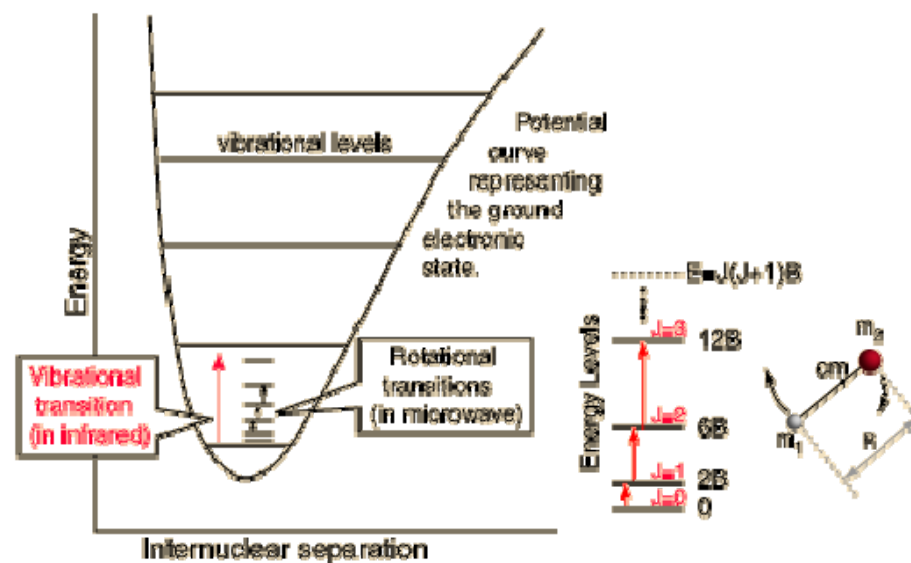


Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

Lecture 2: Rotational and Vibrational Spectra

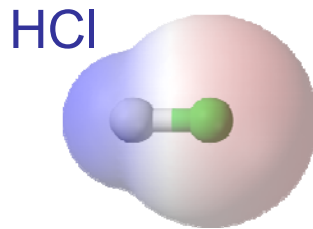
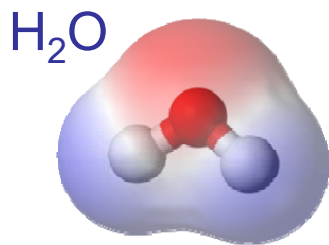
1. Light-matter interaction
2. Rigid-rotor model for diatomic molecule
3. Non-rigid rotation
4. Vibration-rotation for diatomics



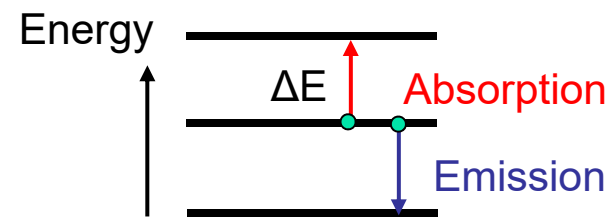
1. Light-matter interaction

■ Possibilities of interaction

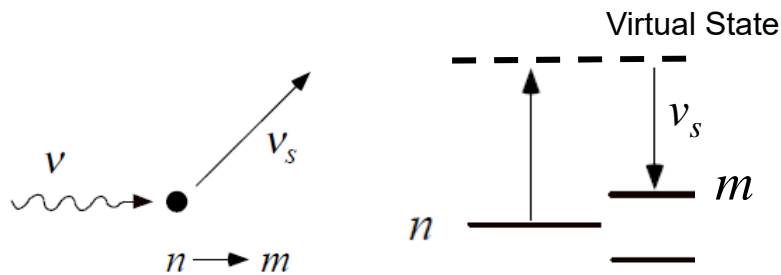
- Permanent electric dipole moment
- Rotation and vibration produce oscillating dipole (Emission/Absorption)



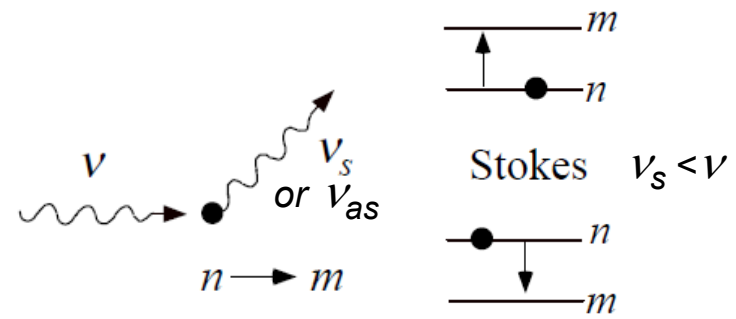
$\mu = qd$
*What if
 Homonuclear?*



- Elastic scattering (Rayleigh), $\nu_s = \nu$
- Inelastic scattering (Raman), $\nu_s \neq \nu$



