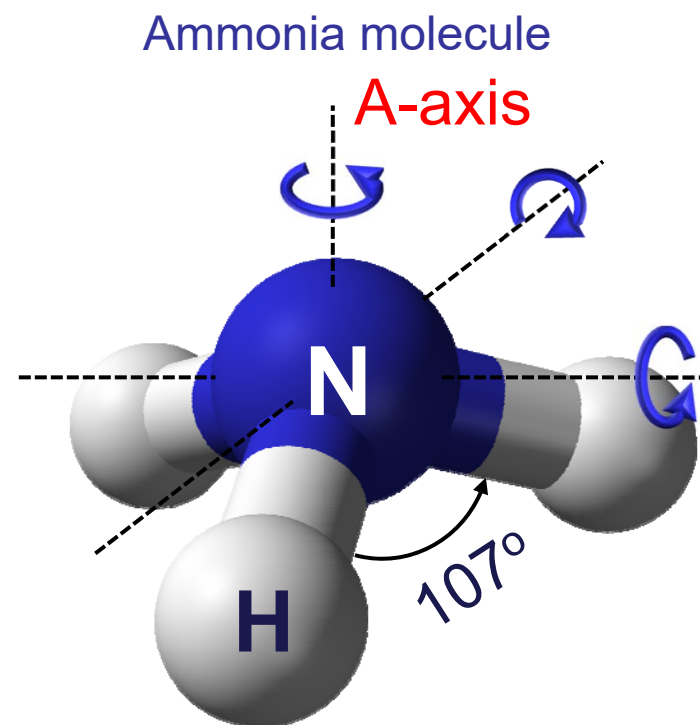


# Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

## 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:  $F(J), cm^{-1} = \underbrace{BJ(J+1)}_{R.R.} - DJ^2(J+1)^2$  ↗ Centrifugal distortion constant

Rotational constant:  $B, cm^{-1} = \frac{h}{8\pi^2 I_c}$

Selection Rule:  $J' = J'' + 1 \rightarrow \Delta J = +1$

Line position:  $\bar{\nu}_{J''+1 \leftarrow J''} = 2B(J''+1) - 4D(J''+1)^3$

✎ Notes:

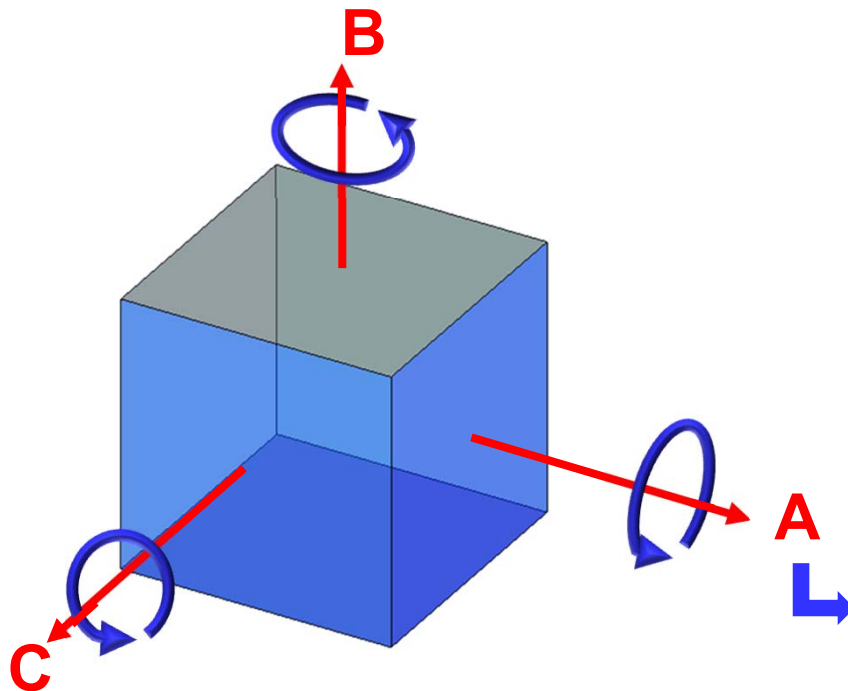
1. D is small, i.e.,  $D/B = 4(B/\bar{\nu}_{vib})^2 \ll 1$
2. E.g., for NO,  $\left(\frac{D}{B}\right)_{NO} = 4\left(\frac{B}{\omega_e}\right)^2 \approx 4\left(\frac{1.7}{1900}\right)^2 \approx 3 \times 10^{-6}$

→ Even @ J=60,  $D/B \cdot J^2 \sim 0.01$

*What about polyatomics ( $\geq 3$  atoms)?*

# 1. From diatomic to polyatomic

- 3D-body rotation

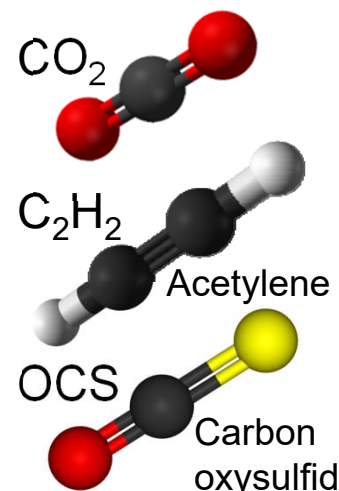
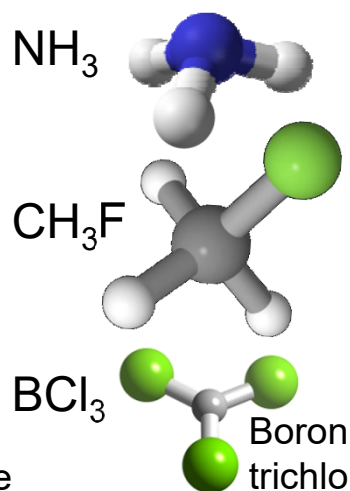
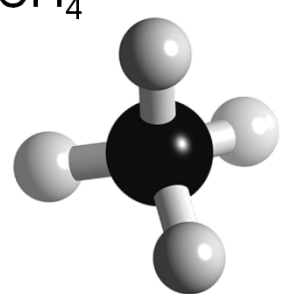
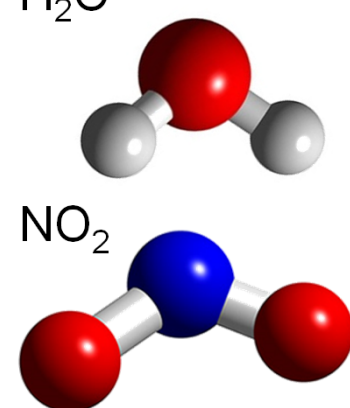


- Convention:  
A-axis is the “unique” or “figure” axis, along which lies the molecule’s defining symmetry

- 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  $I_A$ ,  $I_B$ ,  $I_C$

## 2. Classification of polyatomic molecules

### Types of molecules

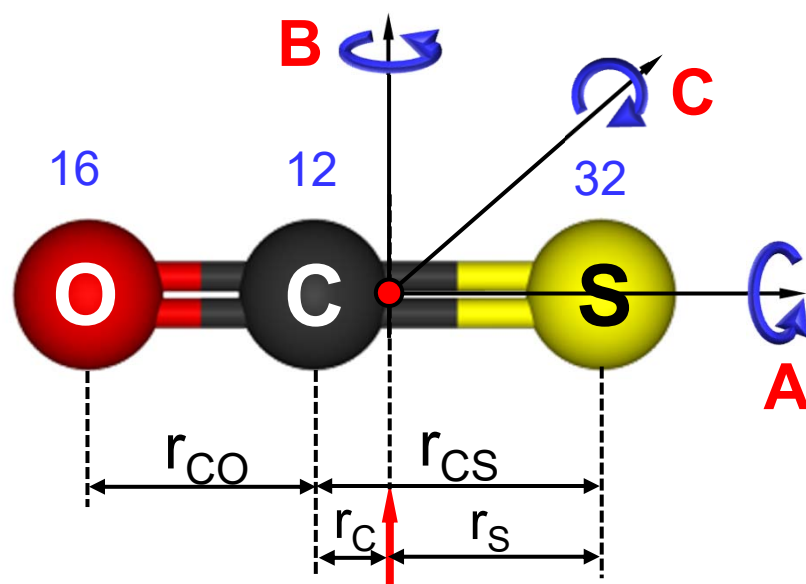
Type	Linear Molecules	Symmetric Tops	Spherical Tops	Asymmetric Rotors
Relative magnitudes of $I_{A,B,C}$	$I_B = I_C; I_A \approx 0^*$	$I_B = I_C \neq I_A$ $I_A \neq 0$	$I_A = I_B = I_C$	$I_A \neq I_B \neq I_C$
Examples	 <p>CO<sub>2</sub></p> <p>C<sub>2</sub>H<sub>2</sub> Acetylene</p> <p>OCS Carbon oxysulfide</p>	 <p>NH<sub>3</sub></p> <p>CH<sub>3</sub>F</p> <p>BCl<sub>3</sub> Boron trichloride</p>	 <p>CH<sub>4</sub></p>	 <p>H<sub>2</sub>O</p> <p>NO<sub>2</sub></p>
	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

