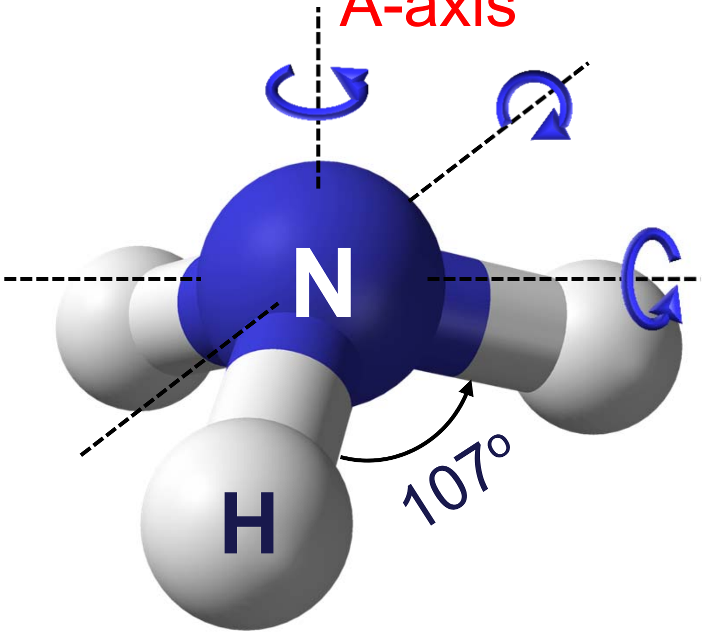
Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

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

Ammonia molecule



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

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:

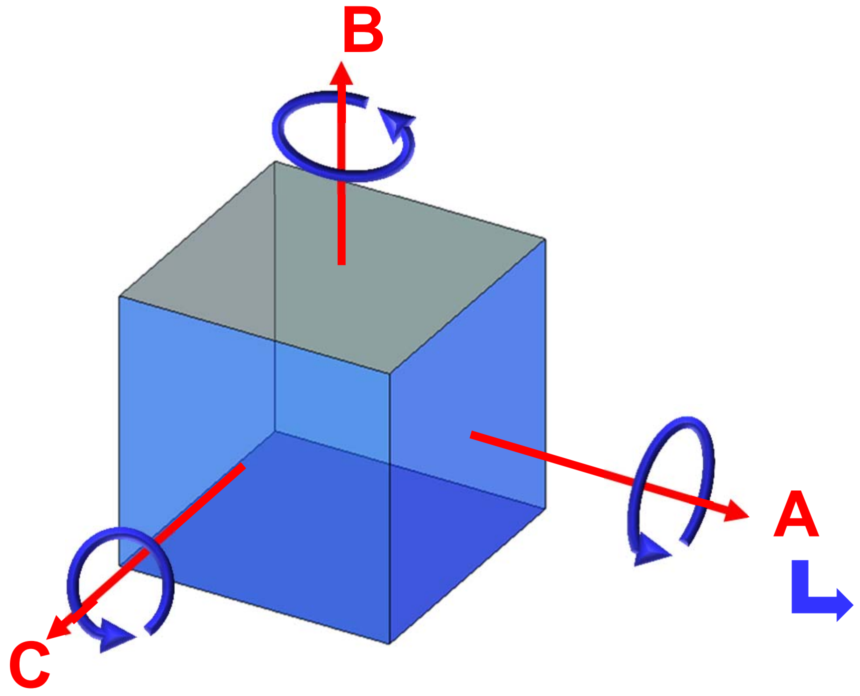
1. D_v is small, i.e., $D/B = 4(B/\bar{\nu}_{vib})^2 << 1$
2. E.g., for NO, $\left(\frac{D}{B}\right)_{NO} = 4\left(\frac{B}{\omega_e}\right)^2 \approx 4\left(\frac{1.7}{1900}\right)^2 \approx 3\times10^{-6}$

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

What about polyatomics (≥3 atoms)?

1. From diatomic to polyatomic

- 3D-body rotation



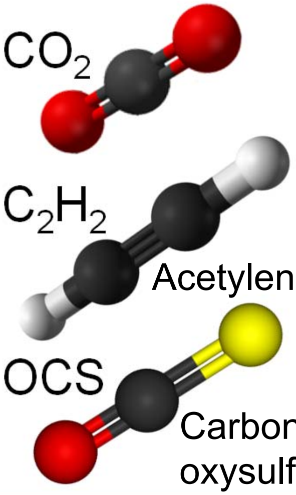
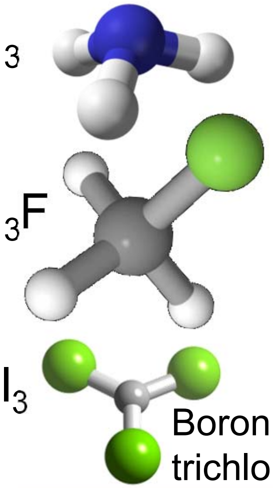
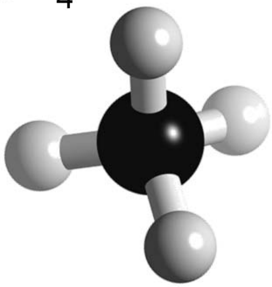
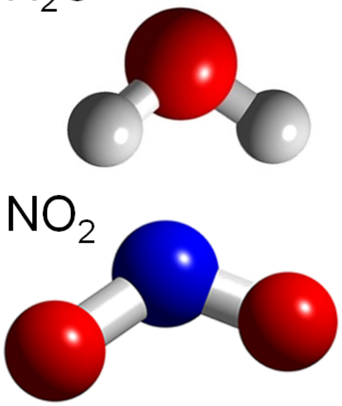
- Convention:

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	CO_2 C_2H_2 Acetylene OCS Carbon oxysulfide 	NH_3 CH_3F BCl_3 Boron trichloride 	CH_4 	H_2O NO_2 

Relatively simple

No dipole moment
Not microwave active

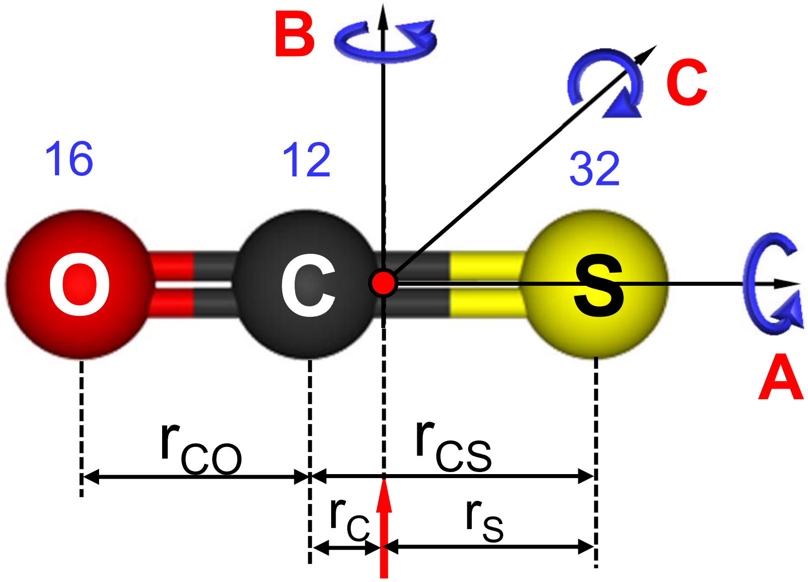
Largest category
Most complex

*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)