Inelastic scattering



anti-Stokes $\nu_{as} > \nu$

1. Light-matter interaction

■ Elements of spectra:

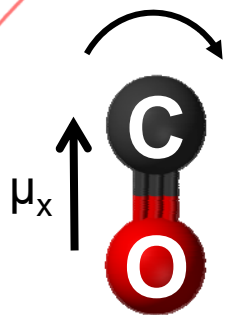
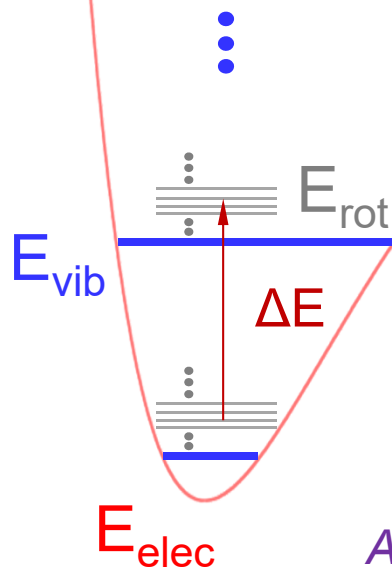
- Line position
- Line strength
- Line shapes



- Line position (λ) is determined by difference between energy levels
- **What determines the energy levels?**
- **Quantum Mechanics!**

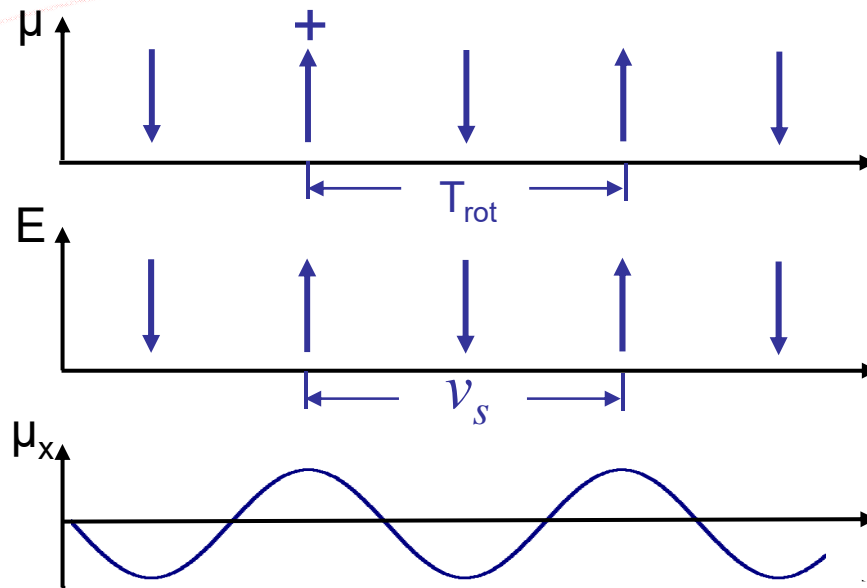
■ Internal Energy:

$$E_{\text{int}} = E_{\text{elec}}(n) + E_{\text{vib}}(v) + E_{\text{rot}}(J)$$



Rotation: Microwave Region (ΔJ)

Electric dipole moment: $\vec{\mu} = \sum_i q_i \vec{r}_i$



Are some molecules
"Microwave inactive"?

YES, e.g., H_2 , Cl_2 , CO_2

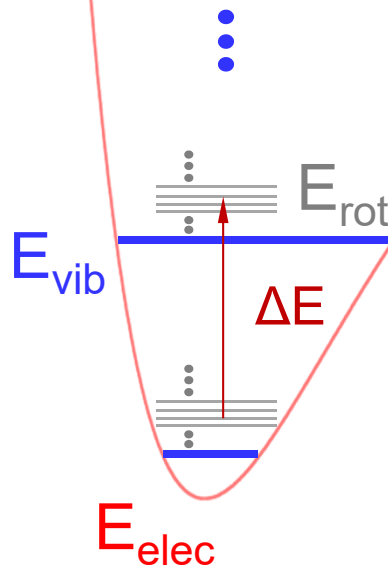
1. Light-matter interaction

- Elements of spectra:

- Line position
- Line strength
- Line shapes

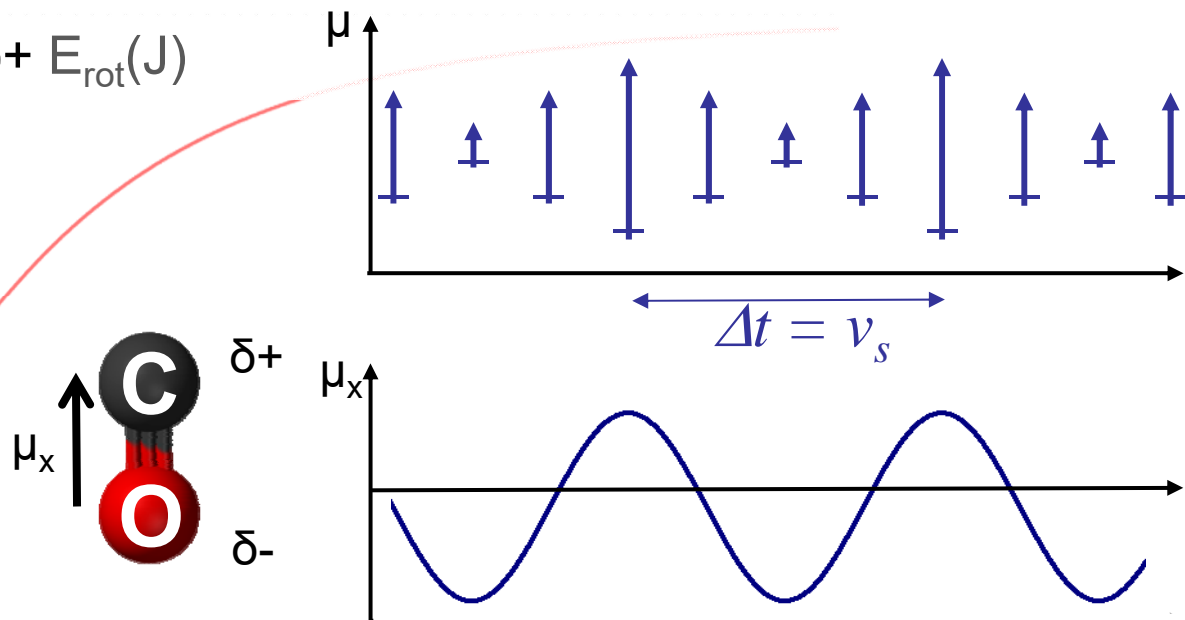
- Internal Energy :

$$E_{\text{int}} = E_{\text{elec}}(n) + E_{\text{vib}}(\nu) + E_{\text{rot}}(J)$$



Rotation: Microwave Region (ΔJ)

Vibration: Infrared Region ($\Delta \nu$, J)