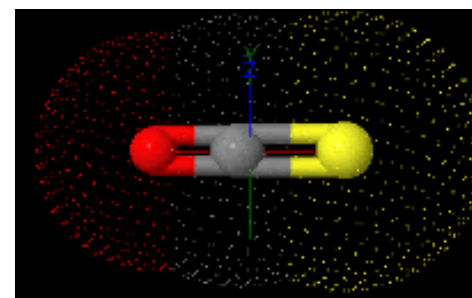
$$r_{CO} = 1.165 \text{ \AA}$$

$$r_{CS} = 1.558 \text{ \AA}$$

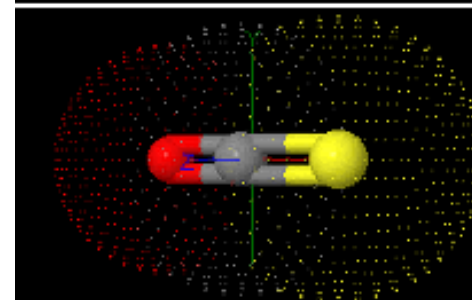
$$I_B = I_C; I_A \approx 0$$

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

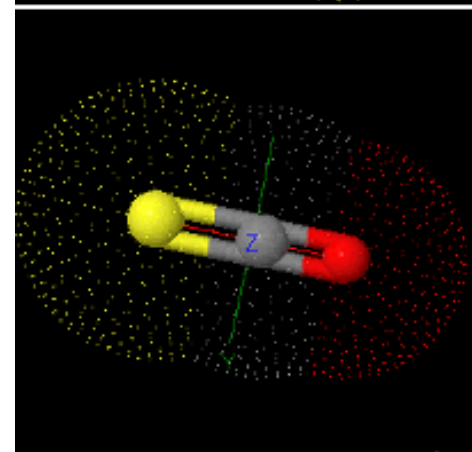
A



B



C



## 2. Classification of polyatomic molecules

- Symmetric tops

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

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

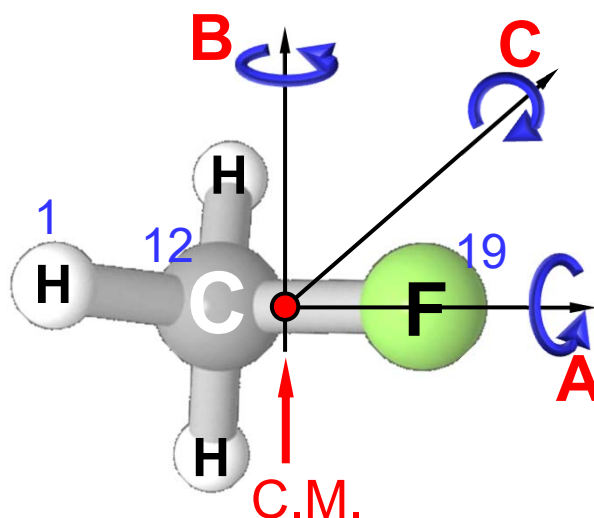
$$B, \text{cm}^{-1} = \frac{h}{8\pi^2 I_B c}$$

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

### Prolate

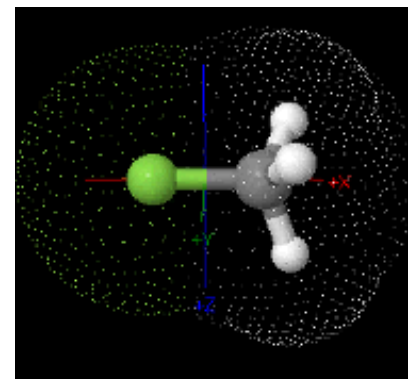
$$I_A < I_B = I_C, A > B = C$$

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

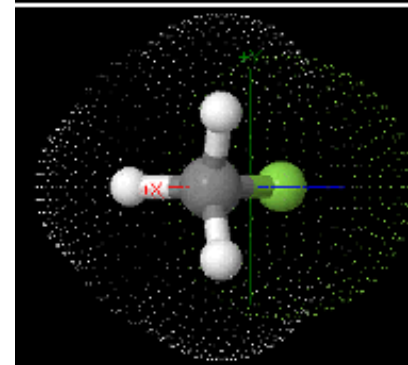


Tripod-like (tetrahedral bonding)

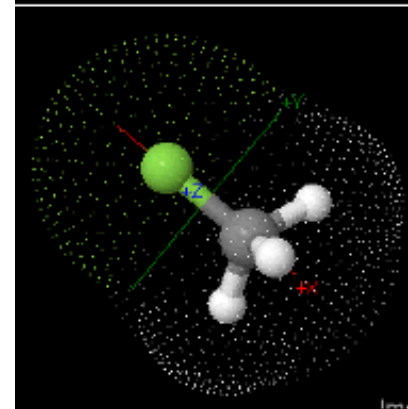
**A**



**B**



**C**



## 2. Classification of polyatomic molecules

### Symmetric tops

#### Oblate

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

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

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

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

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

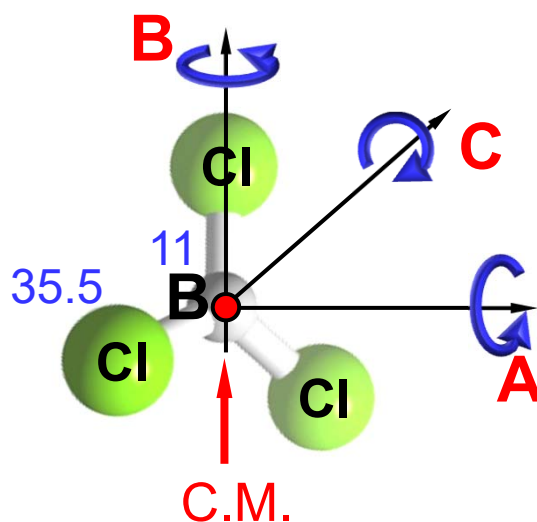
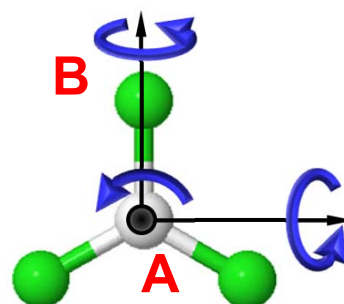
$$C, \text{cm}^{-1} = \frac{h}{8\pi^2 I_C c}$$

No elec.  
dipole mom.  
→ no QM  
selection rule

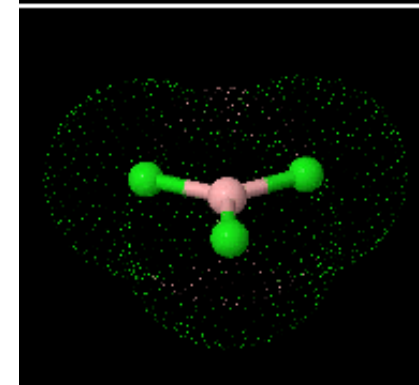
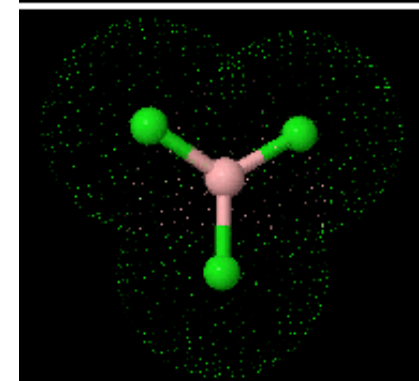
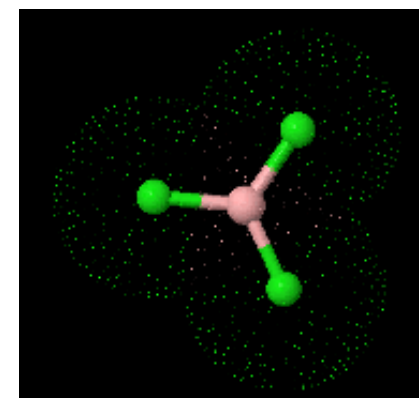
**A**

**B**

**C**



Planar view

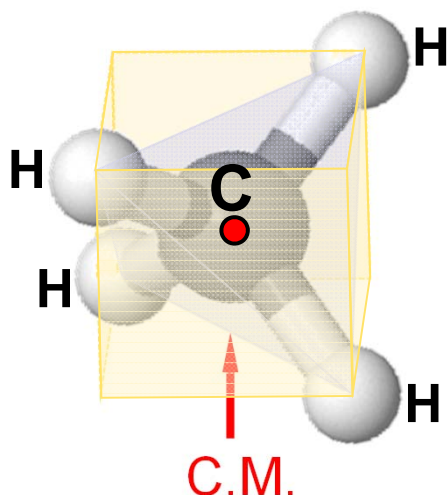


## 2. Classification of polyatomic molecules


- Spherical tops

$$I_A = I_B = I_C$$

E.g., CH<sub>4</sub> (methane)