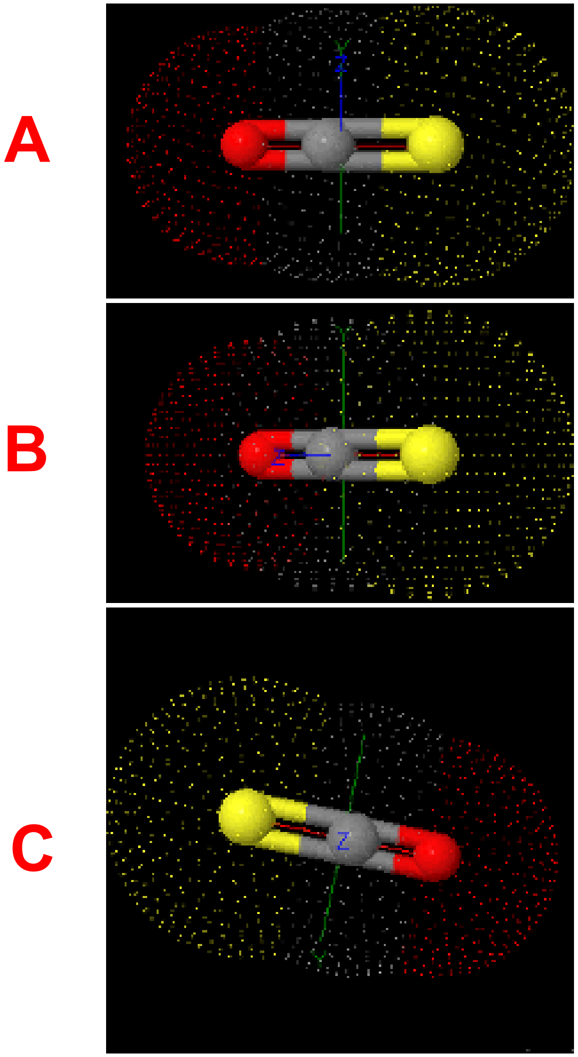


Center of mass

$r_{CO} = 1.165Å$
$r_{CS} = 1.558Å$

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

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



2. Classification of polyatomic molecules

- Symmetric tops

$$\boxed{I_B=I_C\neq I_A;\ I_A\neq 0}$$

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

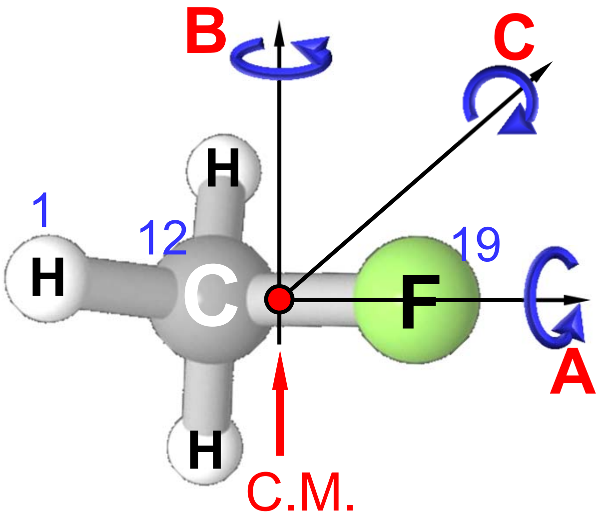
$$B, cm^{-1} = \frac{h}{8\pi^2 I_B c}$$

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

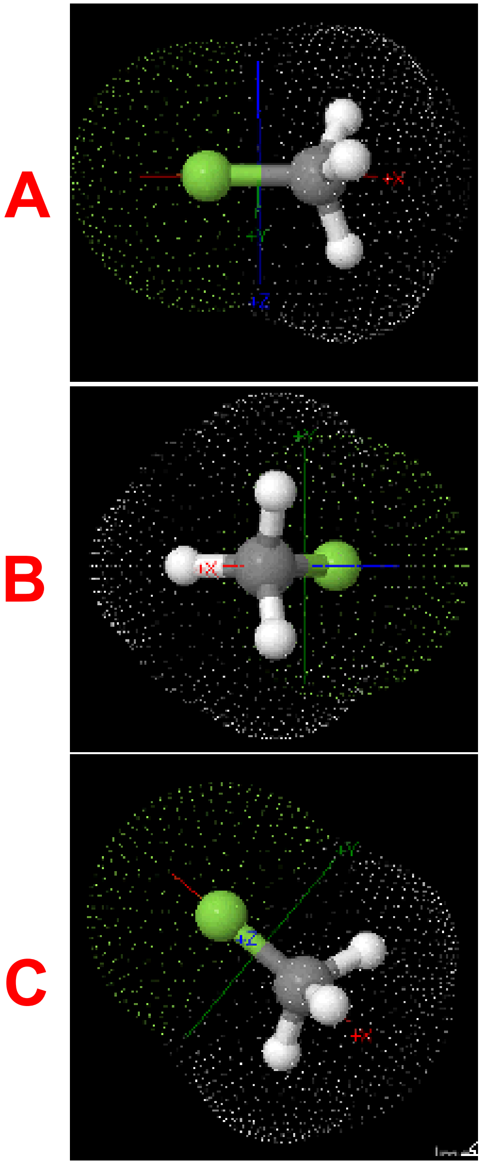
Prolate

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

E.g., CH_3F



Tripod-like (tetrahedral bonding)



2. Classification of polyatomic molecules

- Symmetric tops

$$\boxed{I_B=I_C\neq I_A;\ I_A\neq 0}$$

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

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

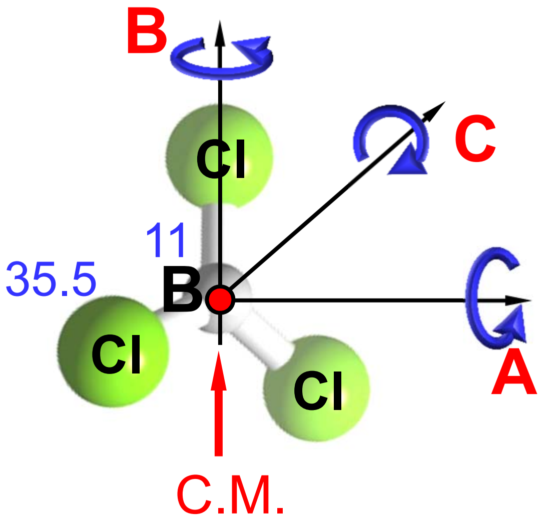
$$C, cm^{-1} = \frac{h}{8\pi^2 I_C c}$$

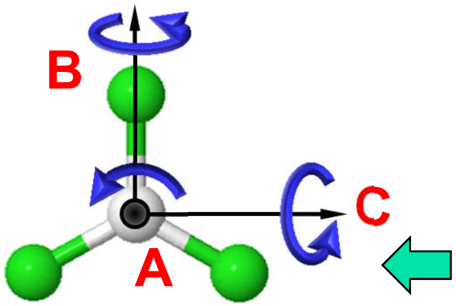
Oblate

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

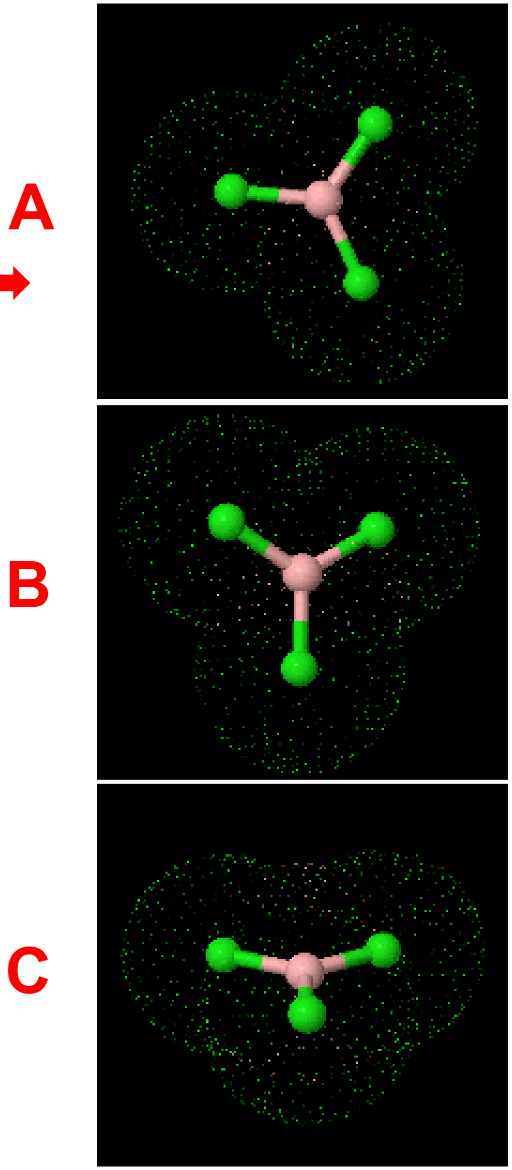
E.g., BCl_3 (Planar)