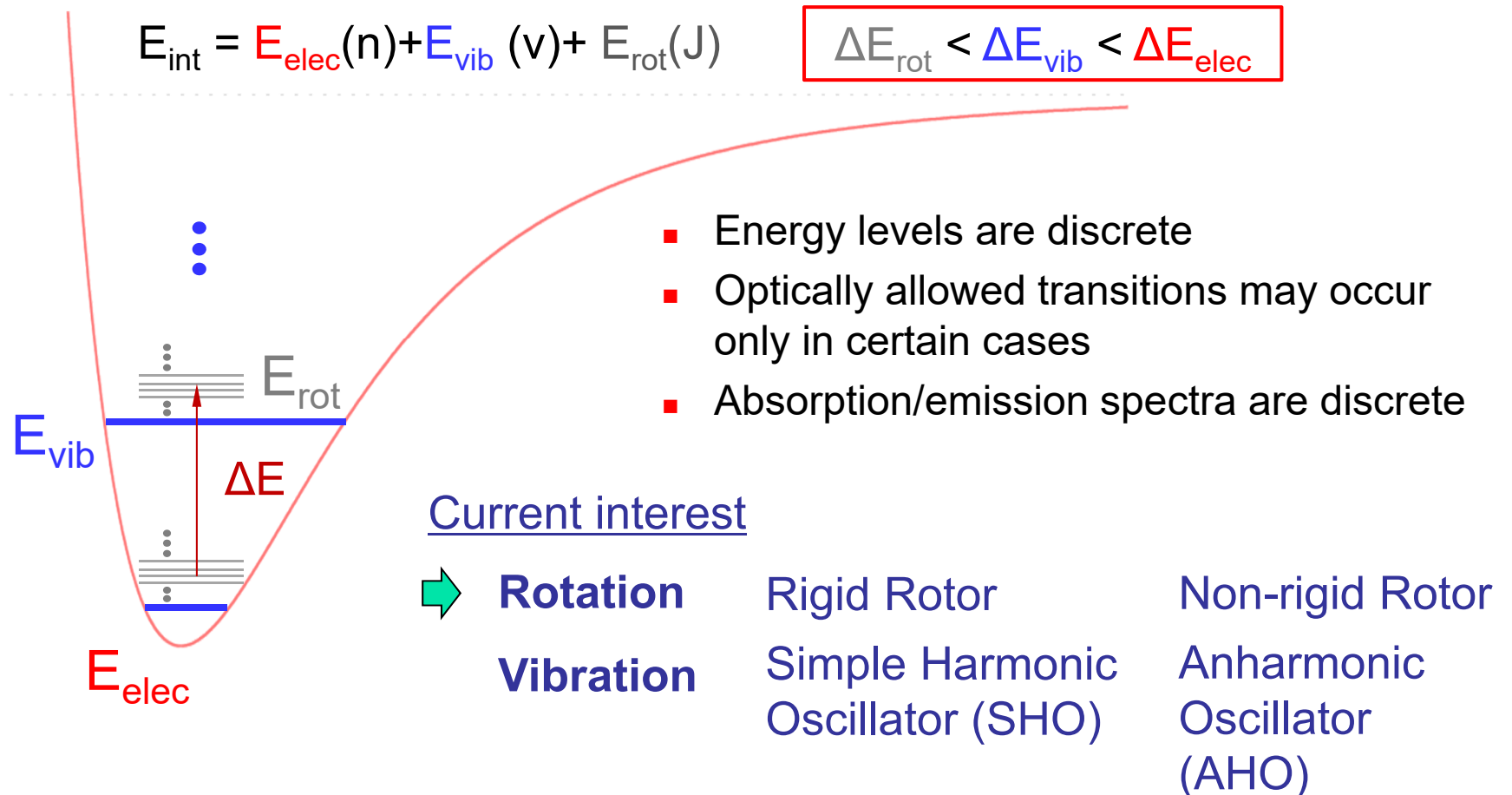
Heteronuclear diatomic case is IR-active

Are some vibrations "Infra-red inactive"?

Yes, e.g., symmetric stretch of CO_2

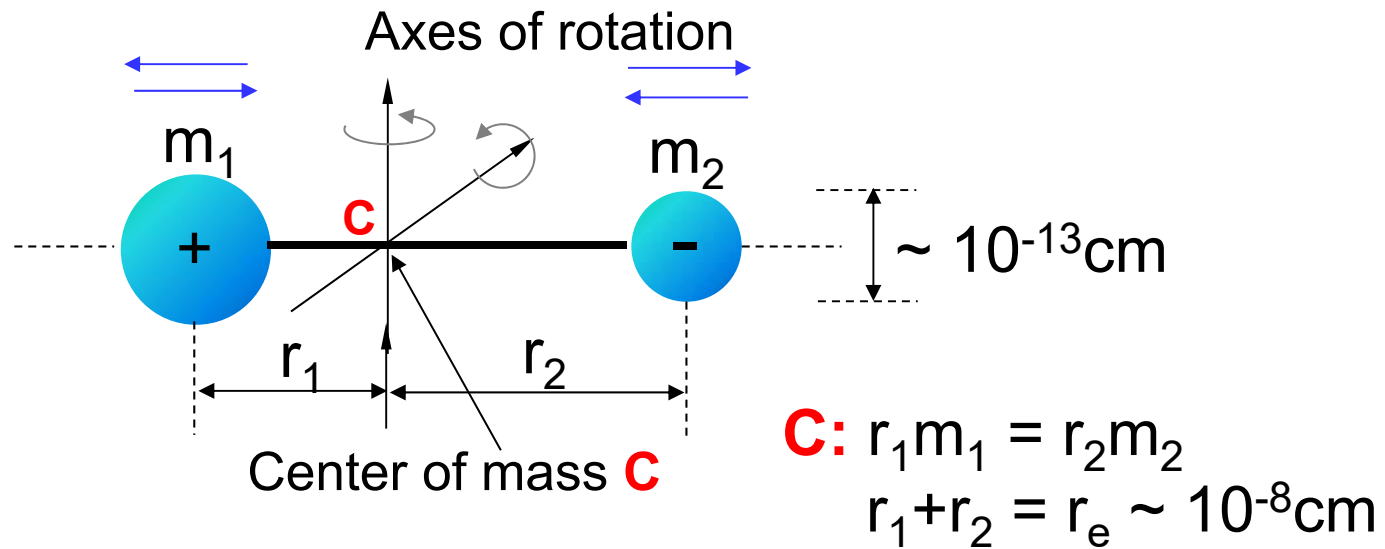
1. Light-matter interaction

■ Summary



2. Rigid-Rotor model of diatomic molecule

- Rigid Rotor



Assume:

- Point masses ($d_{\text{nucleus}} \sim 10^{-13}\text{cm}$, $r_e \sim 10^{-8}\text{cm}$)
- $r_e = \text{const.}$ ("rigid rotor")

➡ Relax this later

2. Rigid-Rotor model of diatomic molecule

■ Classical Mechanics

■ Moment of Inertia

$$I = \sum m_i r_i^2 = \mu r_e^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \text{reduced mass}$$

↪ 2-body problem changed to single point mass

■ Quantum Mechanics

Value of ω_{rot} is quantized

$$I\omega_{\text{rot}} = \sqrt{J(J+1)}(\hbar = h/2\pi)$$



Rot. quantum number = 0, 1, 2, ...
 $\therefore E_{\text{rot}}$ is quantized!

■ Rotational Energy

$$E_{\text{rot}} = \frac{1}{2} I \omega_{\text{rot}}^2 = \frac{1}{2I} (I\omega_{\text{rot}})^2 = \frac{1}{2I} J(J+1)\hbar^2 = J(J+1) \frac{h^2}{8\pi^2 I}$$

Convention is to denote rotational energy as $F(J)$, cm^{-1}

$$F(J), \text{cm}^{-1} = \frac{E_{\text{rot}}}{hc} = \left[\frac{h}{8\pi^2 Ic} \right] J(J+1) = BJ(J+1)$$

Note : $E, J = h\nu = \frac{hc}{\lambda} = hc(\bar{\nu}, \text{cm}^{-1})$ so (energy, cm^{-1}) = (energy, J)/hc

2. Rigid-Rotor model of diatomic molecule

- Rotational spectrum

Schrödinger's Equation:
$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - U(x)]\psi(x) = 0$$

Transition probability $\propto \int \psi_m \mu \psi_n^* d\tau \rightarrow \underline{\Delta J = \pm 1}$

ψ	Wave function
ψ^*	Complex conjugate
μ	Dipole moment

Selection Rules for rotational transitions

$$\Delta J = \begin{matrix} \text{' (upper)} \\ \downarrow \\ J' \end{matrix} - \begin{matrix} \text{' (lower)} \\ \downarrow \\ J'' \end{matrix} = +1$$

Recall: $F(J) = BJ(J+1)$

e.g., $\bar{\nu}_{J=1 \leftarrow J=0} = F(J=1) - F(J=0) = 2B - 0 = 2B$

2. Rigid-Rotor model of diatomic molecule

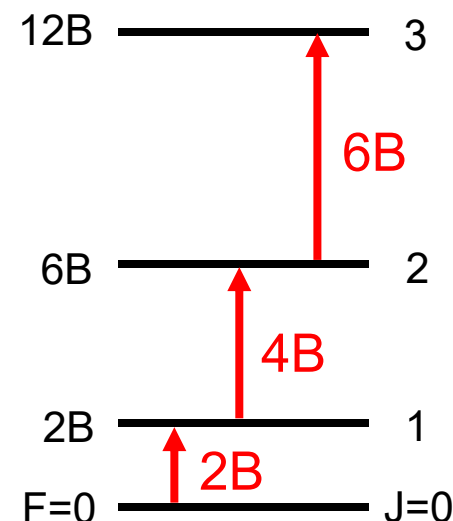
- Rotational spectrum

Remember that: $F(J) = BJ(J+1)$

E.g., $\bar{\nu}_{J=1 \leftarrow J=0} = F(J=1) - F(J=0) = 2B - 0 = 2B$

J	F	1 st diff = $\bar{\nu}$	2 nd diff = spacing
0	0		
1	2B	2B	2B
2	6B	4B	2B
3	12B	6B	2B
4	20B	8B	2B

Lines every 2B!