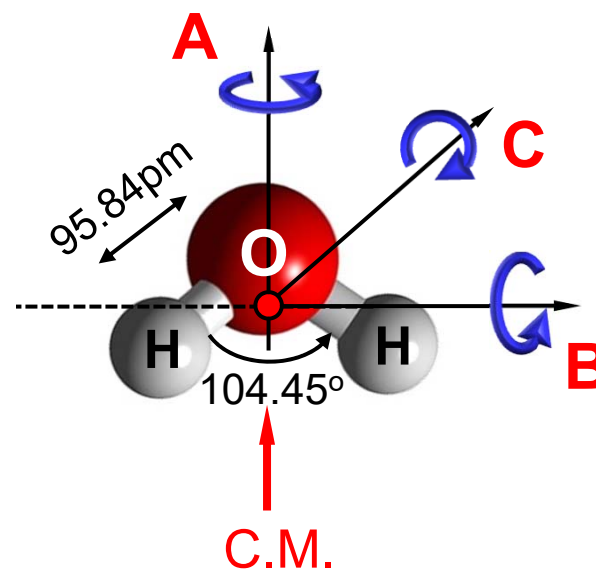
Cube w/ C at center  
and H at diagonal  
corners

 Symmetric, but  
No dipole moment  
↓  
No rotational  
spectrum

- Asymmetric rotors

$$I_A \neq I_B \neq I_C$$

E.g., H<sub>2</sub>O



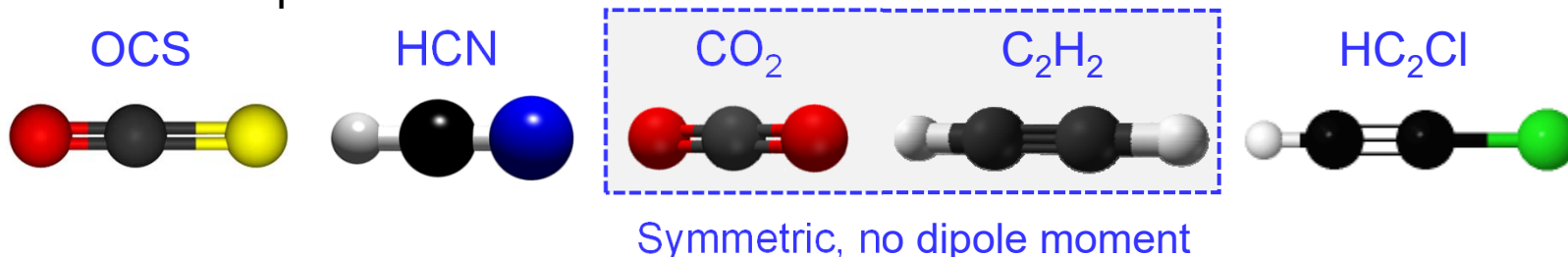
 Complex and not  
addressed here



### 3. Rotational spectra of polyatomic molecules

- Linear molecules ( $I_B = I_C$ ;  $I_A \approx 0$ )

- Examples



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

$$F(J) = BJ(J+1) - DJ^2(J+1)^2$$

$$\bar{\nu}(J) = 2B(J+1) - 4D(J+1)^3$$

↑  
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

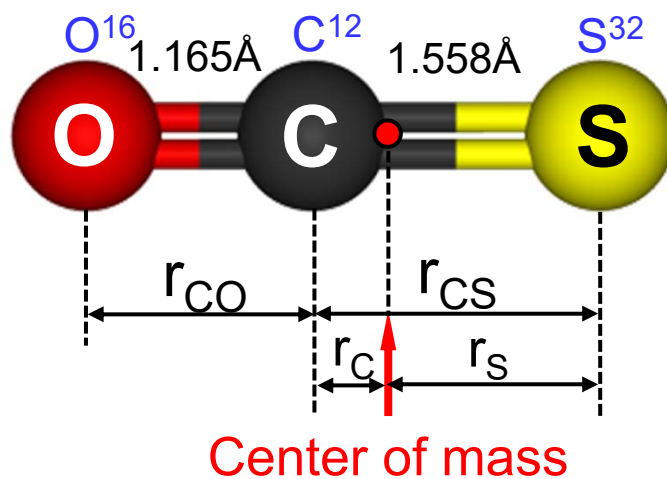
- Linear molecules ( $I_B = I_C$ ;  $I_A \approx 0$ )

- 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:

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

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



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 → 2 quantum numbers

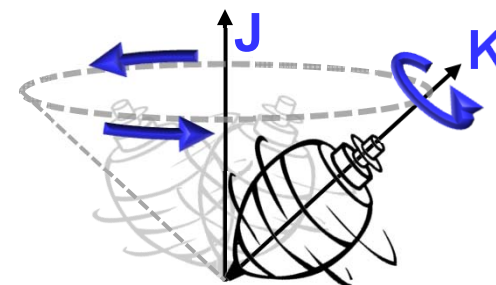
- **J** (total angular momentum): 0, 1, 2, ...
- **K** (angular momentum about A): J, J-1, ..., 1, 0, -1, ... -J
- + & - allowed, w/o change in energy

→ 2J+1 possibilities of K for each J

- Quantized angular momentum

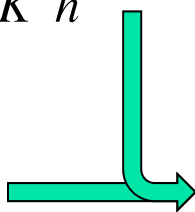
As before:  $I_A^2 \omega_A^2 + I_B^2 \omega_B^2 + I_C^2 \omega_C^2 = J(J+1)\hbar^2$

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

$$\bar{\nu}_{J,K} = F(J+1, K) - F(J, K) = 2B (J+1) \text{ [cm}^{-1}\text{]}$$



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



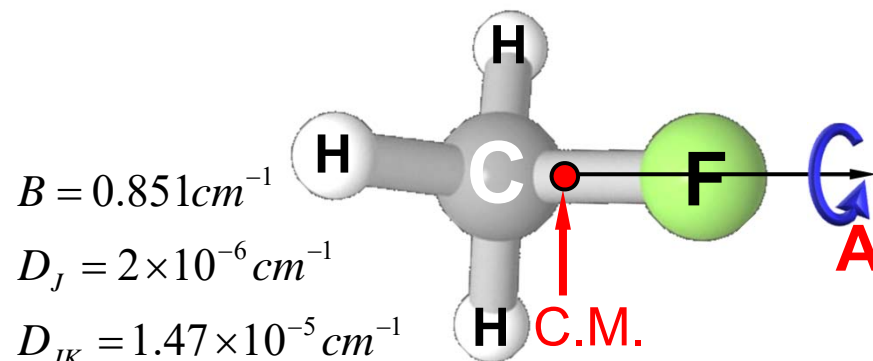
Centrifugal distortion const.  $D_J$ ,  $D_K$ ,  $D_{JK}$

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

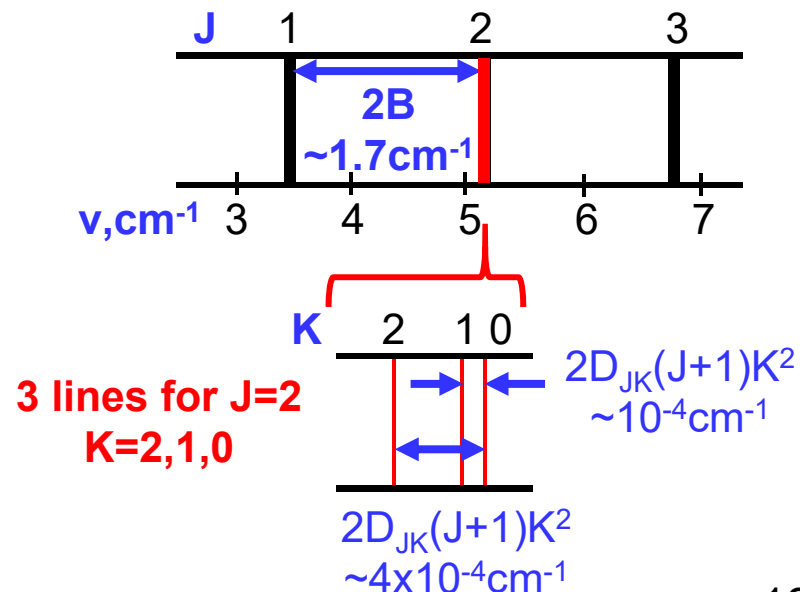
$$\bar{\nu}_{J,K} = 2(J+1) \left[ B - 2D_J(J+1)^2 - D_{JK}K^2 \right] \text{ [cm}^{-1}\text{]}$$

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

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



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



### 3. Rotational spectra of polyatomic molecules

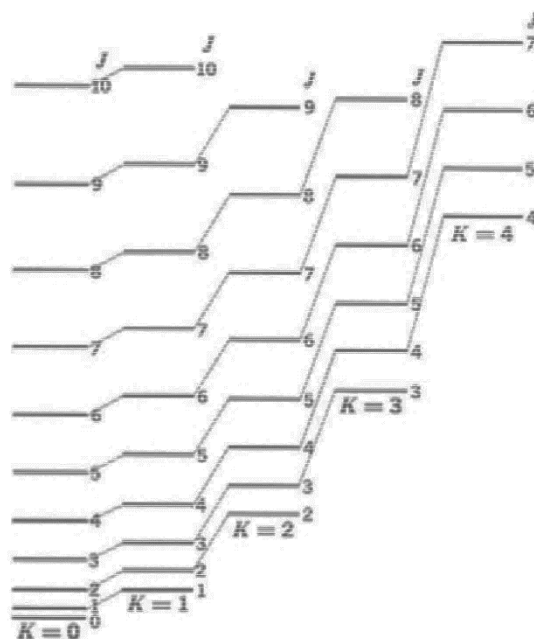
- Symmetric tops ( $I_B = I_C \neq I_A$ ;  $I_A \neq 0$ )  $\rightarrow$  gets complex fast!