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





Planar view

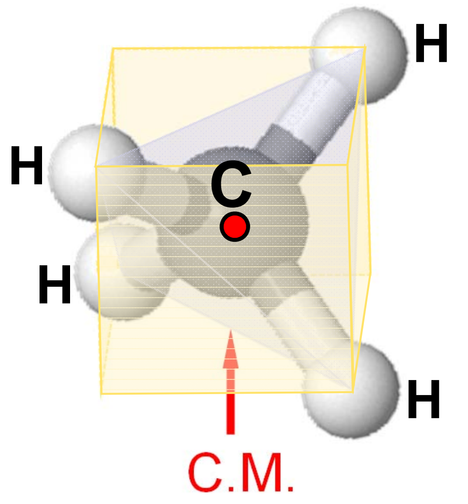


2. Classification of polyatomic molecules

- Spherical tops

$I_A = I_B = I_C$

E.g., CH_4 (methane)



Cube w/ C at center and H at diagonal corners

Symmetric, but

No dipole moment

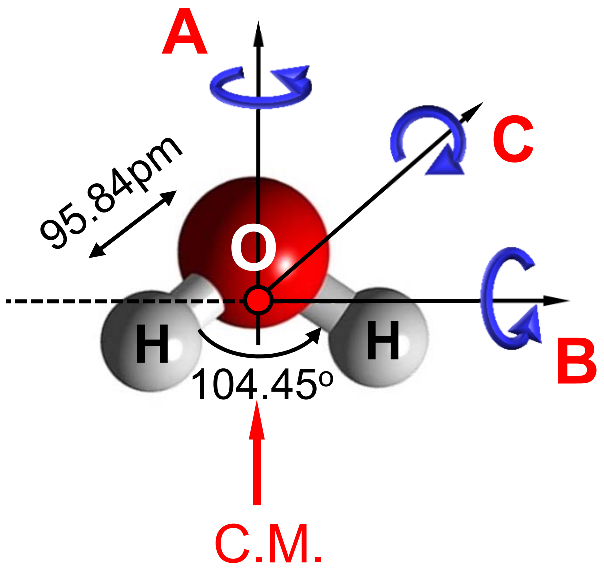
↓

No rotational spectrum

- Asymmetric rotors

$I_A \neq I_B \neq I_C$

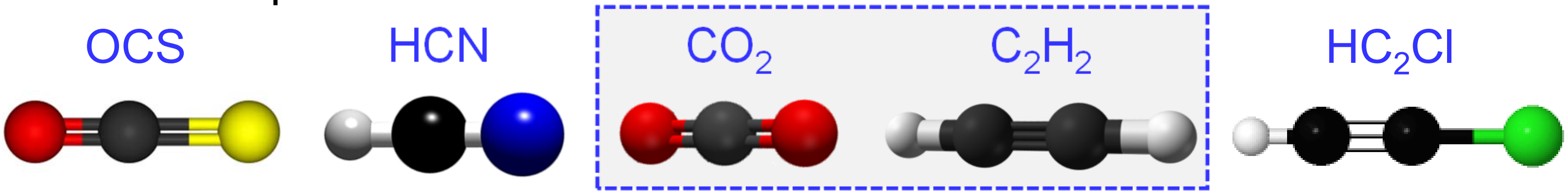
E.g., H_2O



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_2H_2 HC_2Cl

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

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

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

Rotational const.

Centrifugal distortion const.

Note: Larger I, smaller B (& line spacing) than diatomics

(" is suppressed, i.e. J=J")

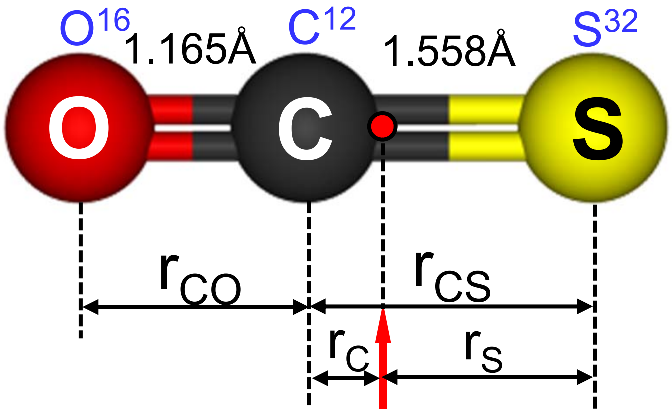
3. Rotational spectra of polyatomic molecules

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

N atoms → 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)



Center of mass

Use 2 isotopes for 2 equations:

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

↓

Solve for r_{CO}, r_{CS}

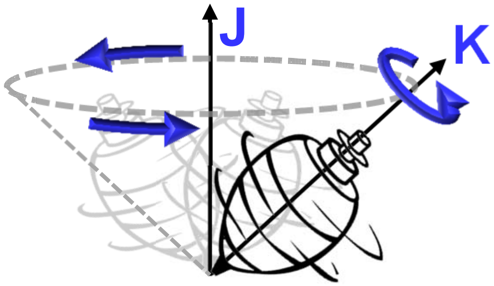
3. Rotational spectra of polyatomic molecules

- Symmetric tops ($I_B=I_C\neq I_A$; $I_A\neq 0$)
  - 2 main directions of rotation → 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

$$E_{J,K} = \frac{1}{2}\sum_i I_i\omega_i^2 \longrightarrow \boxed{F(J,K) = BJ(J+1) + (A-B)K^2}$$

✏ 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
    - **ΔJ** = +1   Remember that ΔJ = J' – J"
    - **ΔK** = 0

      ➡ No dipole moment for rotation about A-axis
      No change in K will occur with abs./emis.
  - Line positions

$$\boxed{\bar{\nu}_{J.K} = F(J+1,K) - F(J,K) = 2BJ(J+1) \quad \left[cm^{-1}\right]}$$

✎ 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}

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

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

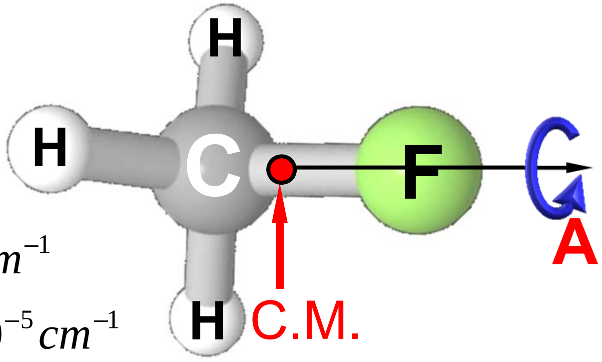
✎ Note: Each J has 2J+1 components, but only J+1 frequencies

E.g., CH_3F, Methyl Fluoride

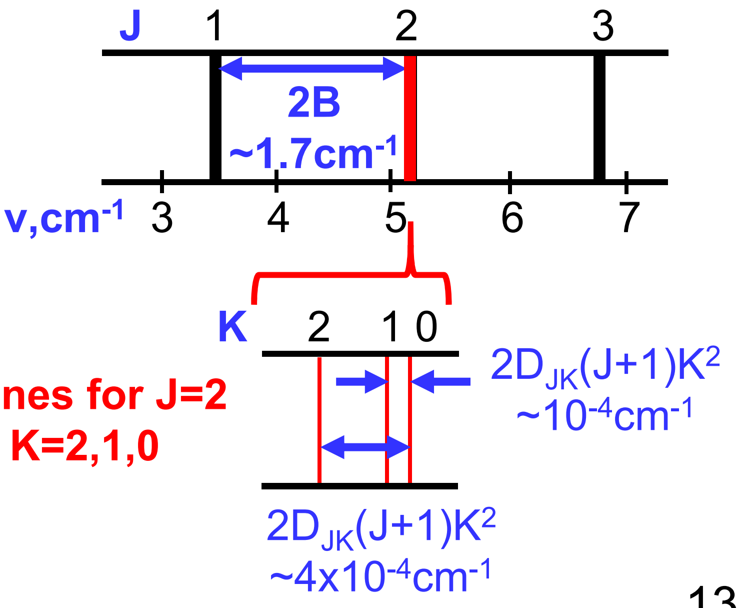
$B = 0.851 cm^{-1}$

$D_J = 2 \times 10^{-6} cm^{-1}$

$D_{JK} = 1.47 \times 10^{-5} cm^{-1}$



If J≈20, J^2≈400, $2DJ^2$≈1.6×10^{-3}, $2DJ^2/B$≈.2%



3 lines for J=2
K=2,1,0

3. Rotational spectra of polyatomic molecules

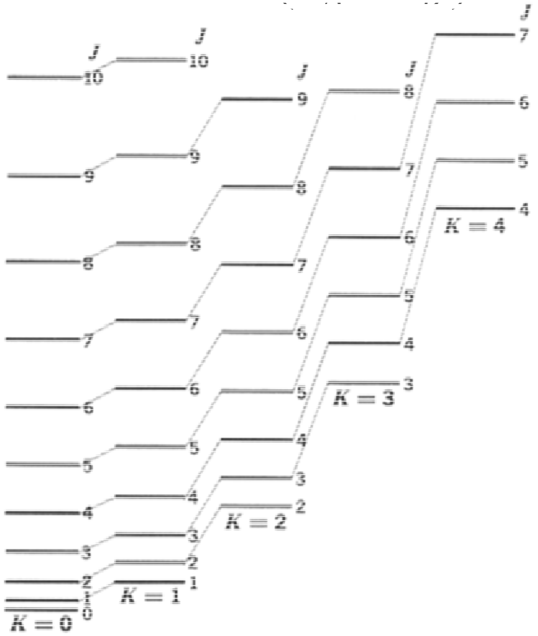
- Symmetric tops ($I_B=I_C\neq I_A$; $I_A\neq 0$) → gets complex fast!