In general: $\bar{\nu}_{J+1 \leftarrow J} = \bar{\nu}_{J' \leftarrow J''} = B(J''+1)(J''+2) - BJ''(J''+1)$

$$\bar{\nu}_{J' \leftarrow J''}, cm^{-1} = 2B(J''+1)$$

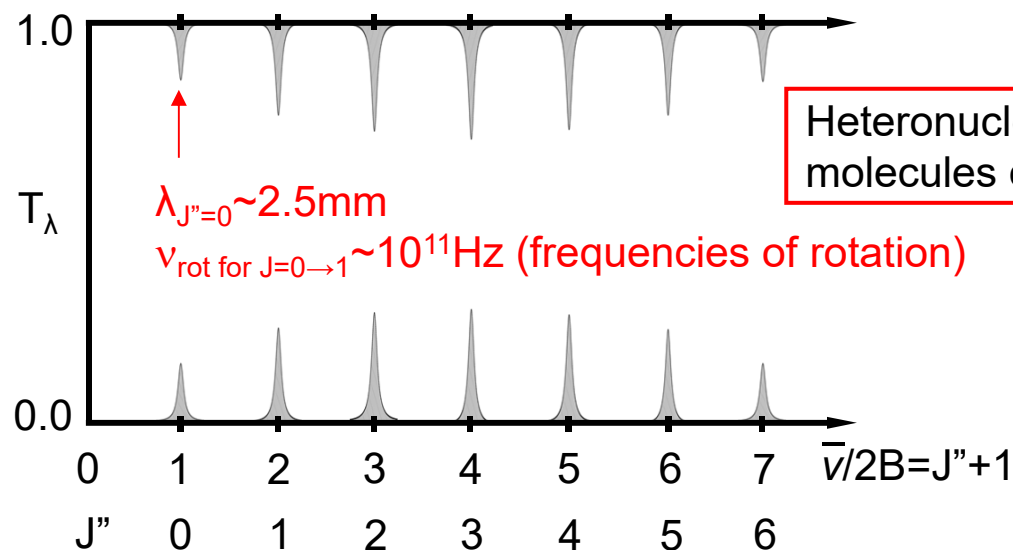
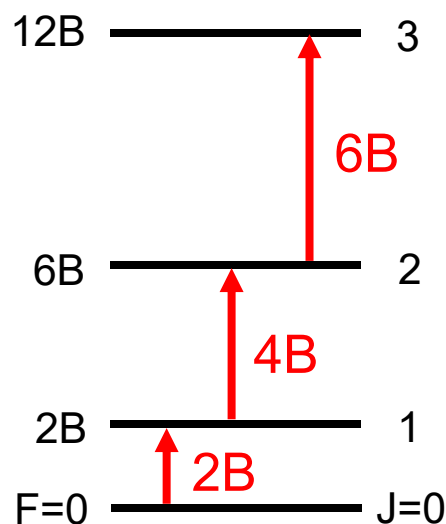
Let's look at absorption spectrum

2. Rigid-Rotor model of diatomic molecule

■ Rotational spectrum

Recall: $F(J) = BJ(J+1)$

E.g., $\bar{\nu}_{J=1 \leftarrow J=0} = F(J=1) - F(J=0) = 2B - 0 = 2B$



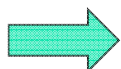
Note:

1. Uniform spacing (easy to identify/interpret)
2. $B_{\text{CO}} \sim 2\text{ cm}^{-1} \Rightarrow \lambda_{J''=0} = 1/\bar{\nu} = 1/4\text{ cm} = 2.5\text{mm}$ (microwave/mm waves)
3. $\nu_{\text{rot}, J=1} = c/\lambda = 3 \times 10^{10}/0.25\text{ Hz} = 1.2 \times 10^{11}\text{Hz}$ (microwave)

2. Rigid-Rotor model of diatomic molecule

- Usefulness of rotational spectra

Measured spectra



Physical characteristics of molecule

$$\begin{array}{c} \text{Line spacing} \\ = 2B \end{array} \Rightarrow B = \frac{h}{8\pi^2 I c} \Rightarrow I = \mu r_e^2 \Rightarrow \mathbf{r_e} \text{ Accurately!}$$

Example: CO

$$B = 1.92118 \text{ cm}^{-1} \rightarrow r_{\text{CO}} = 1.128227 \text{ \AA}$$



$$10^{-6} \text{ \AA} = 10^{-16} \text{ m!}$$

2. Rigid-Rotor model of diatomic molecule

- Intensities of spectral lines

Equal probability assumption (crude but useful)

- ✓ Abs. (or emiss.) probability per molecule is (crudely) independent of J
- ✓ Abs. (or emiss.) spectrum varies w/ J like Boltzmann distribution

↓ Degeneracy is a QM result associated w/ possible directions of Angular Momentum vector

Recall:
$$\frac{N_J}{N} = \frac{(2J+1)\exp(-E_J/kT)}{Q_{rot}} = \frac{(2J+1)\exp[-\theta_r J(J+1)/T]}{T/\theta_r}$$

$$\frac{E_J}{k} = \frac{hcF(J)}{k} = \left(\frac{hc}{k}\right)BJ(J+1) = \theta_r J(J+1)$$

Partition function:
$$Q_{rot} = \frac{1}{\sigma} \frac{kT}{hcB} = \frac{1}{\sigma} \frac{T}{\theta_r}$$

↑ Symmetric no. (ways of rotating to achieve same orientation) = 1 for microwave active

Define rotational T:
$$\theta_r [K] = \left(\frac{hc}{k}\right)B$$

CO: $\sigma=1 \rightarrow$ microwave active!