#### Prolate

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

$$F(J, K) = BJ(J+1) + (A-B)K^2$$

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



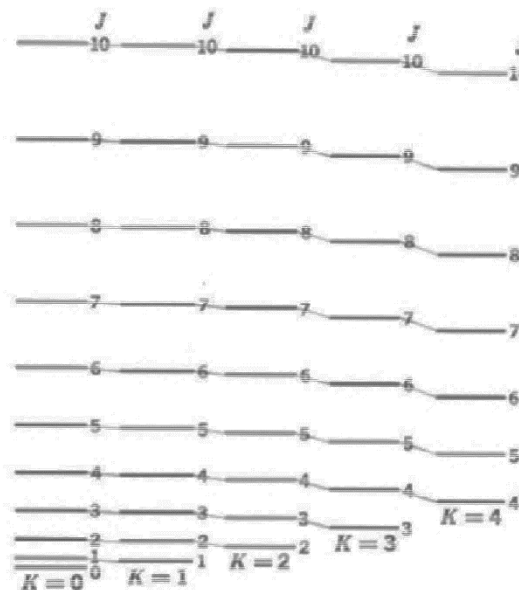
Example  
energy levels

#### Oblate

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

$$F(J, K) = BJ(J+1) + (A-B)K^2$$

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



### 3. Rotational spectra of polyatomic molecules

- Rotational partition function

Linear	Symmetric top	Spherical top	Asymmetric rotor
$B=C; I_A \approx 0$	$B=C \neq A; I_A \neq 0$	$A=B=C$	$A \neq B \neq C$
$Q_{rot} = \frac{kT}{\sigma hcB}$	$Q_{rot} = \frac{1}{\sigma} \sqrt{\frac{\pi}{AB^2} \left( \frac{kT}{hc} \right)^3}$	$Q_{rot} = \frac{1}{\sigma} \sqrt{\frac{\pi}{B^3} \left( \frac{kT}{hc} \right)^3}$	$Q_{rot} = \frac{1}{\sigma} \sqrt{\frac{\pi}{ABC} \left( \frac{kT}{hc} \right)^3}$

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

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

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

$\sigma$  – molecule-dependent symmetry factor

Molecule	$\sigma$	Molecule Type
CO <sub>2</sub>	2	Linear
NH <sub>3</sub>	3	Symmetric Top
CH <sub>4</sub>	12	Spherical Top
H <sub>2</sub> O	2	Asymmetric Rotor



### 3. Rotational spectra of polyatomic molecules: Summary

---

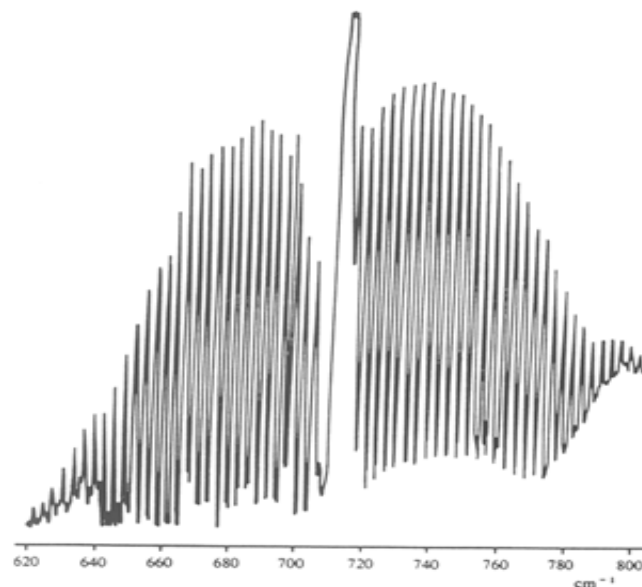
- Linear (diatomic & polyatomic) and symmetric top molecules give similar (equal spacing) spectra at rigid rotor level
- High resolution needed to detect corrections / splittings
- Spectra  $\rightarrow$  microscopic parameters ( $r_e$ , angles)
- Isotopes useful for spectral studies



## 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





# 1. Number of vibrational modes

- N-atom molecule

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

Total: **3N**

Center of Mass: **3** coordinates (3 translational modes)

Rotation:

Linear molecules  
**2** angular coordinates  
(rot. modes)

Nonlinear molecules  
**3** angular coordinates  
(rot. modes)

Vibration:

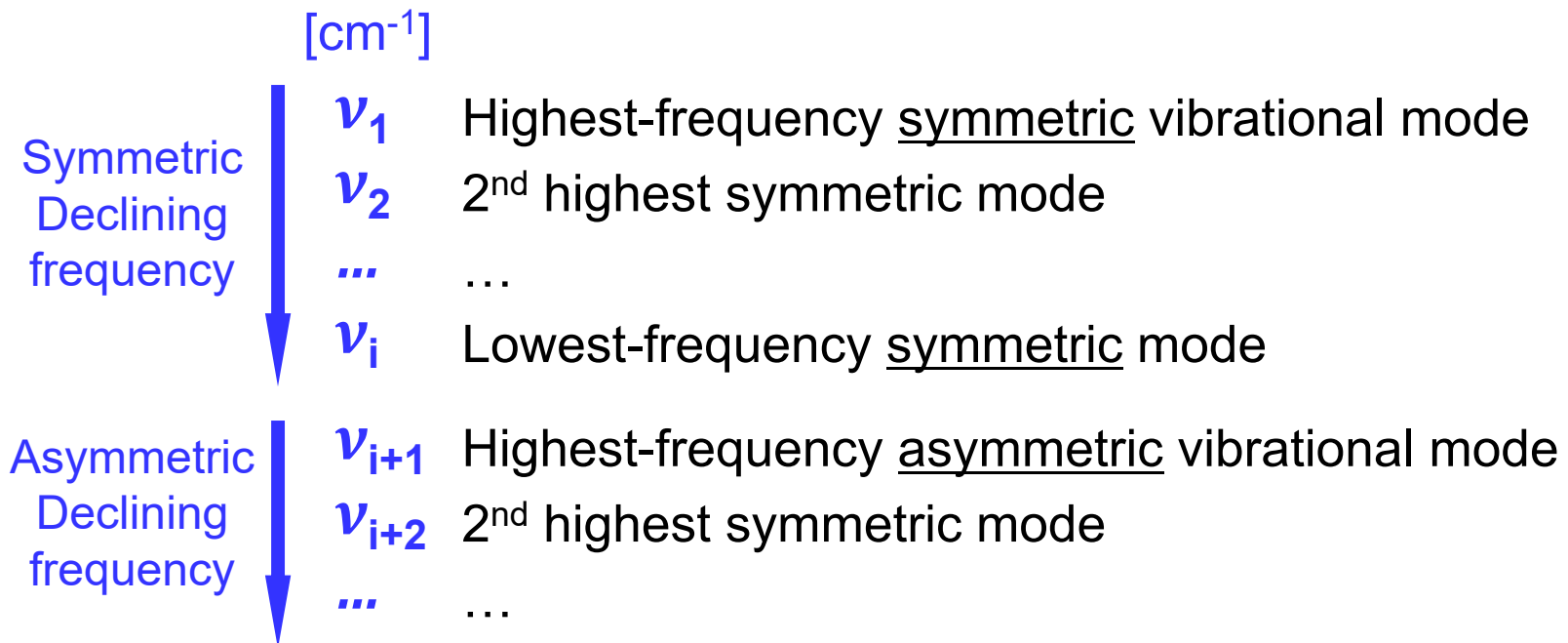
Linear molecules  
**3N-5** vibrational coordinates  
(vib. modes)

Nonlinear molecules  
**3N-6** vibrational coordinates  
(vib. modes)



## 4.2. Types of bands

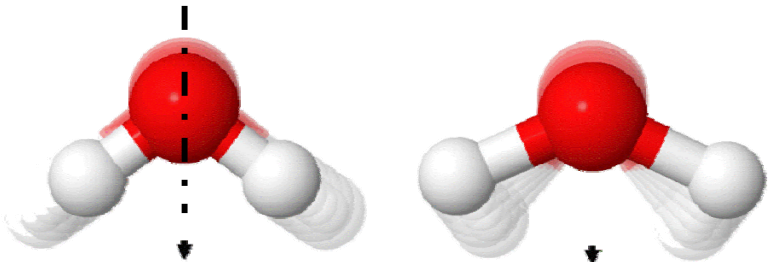
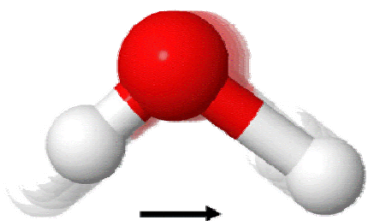
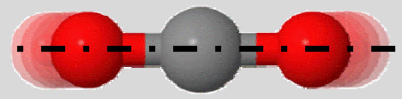
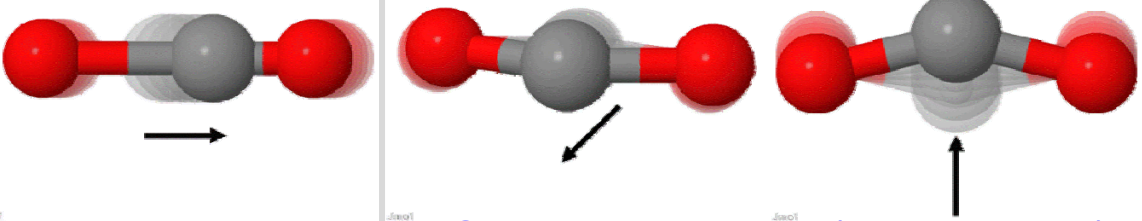
- Numbering (identification) convention of vibrational modes
  - Symmetry
  - Decreasing energy