Prolate

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

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

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

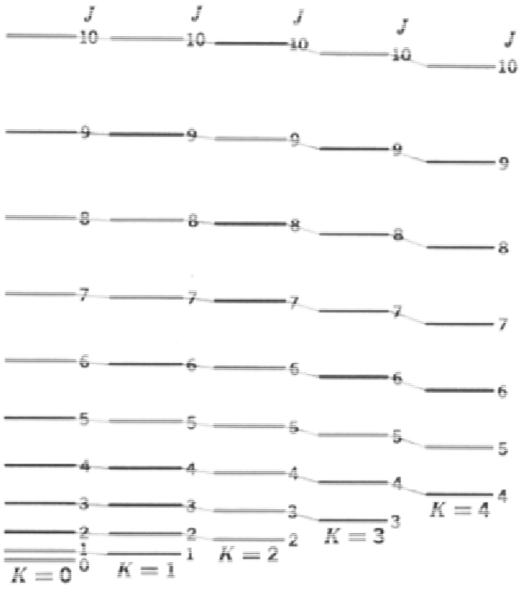


Oblate

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

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

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



Example energy levels

3. Rotational spectra of polyatomic molecules

- Rotational partition function

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

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

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

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

σ – molecule-dependent symmetry factor

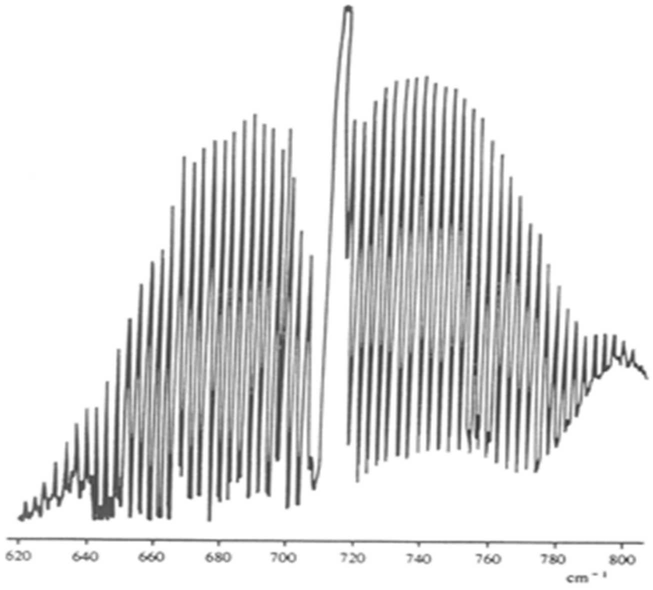
Molecule	σ	Molecule Type
CO_2	2	Linear
NH_3	3	Symmetric Top
CH_4	12	Spherical Top
H_2O	2	Asymmetric Rotor

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 → 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

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 angular coordinates (vib. modes)

4.2. Types of bands

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

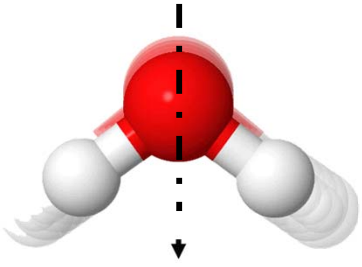
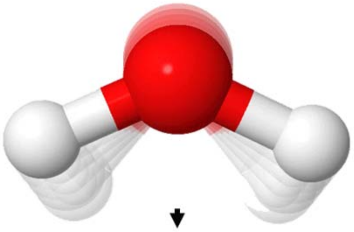
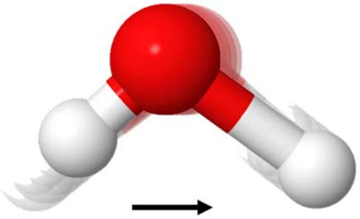
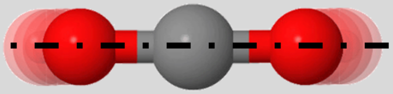
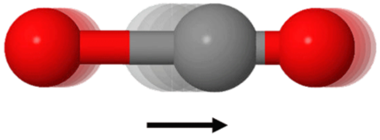
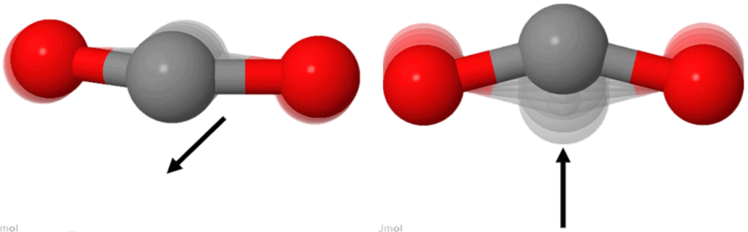
[cm^{-1}]

Symmetric Declining frequency	ν_1	Highest-frequency <u>symmetric</u> vibrational mode
	ν_2	2nd highest symmetric mode
	…	…
	ν_i	Lowest-frequency <u>symmetric</u> mode
Asymmetric Declining frequency	ν_{i+1}	Highest-frequency <u>asymmetric</u> vibrational mode
	ν_{i+2}	2nd highest symmetric mode
	…	…

✎ <u>Exception</u>: the perpendicular vibration for linear XY_2 and XYZ molecules is always called $\boldsymbol{\nu_2}$

4.2. Types of bands

- Parallel and perpendicular modes

Examples:	**Parallel (||)** Dipole changes are || to the main axis of symmetry		**Perpendicular (⊥)** Dipole changes are ⊥ to the main axis of symmetry
H_2O (3x3-6=3 vib. modes)	 Symmetric stretch $\nu_1=3652\text{cm}^{-1}$	 Symmetric bending $\nu_2=1595\text{cm}^{-1}$	 Asymmetric stretch $\nu_3=3756\text{cm}^{-1}$
CO_2 (3x3-5=4 vib. modes)	 No dipole moment Not IR-active! Symmetric stretch $\nu_1=1330\text{cm}^{-1}$	 Asymmetric stretch $\nu_3=2349\text{cm}^{-1}$	 Symmetric bending (2 degenerate) $\nu_2=667\text{cm}^{-1}$

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 CO_2

Mode	Frequency [cm^{-1}]	Type	Description	IR	Raman
ν_1	1388	--	Symmetric stretch	Not active	Active
ν_2	667	$\perp$	Symmetric bend (Degenerate)	Strong	Not active
ν_3	2349	$\parallel$	Asymmetric stretch	Very strong	Not active

Vibrational modes of HCN

Mode	Frequency [cm^{-1}]	Type	Description	IR	Raman
ν_1	3310	$\parallel$	Symmetric stretch	Strong	Weak
ν_2	715	$\perp$	Symmetric bend (Degenerate)	Very strong	Weak
ν_3	2097	$\parallel$	Asymmetric stretch	Weak	Strong