N₂: $\sigma=2 \rightarrow$ microwave inactive!

2. Rigid-Rotor model of diatomic molecule

- Intensities of spectral lines

Rotational Characteristic Temperature: $\theta_r [K] = \left(\frac{hc}{k} \right) B$

Species	$\theta_{rot} [K]$
O ₂	2.1
N ₂	2.9
NO	2.5
Cl ₂	0.351

$$\frac{hc}{k} = 1.44 K / cm^{-1}$$

$$\frac{N_J}{N} = \frac{(2J+1) \exp[-\theta_r J(J+1)/T]}{T / \theta_r}$$

Strongest peak: occurs where the population is at a local maximum

$$\frac{d(N_J / N)}{dJ} = 0 \quad \Rightarrow \quad J_{\max} = (T / 2\theta_{rot})^{1/2} - 1/2 = f(T / \theta_{rot})$$



2. Rigid-Rotor model of diatomic molecule

- Effect of isotopic substitution

Recall: $B = \frac{h}{8\pi^2 I_C}$

Changes in nuclear mass (neutrons) do not change r_0

- r depends on binding forces, associated w/ charged particles
- Can determine mass from B

Therefore, for example:

$$\frac{B(^{12}\text{C}^{16}\text{O})}{B(^{13}\text{C}^{16}\text{O})} = \frac{1.92118}{1.83669} \Rightarrow m_{^{13}\text{C}} = 13.0007$$

$(m_{^{12}\text{C}} = 12.00)$

➡ Agrees to 0.02% of other determinations

3. Non-Rigid Rotation

- Two effects; follows from $B \propto 1/r^2$

- Vibrational stretching $r(v)$

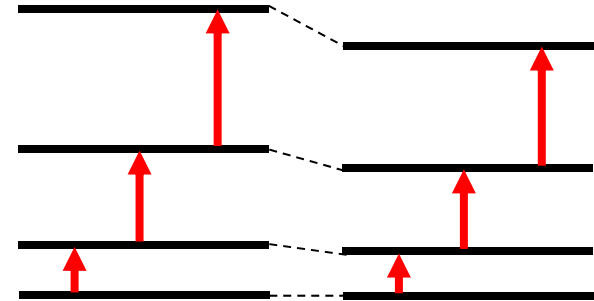
$v \uparrow \quad r \uparrow \quad B \downarrow$

- Centrifugal distortion $r(J)$

$J \uparrow \quad r \uparrow \quad B \downarrow$



Effects shrink line spacings/energies



Result: $F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2$



$$\bar{\nu}_{J' \leftarrow J'', v} = 2B_v(J''+1) - 4D_v(J''+1)^3$$

Centrifugal distribution constant

Notes: 1. But D is small; where $D = \frac{4B^3}{\omega_e^2} \ll B$

since $\left(\frac{D}{B}\right)_{NO} = 4\left(\frac{B}{\omega_e}\right)^2 \approx 4\left(\frac{1.7}{1900}\right)^2 \approx 3 \times 10^{-6}$

→ D/B smaller for “stiff/hi-freq” bonds

3. Non-Rigid Rotation

- Notes: 1. D is small; $D = \frac{4B^3}{\omega_e^2} \ll B$

$$\text{e.g., } \left(\frac{D}{B}\right)_{NO} = 4\left(\frac{B}{\omega_e}\right)^2 \approx 4\left(\frac{1.7}{1900}\right)^2 \approx 3 \times 10^{-6}$$