Exception: the perpendicular vibration for linear XY<sub>2</sub> and XYZ molecules is always called  $\nu_2$

## 4.2. Types of bands

- Parallel and perpendicular modes

Examples:	<b>Parallel (<math>\parallel</math>)</b> Dipole changes are $\parallel$ to the main axis of symmetry	<b>Perpendicular (<math>\perp</math>)</b> Dipole changes are $\perp$ to the main axis of symmetry
$\text{H}_2\text{O}$ $(3 \times 3 - 6 = 3)$ vib. modes)	 <p>Symmetric stretch <math>\nu_1 = 3652 \text{ cm}^{-1}</math></p> <p>Symmetric bending <math>\nu_2 = 1595 \text{ cm}^{-1}</math></p>	 <p>Asymmetric stretch <math>\nu_3 = 3756 \text{ cm}^{-1}</math></p>
$\text{CO}_2$ $(3 \times 3 - 5 = 4)$ vib. modes)	 <p>No dipole moment Not IR-active! Symmetric stretch <math>\nu_1 = 1330 \text{ cm}^{-1}</math></p>	 <p>Asymmetric stretch <math>\nu_3 = 2349 \text{ cm}^{-1}</math></p> <p>Symmetric bending (2 degenerate) <math>\nu_2 = 667 \text{ cm}^{-1}</math></p>



## 4.2. Types of bands

- Parallel and perpendicular modes

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

Vibrational modes of CO<sub>2</sub>

Mode	Frequency [cm <sup>-1</sup> ]	Type	Description	IR	Raman
$\nu_1$	1388	--	Symmetric stretch	Not active	Active
$\nu_2$	667	$\perp$	Symmetric bend (Degenerate)	Strong	Not active
$\nu_3$	2349		Asymmetric stretch	Very strong	Not active

Vibrational modes of HCN

Mode	Frequency [cm <sup>-1</sup> ]	Type	Description	IR	Raman
$\nu_1$	3310		Symmetric stretch	Strong	Weak
$\nu_2$	715	$\perp$	Symmetric bend (Degenerate)	Very strong	Weak
$\nu_3$	2097		Asymmetric stretch	Weak	Strong



## 4.2. Types of bands

- Terminology for different types of vibrational bands

Fundamental Bands:  $\nu_i$ , the  $i^{\text{th}}$  vibrational mode;  $\Delta\nu = \nu' - \nu'' = 1$  for the  $i^{\text{th}}$  mode

1<sup>st</sup> Overtone:  $2\nu_i$ ;  $\Delta\nu = \nu' - \nu'' = 2$  for the  $i^{\text{th}}$  mode

2<sup>nd</sup> Overtone:  $3\nu_i$ ;  $\Delta\nu = \nu' - \nu'' = 3$  for the  $i^{\text{th}}$  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

$$Q_{vib} = \prod_i^{\text{modes}} \left[ 1 - \exp\left(-\frac{hc\omega_{e,i}}{kT}\right) \right]^{-g_i}$$

E.g.,  $\text{NH}_3$ :  $3N-6 = 6$  vib. modes

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

Degenerate

Vibration	Frequency [cm <sup>-1</sup> ]	Type	Description
$\nu_1$	3337		Symmetric stretch
$\nu_2$	950		Symmetric bend
$\nu_3$	3444	⊥	Asymmetric stretch (Degenerate)
$\nu_4$	1627	⊥	Asymmetric bend (Degenerate)



## 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.,  $\text{NH}_3$
  - 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.,  $2\nu_2 \text{ CO}_2$  (i.e.  $2 \times 667 \text{ cm}^{-1} = 1334 \text{ cm}^{-1}$ )  $\approx \nu_1, \text{ CO}_2$



## 4.4. Rovibrational spectra of polyatomic molecules

- Linear polyatomic molecules

(limit consideration to fundamental transitions)

Energy:  $T(\nu_i, J) = G(\nu_i) + F(J)$

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

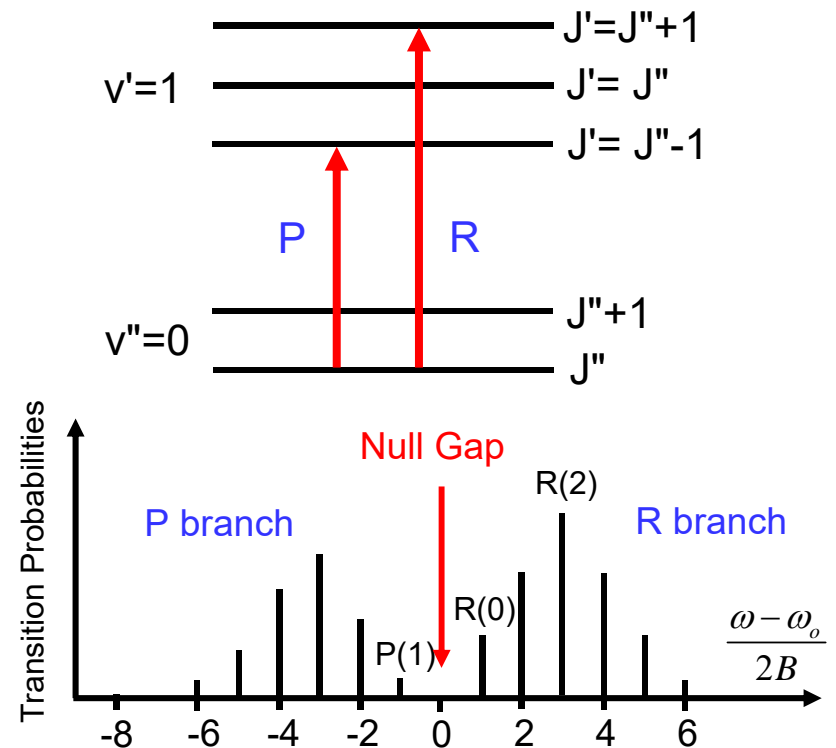
Selection Rule:  $\Delta \nu_i = 1$   
 $\Delta J = \pm 1$   
 (*R* and *P* branches)  
 $\Delta \nu_j = 0, j \neq i$

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

Example:  $\text{HCN}(\nu_1, \nu_3)$



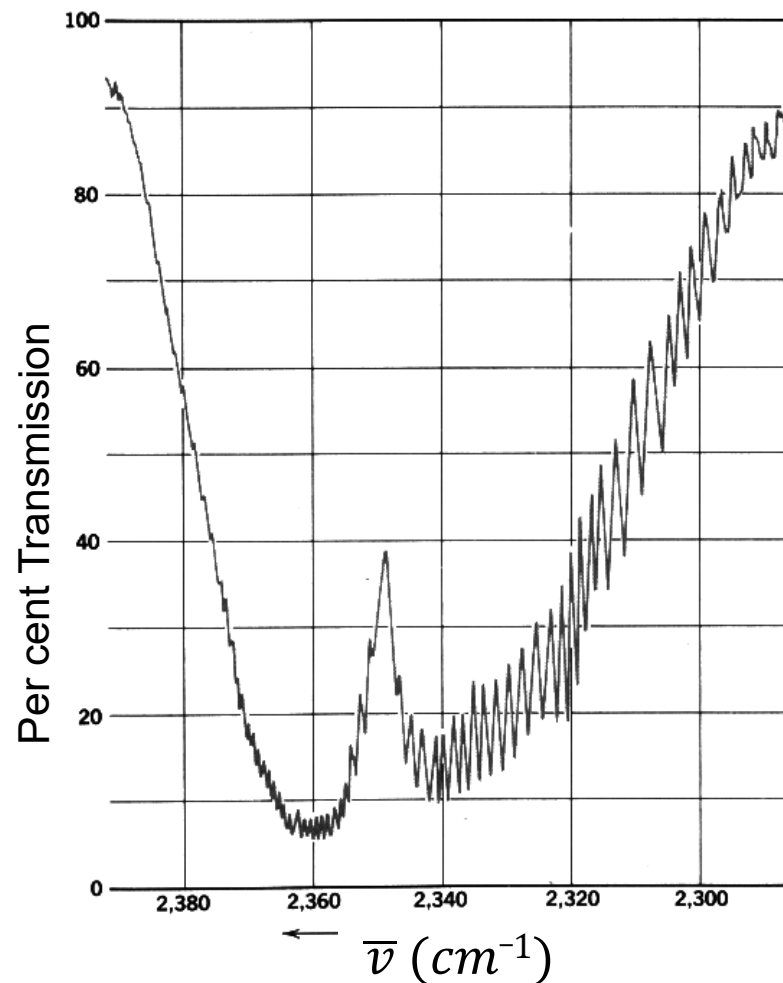
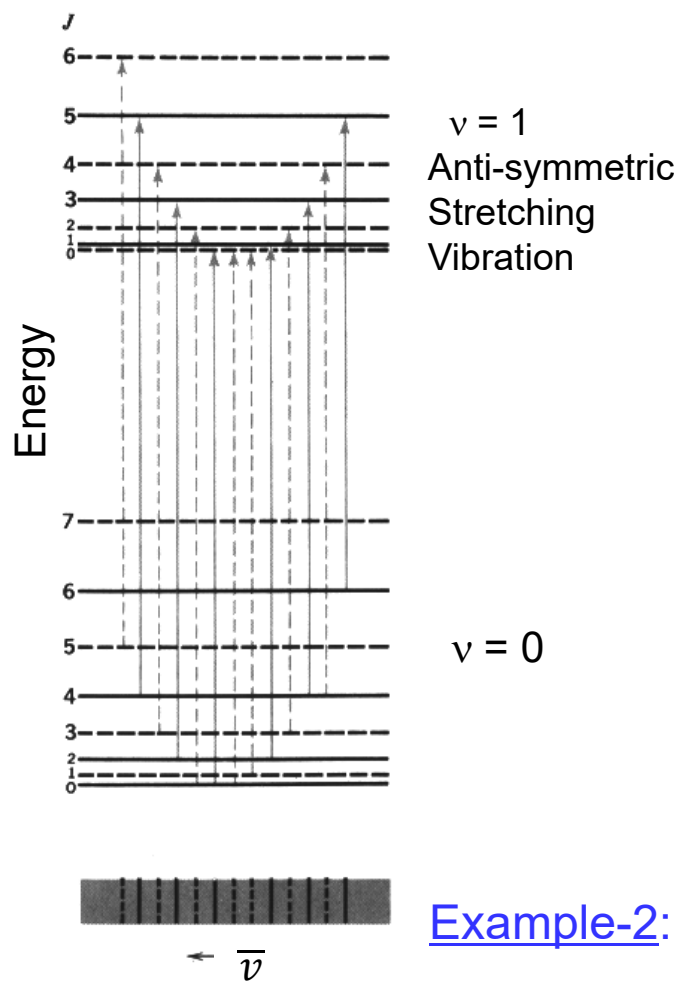
Note: No  $\nu_1$  parallel band for  $\text{CO}_2$