4.2. Types of bands

- Terminology for different types of vibrational bands

Fundamental Bands:	ν_i, the ith vibrational mode;	$\Delta v = v' - v'' = 1$ for the ith mode
1st Overtone:	$2\nu_i$;	$\Delta v = v' - v'' = 2$ for the ith mode
2nd Overtone:	$3\nu_i$;	$\Delta v = v' - v'' = 3$ for the ith mode
Combination bands:	Changes in multiple quantum numbers, e.g., $\nu_1 + \nu_2$; $2\nu_1 + \nu_2$;	 $\Delta v_1 = \Delta v_2 = 1$, i.e., v_1 and v_2 both increase by 1 for absorption or decrease by 1 for emission $\Delta v_1 = 2$ and $\Delta v_2 = 1$
Difference bands:	Quantum number changes with mixed sign $\nu_1 - \nu_2$;	 $v_{1,\text{final}} - v_{1,\text{initial}} = \pm 1$ 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

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

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

Degenerate

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

Vibration	**Frequency [cm^{-1}]**	**Type**	**Description**
ν_1	3337	∥	Symmetric stretch
ν_2	950	∥	Symmetric bend
ν_3	3444	⊥	Asymmetric stretch (Degenerate)
ν_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 ~ 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 ≤ 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., $2\boldsymbol{\nu}_2$ CO_2 (@ 1334cm^{-1}) ≈ $\boldsymbol{\nu}_{1,\,CO2}$

4.4. Rovibrational spectra of polyatomic molecules

- Linear polyatomic molecules

  (limit consideration to fundamental transitions)

  Energy: $T(\mathrm{v}_i, J) = G(\mathrm{v}_i) + F(J)$

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

Selection Rule: $\Delta \mathrm{v}_i = 1$

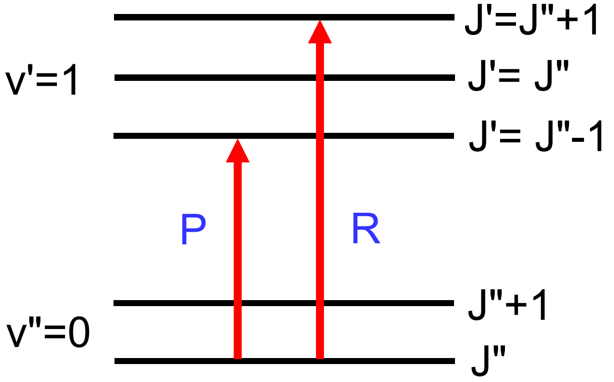
$\Delta J = \pm 1$

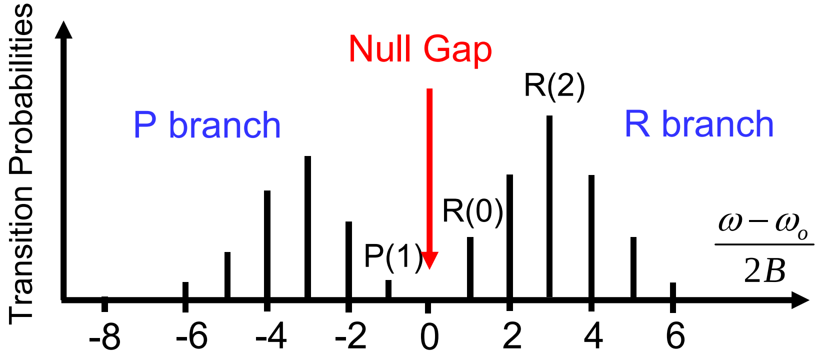
(R and P branches)

$\Delta \mathrm{v}_j = 0,\ j \neq i$

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

Example: HCN(ν_1, ν_3)

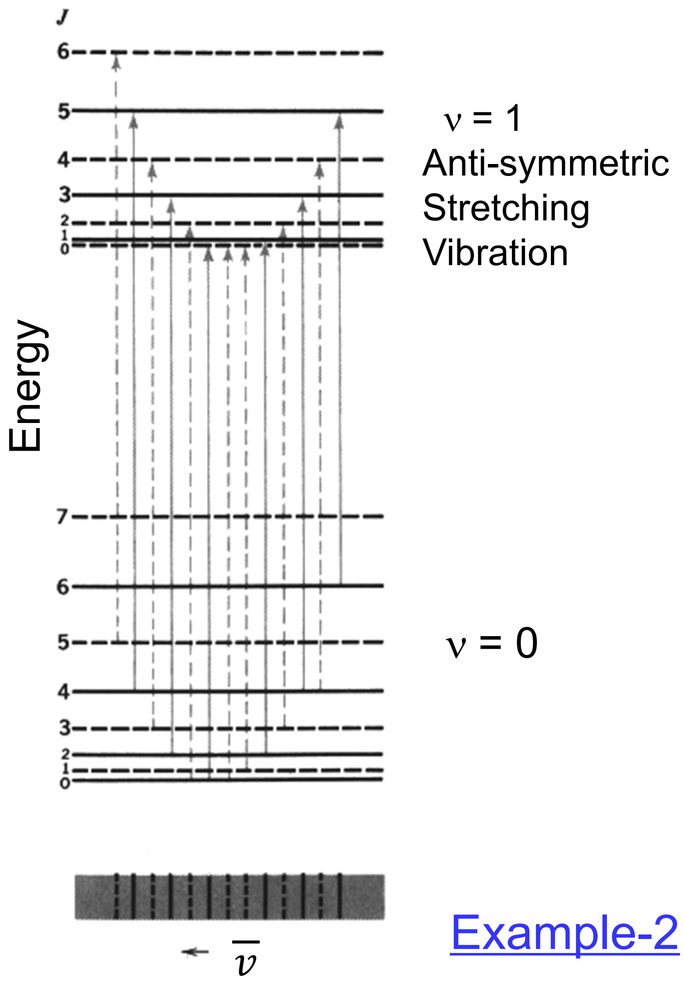


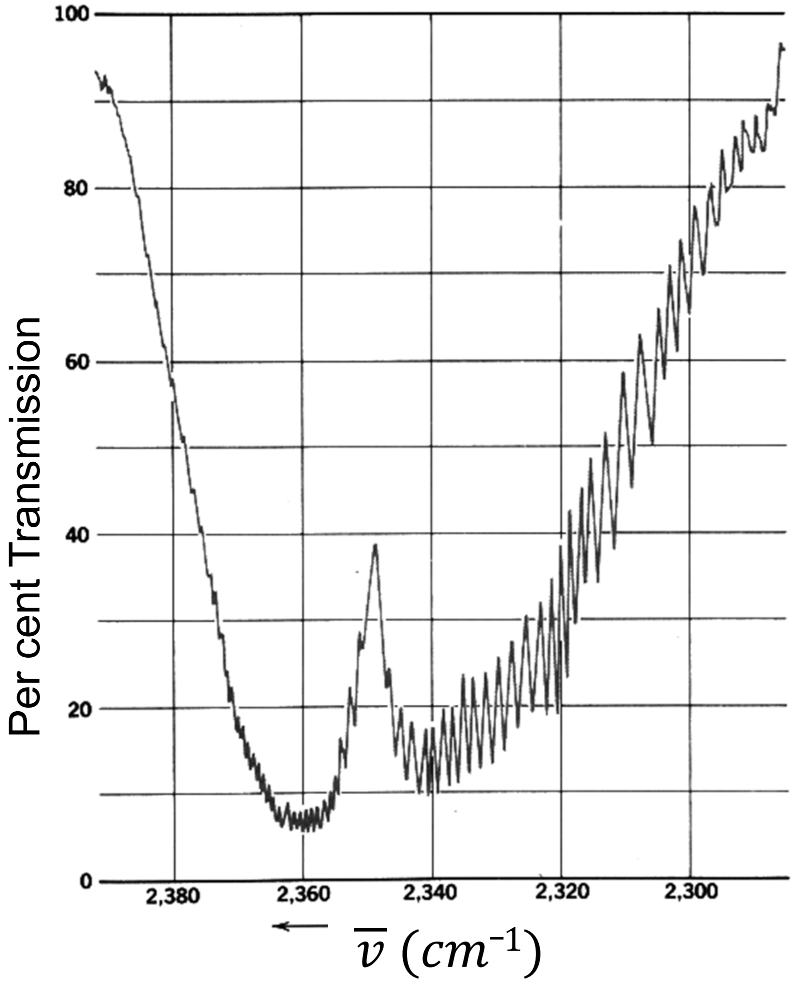


Note: No ν_1 parallel band for CO_2

4.4. Rovibrational spectra of polyatomic molecules

- Linear polyatomic molecules
  - Case I: Parallel band





Example-2: A parallel band of the linear molecule CO_2

4.4. Rovibrational spectra of polyatomic molecules

- Linear polyatomic molecules

  (limit consideration to fundamental transitions)