## 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

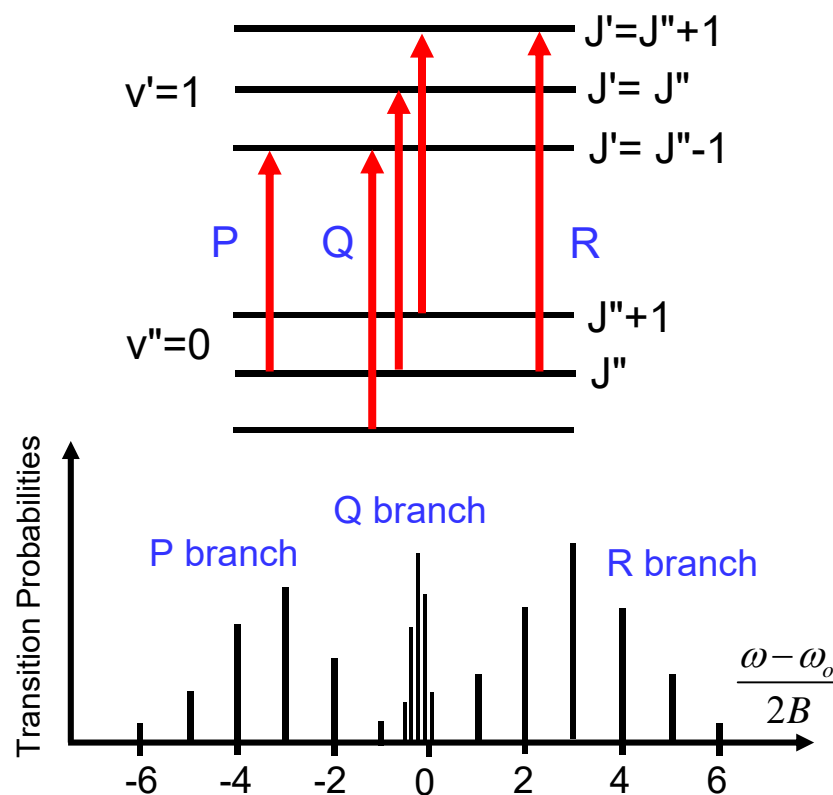
Selection Rule:  $\Delta v_i = 1$

$$\Delta J = \pm 1, 0$$

(R, P and Q branches)

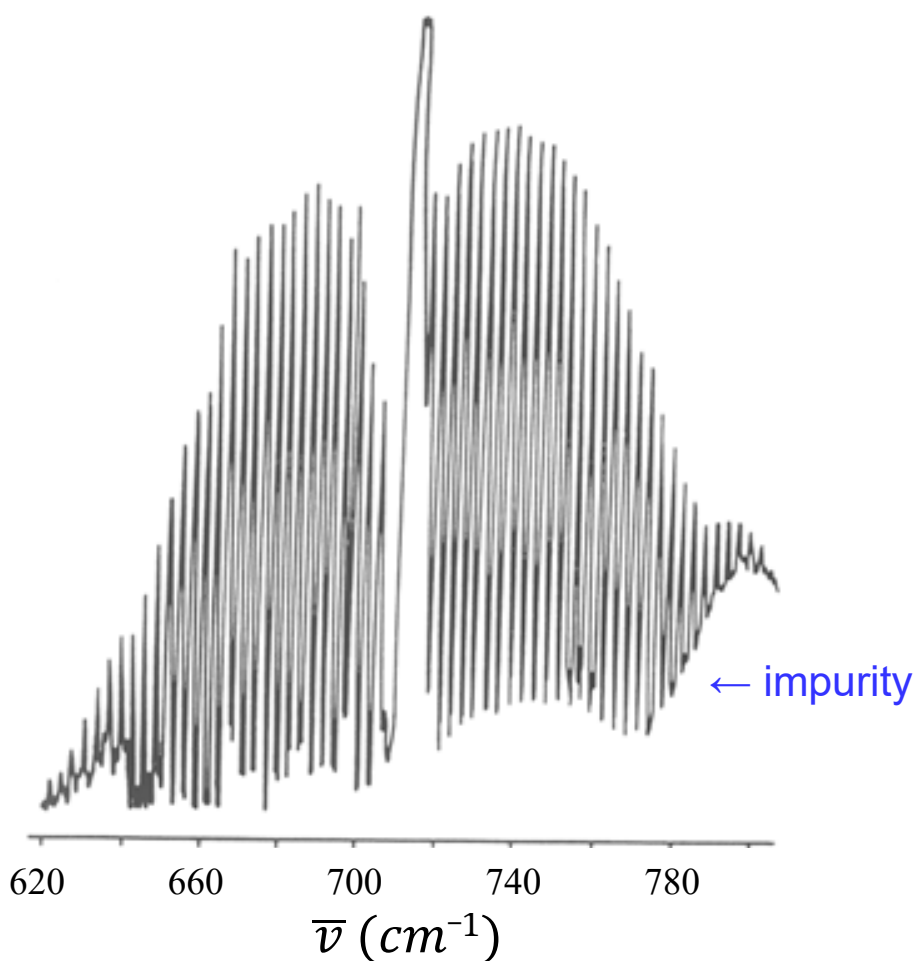
$$\Delta v_j = 0, j \neq i$$

1. If  $B' = B''$ , all Q branch lines occur at the same frequency
2. If  $B' \neq B''$ ,  $Q(J'') = \omega_0 + \overbrace{(B' - B'')}^{-\alpha < 0} J''(J'' + 1)$   
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

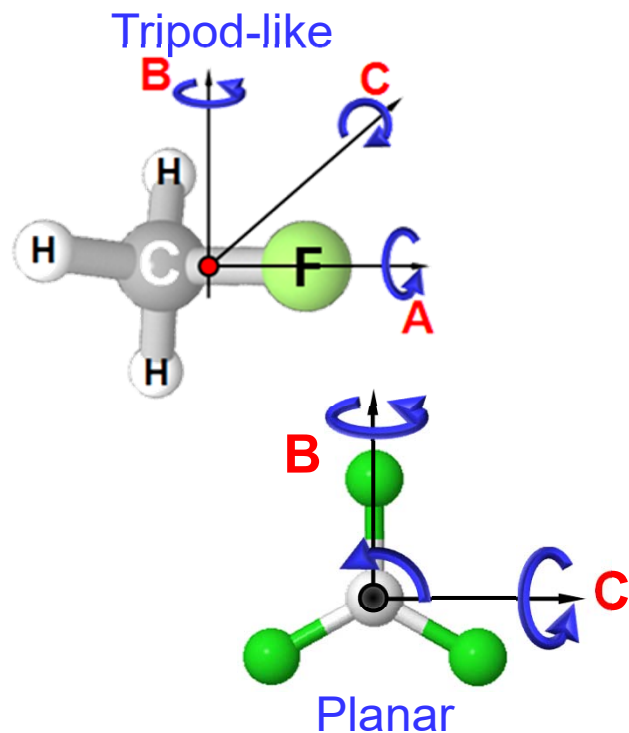
- Symmetric top molecules (e.g.,  $\text{CH}_3\text{F}$ ,  $\text{BCl}_3$ )

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:  $\Delta v_i = 1$

$$\Delta J = \pm 1, 0 \text{ (P, Q, R branches)}$$

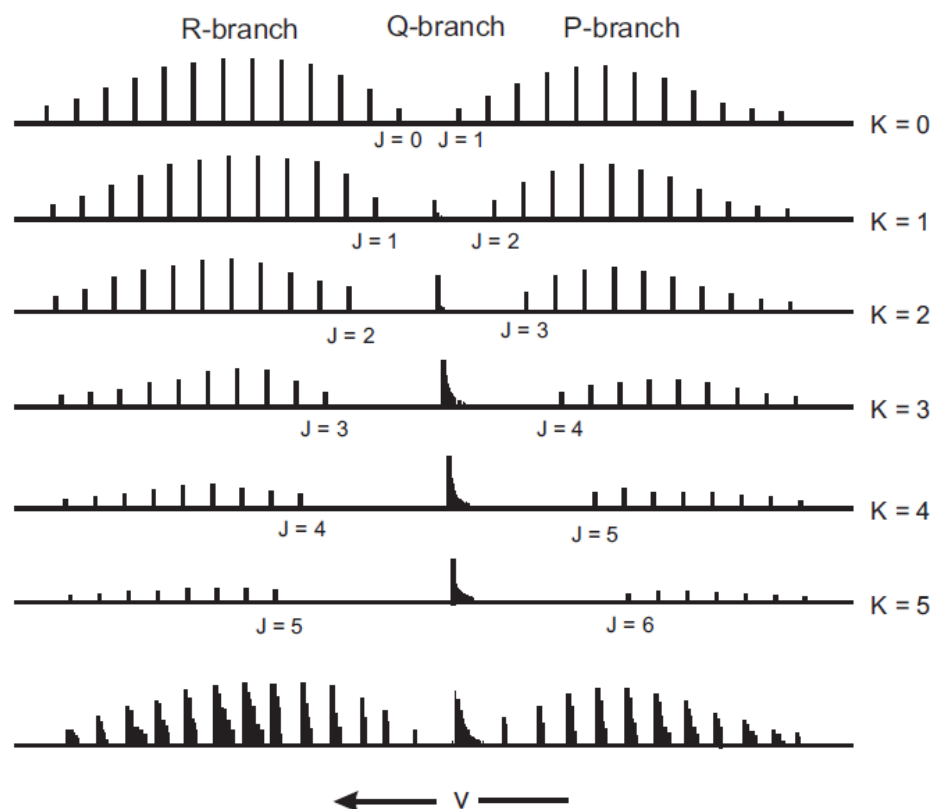
$$\Delta K = 0$$

1.  $2J+1$  values of  $K$  ( $K=J, J-1, \dots, 0, \dots, -J$ )
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.,  $\text{CH}_3\text{F}$ ,  $\text{BCl}_3$ )

- Case I: Parallel bands



Note:

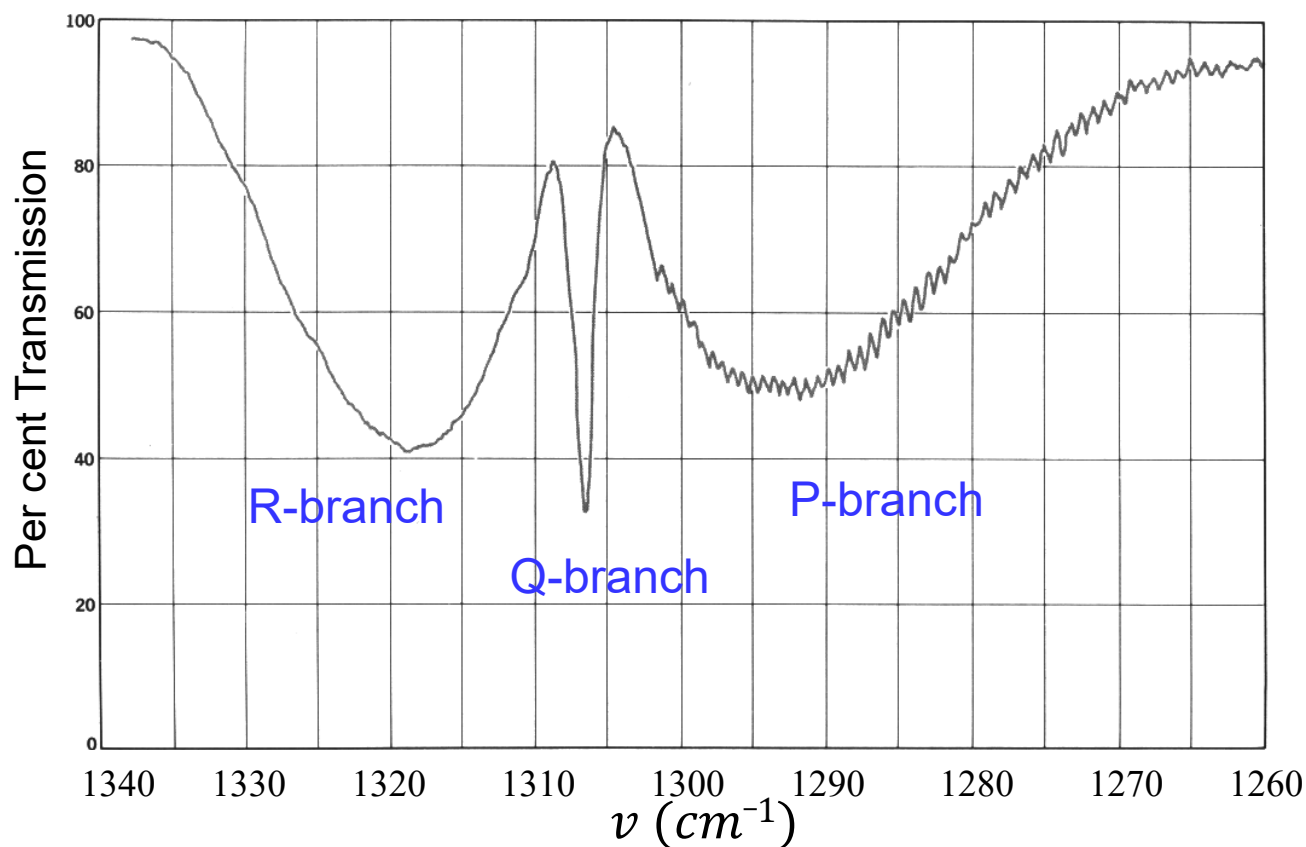
1. Splitting in P and R branch due to a difference in  $(A-B)$  in upper and lower vib. levels
2. Splitting in Q branch due to difference in  $B$  in upper and lower vib. levels
3. For  $K=0$ , spectrum reduces to that of linear molecules, no Q branch
4.  $K$  cannot exceed  $J$

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

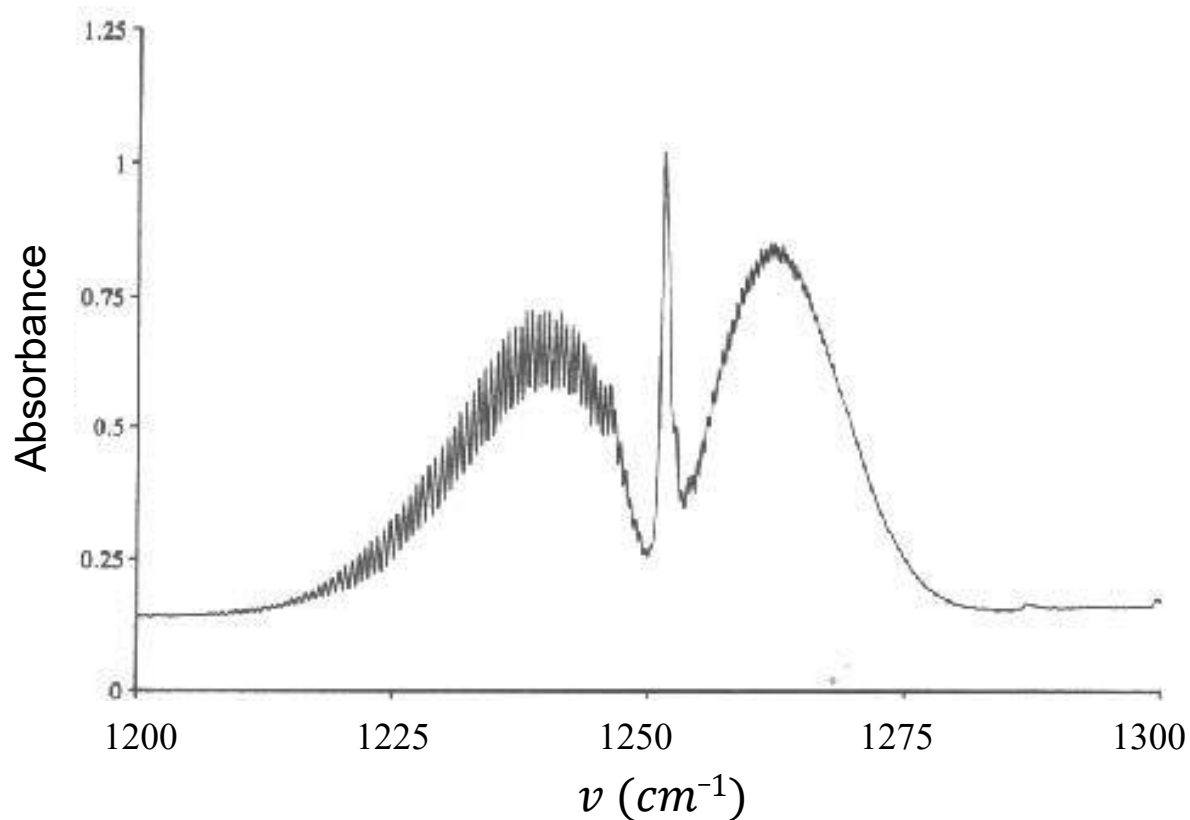
- Case I: Parallel bands



Example-1: A parallel absorption band of the symmetric top molecule  $CH_3Br$ . 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  $\text{cm}^{-1}$ , of the symmetric top molecule  $\text{CH}_3\text{I}$ , showing the typical PQR contour.