  Energy: $T(\mathrm{v}_i, J) = G(\mathrm{v}_i) + F(J)$

  - Case II: Perpendicular bands

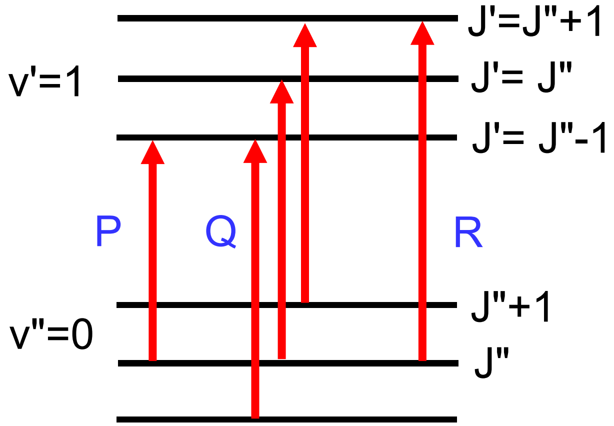
Selection Rule: $\Delta \mathrm{v}_i = 1$

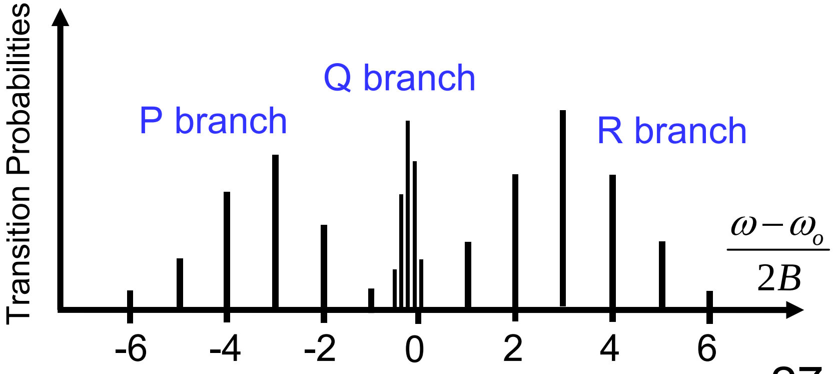
$\Delta J = \pm 1, 0$

(R, P and Q branches)

$\Delta \mathrm{v}_j = 0,\ j \neq i$

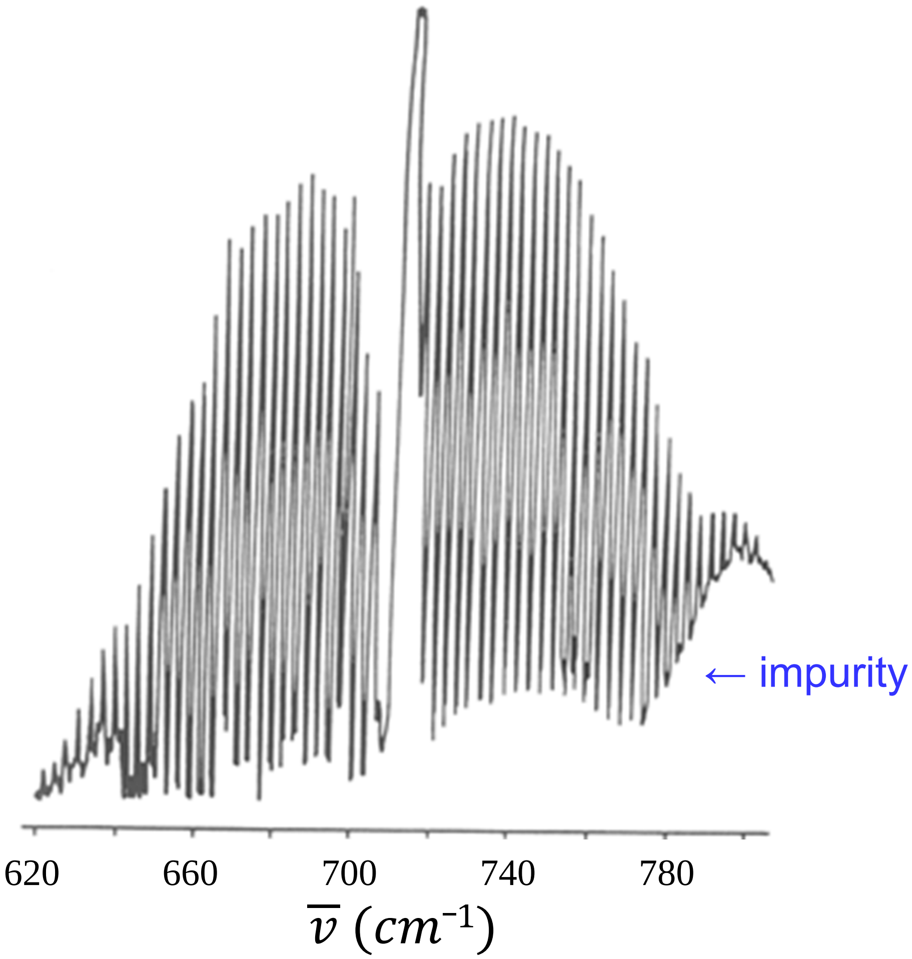
1. If B'=B", all Q branch lines occur at the same frequency
2. If B'≠B", $Q(J'') = \omega_0 + \overbrace{(B' - B'')}^{-\alpha<0} J''(J''+1)$
   Q branch “degrades” to lower frequencies (i.e., to the “red” in wavelength)





4.4. Rovibrational spectra of polyatomic molecules

- Linear polyatomic molecules
  - Case II: Perpendicular bands



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

4.4. Rovibrational spectra of polyatomic molecules

- Symmetric top molecules (e.g., CH_3F, BCl_3)

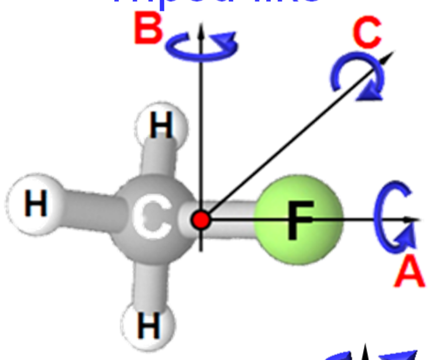
Recall: K – quantum number for angular momentum around axis A

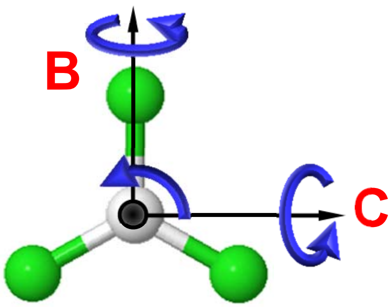
Energy: $T(\mathrm{v}_i, J, K) = G(\mathrm{v}_i) + F(J, K)$

$$= (\mathrm{v}_i + 1/2)\omega_e^i - \omega_e^i x_e^i (\mathrm{v}_i + 1/2)^2 + BJ(J+1) + (A - B)K^2$$