## 4.4. Rovibrational spectra of polyatomic molecules

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

Selection Rule:  $\Delta v_i = 1$

$$\Delta J = \pm 1, 0 \text{ (P, Q, R branches)}$$

$$\Delta K = \pm 1$$

R Branch:  $\Delta J = +1, \Delta K = \pm 1$

$$\bar{\nu}_R = \omega_o + 2B(J+1) + (A-B)(1 \pm 2K)$$

P Branch:  $\Delta J = -1, \Delta K = \pm 1$

$$\bar{\nu}_P = \omega_o - 2BJ + (A-B)(1 \pm 2K)$$

Q Branch:  $\Delta J = 0, \Delta K = \pm 1$

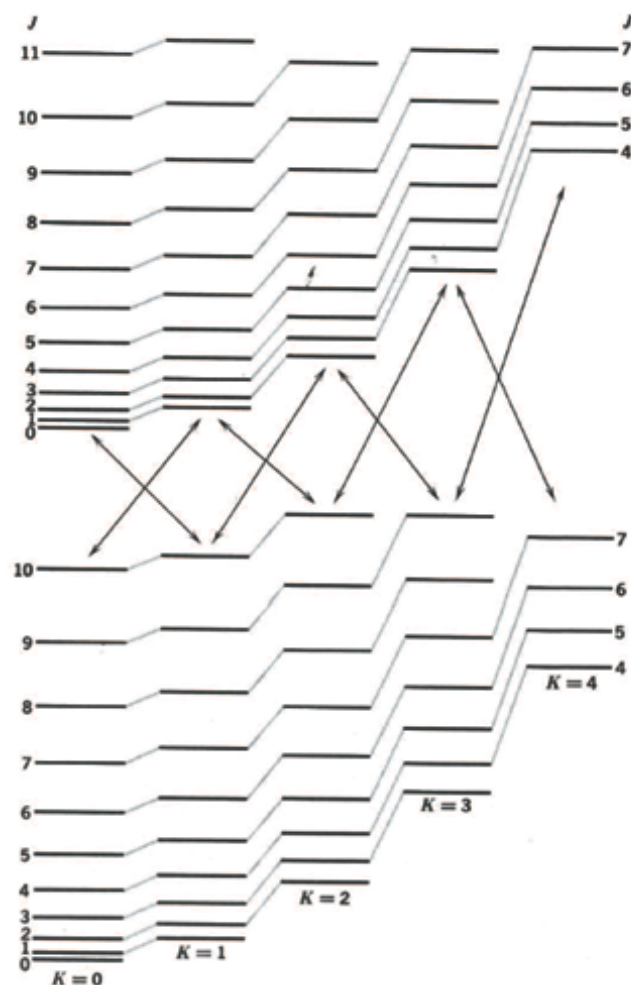
$$\bar{\nu}_Q = \omega_o + (A-B)(1 \pm 2K)$$



Note: Two sets of R, P and Q branches for each lower state value of K

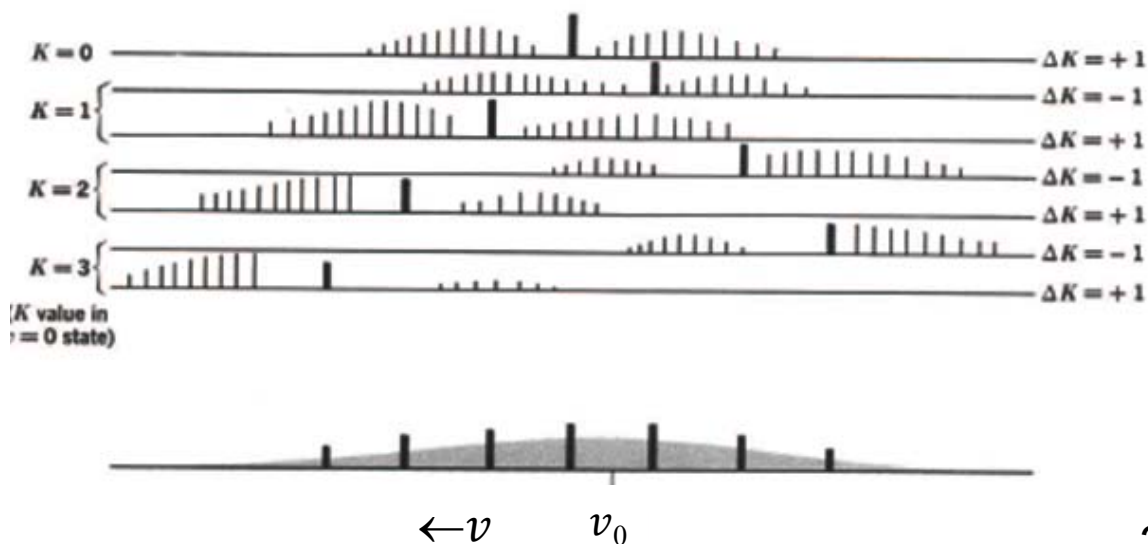
## 4.4. Rovibrational spectra of polyatomic molecules

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



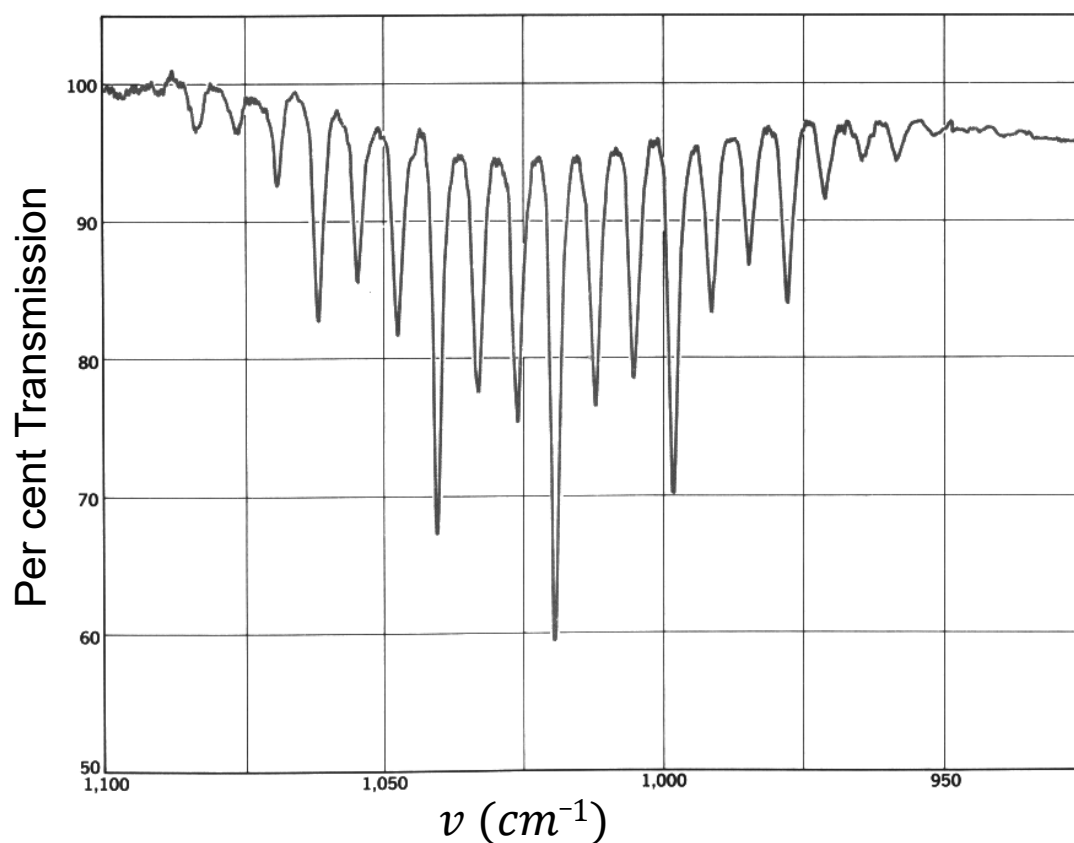
◀ Energy levels of a symmetric top molecule showing transitions that are allowed for a perpendicular band


▼ 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



 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  $\text{CH}_3\text{Cl}$



## Next: Quantitative Emission/Absorption

---

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