- Case I: Parallel bands

Tripod-like





Planar

Selection Rule: $\Delta \mathrm{v}_i = 1$

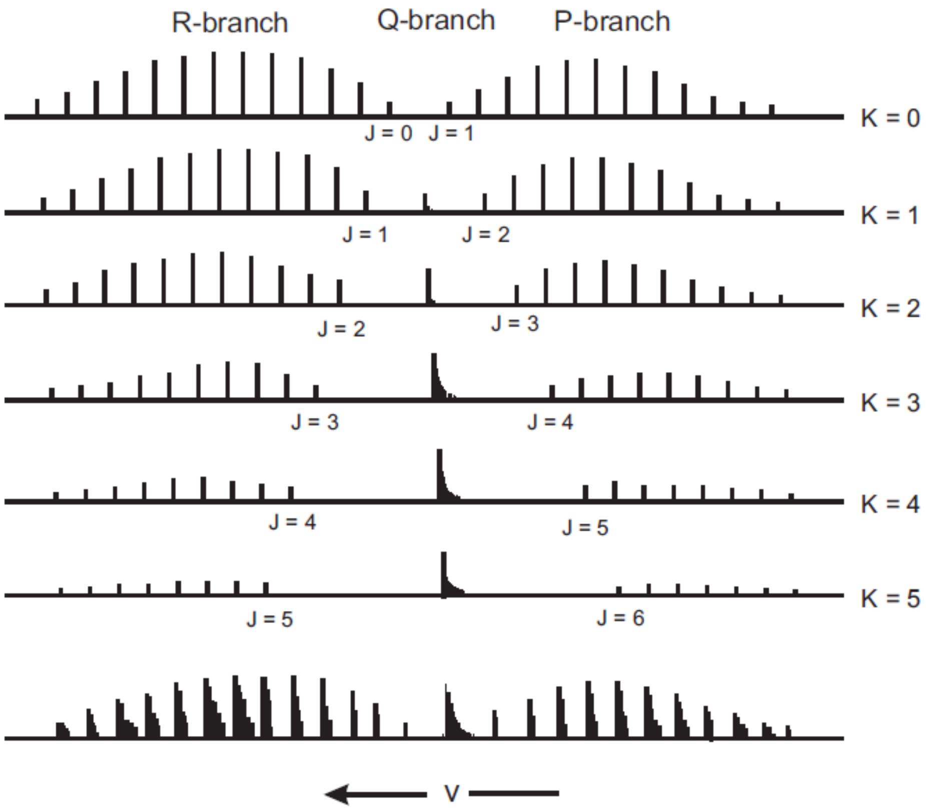
$\Delta J = \pm 1, 0$ (P, Q, R branches)

$\Delta K = 0$

1. 2J+1 values of K (K=J, J-1, …, 0, …, -J)
2. Intensity of Q branch is a function of (I_A/I_B)
3. As $(I_A/I_B) \rightarrow 0$
   symmetric top → linear molecule
   strength of Q branch → 0

4.4. Rovibrational spectra of polyatomic molecules

- Symmetric top molecules (e.g., CH_3F, BCl_3)
  - Case I: Parallel bands



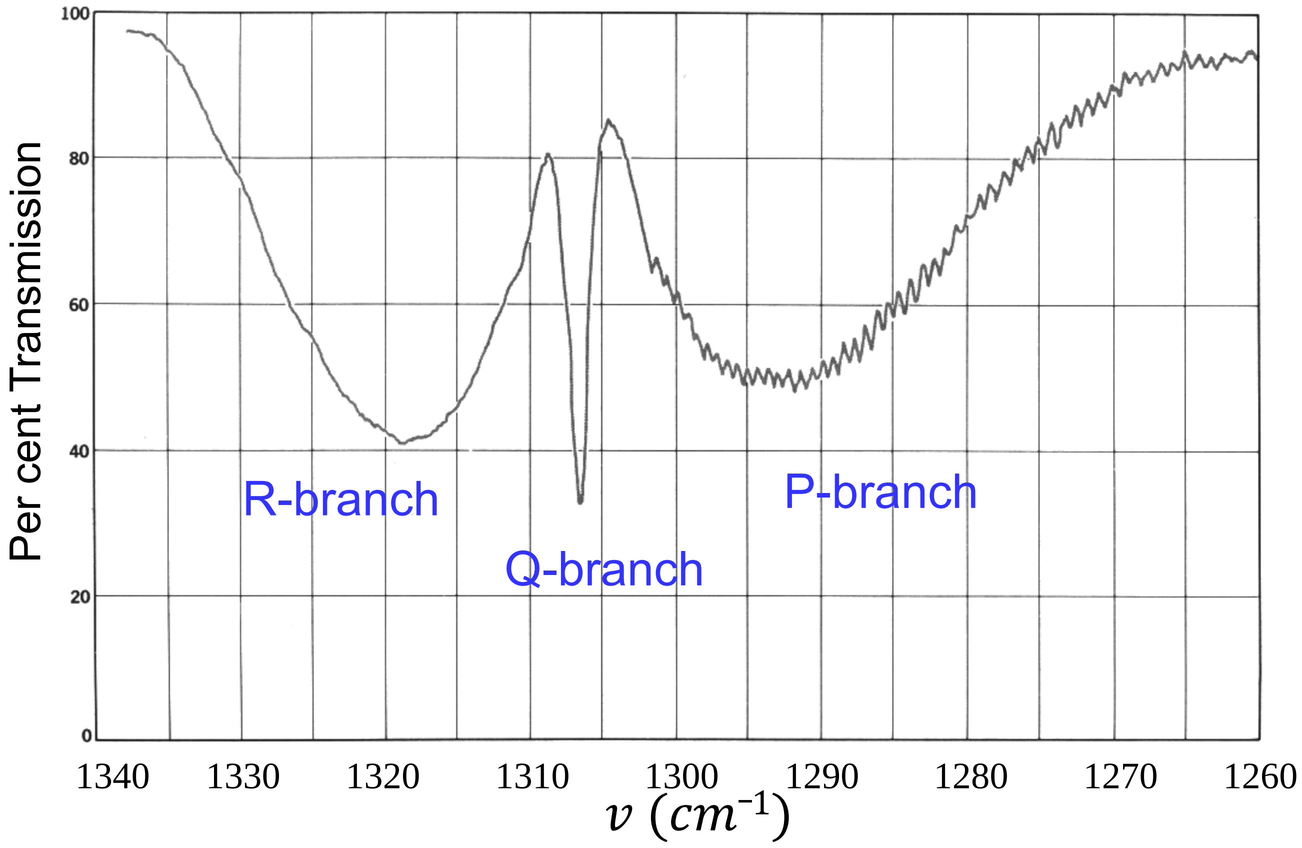
Resolved components of a parallel band showing contributions from each of the K levels of the v=0 state

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

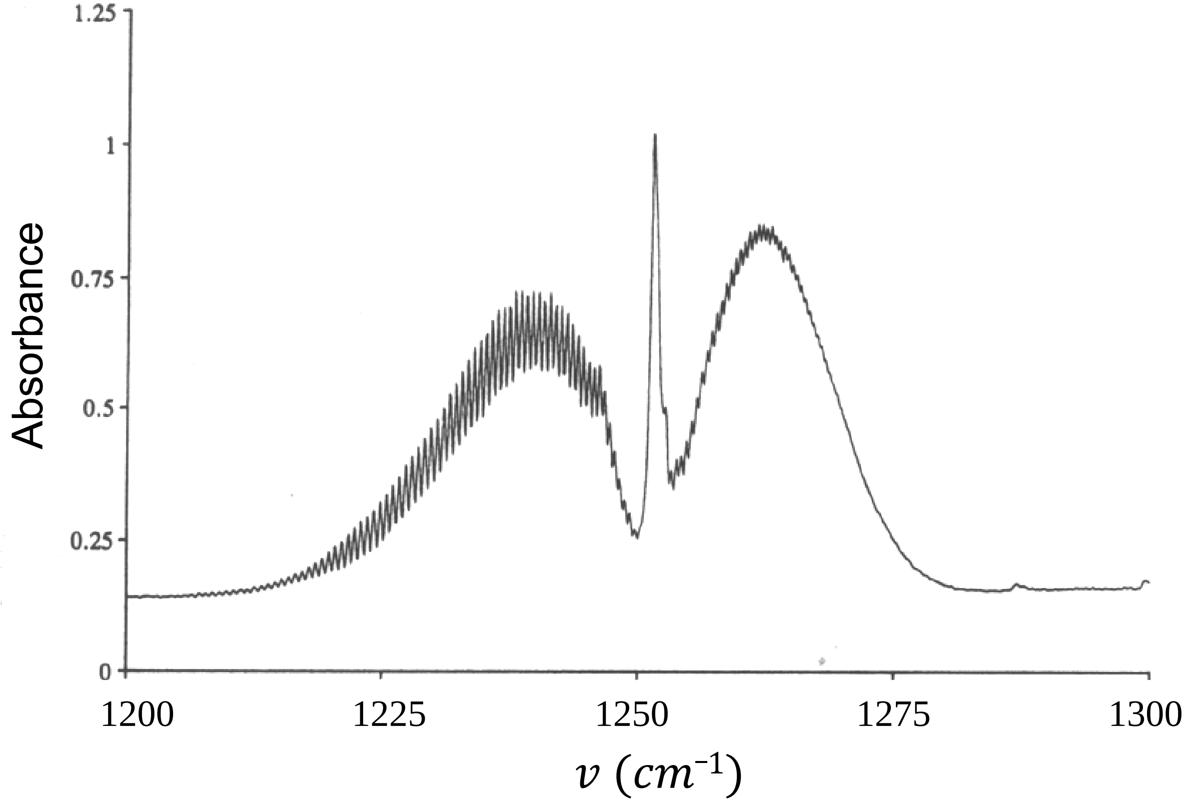
- Symmetric top molecules
  - Case I: Parallel bands



Example-1: A parallel absorption band of the symmetric top molecule 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 cm^{-1}, of the symmetric top molecule CH_3I, showing the typical PQR contour.

4.4. Rovibrational spectra of polyatomic molecules

- Symmetric top molecules (e.g., CH_3F, BCl_3)
  - Case II: Perpendicular bands

Selection Rule:

$$\Delta \mathrm{v}_i = 1$$

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

$$\Delta K = \pm 1$$

R Branch:

$$\Delta J = +1, \Delta K = \pm 1$$

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

P Branch:

$$\Delta J = -1, \Delta K = \pm 1$$

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

Q Branch:

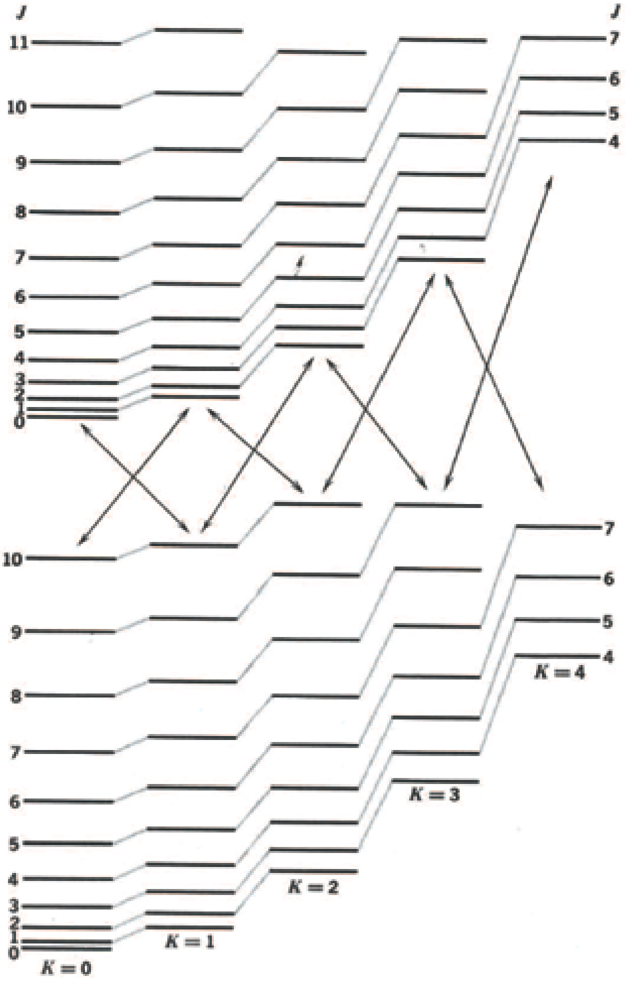
$$\Delta J = 0, \Delta K = \pm 1$$

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

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

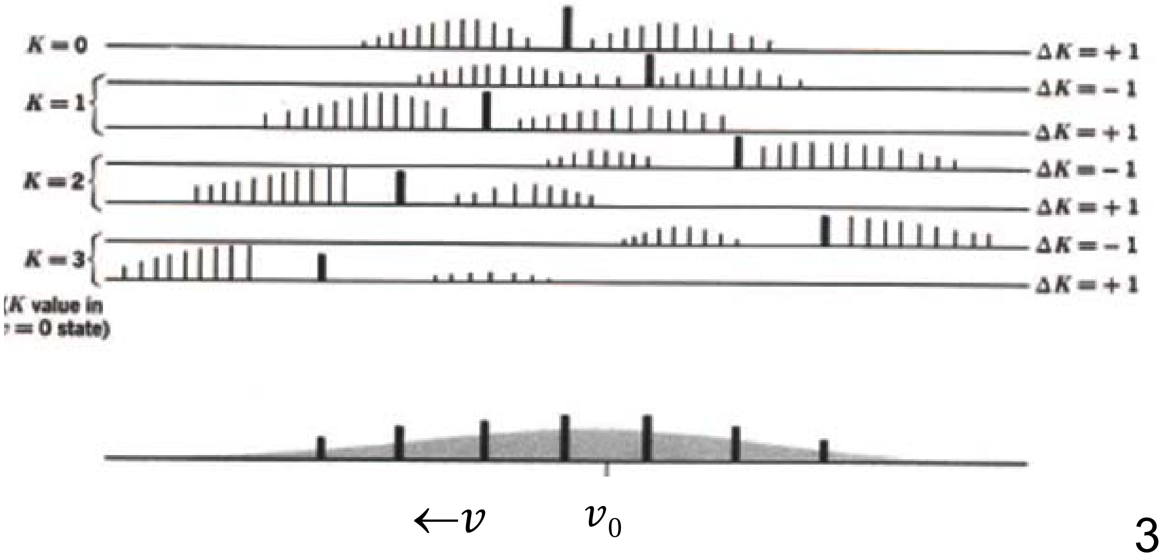
4.4. Rovibrational spectra of polyatomic molecules

- Symmetric top molecules (e.g., CH_3F, BCl_3)
  - Case II: Perpendicular bands



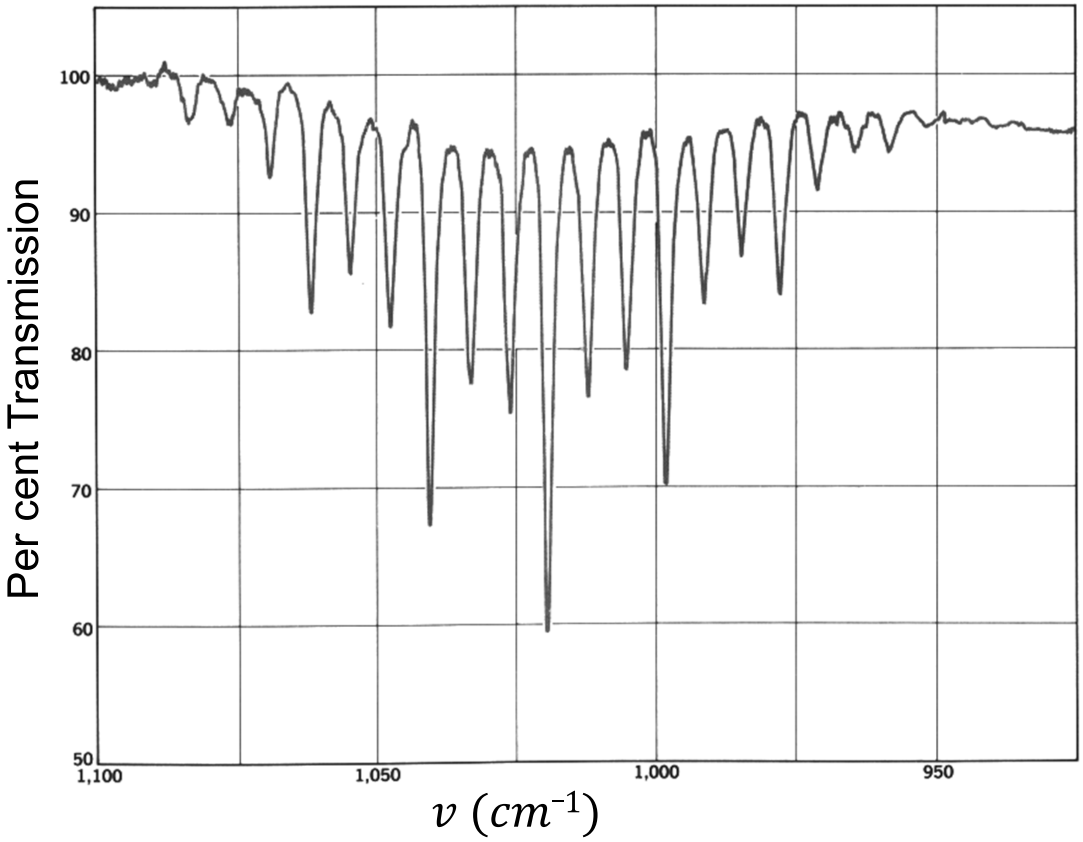
◄ Energy levels of a symmetric top molecule showing transitions that are allowed for a perpendicular band

▼ 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 CH_3Cl

Next: Quantitative Emission/Absorption

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