→ D/B smaller for “stiff/hi-freq” bonds

- 2. v dependence is given by $B_v = B_e - \alpha_e(v + 1/2)$

$$D_v = D_e - \beta_e(v + 1/2)$$

E.g., NO

$$B_e = 1.7046 \text{ cm}^{-1} \quad \alpha_e / B_e \sim 0.01$$

$$\alpha_e = 0.0178 \quad \beta_e / D_e \sim 0.001$$

$$D_e \cong 5.8 \times 10^{-6} ({}^2\Pi_{1/2})$$

$$\beta_e \cong 0.0014 D_e \sim 8 \times 10^{-9} \text{ cm}^{-1}$$

$$\omega_e = 1904.03 ({}^2\Pi_{1/2}); 1903.68 ({}^2\Pi_{3/2})$$

$$\omega_e x_e = 13.97 \text{ cm}^{-1}$$

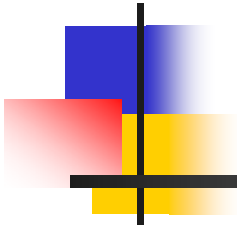
Aside:

$$\beta_e / D_e = \frac{8\omega_e x_e}{\omega_e} - \frac{5\alpha_e}{B_e} - \frac{\alpha_e^2 \omega_e}{24B_e^3} \ll 1$$

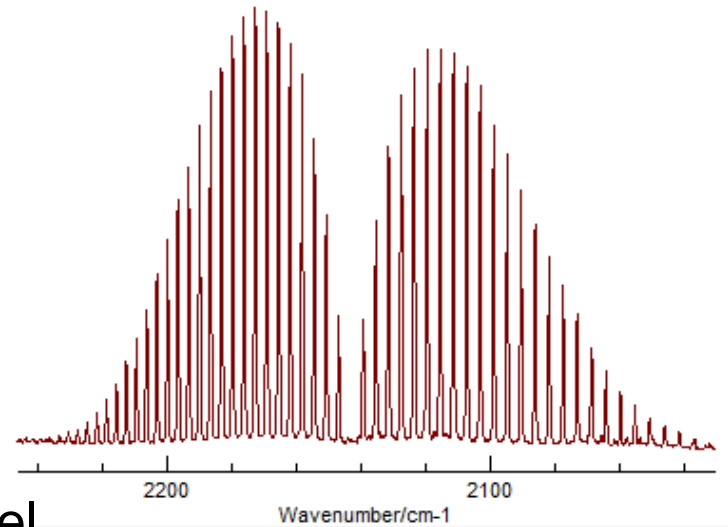
- Herzberg, Vol. I

e denotes “evaluated at equilibrium inter-nuclear separation” r_e

4. Vibration-Rotation Spectra (IR) (often termed Rovibrational)



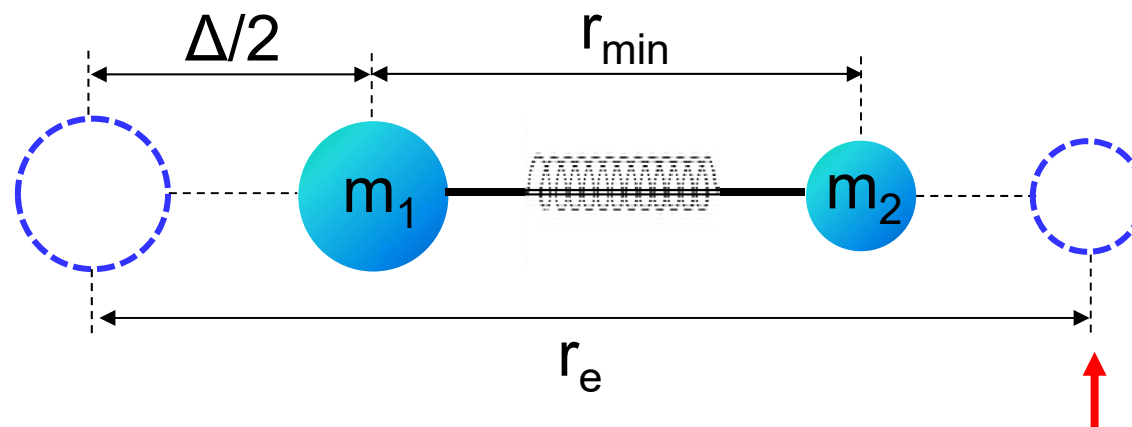
1. Diatomic Molecules
 - Simple Harmonic Oscillator (SHO)
 - Anharmonic Oscillator (AHO)
2. Vibration-Rotation spectra – Simple model
 - R-branch / P-branch
 - Absorption spectrum
3. Vibration-Rotation spectra – Improved model
4. Combustion Gas Spectra



Vibration-Rotation spectrum of CO
(from FTIR)

4.1. Diatomic Molecules

- Simple Harmonic Oscillator (SHO)



Molecule at instant of greatest compression

Equilibrium position (balance between attractive + repulsive forces) – i.e. min energy position

*As usual, we begin w. classical mechanics
+ incorporate QM only as needed*

4.1. Diatomic Molecules

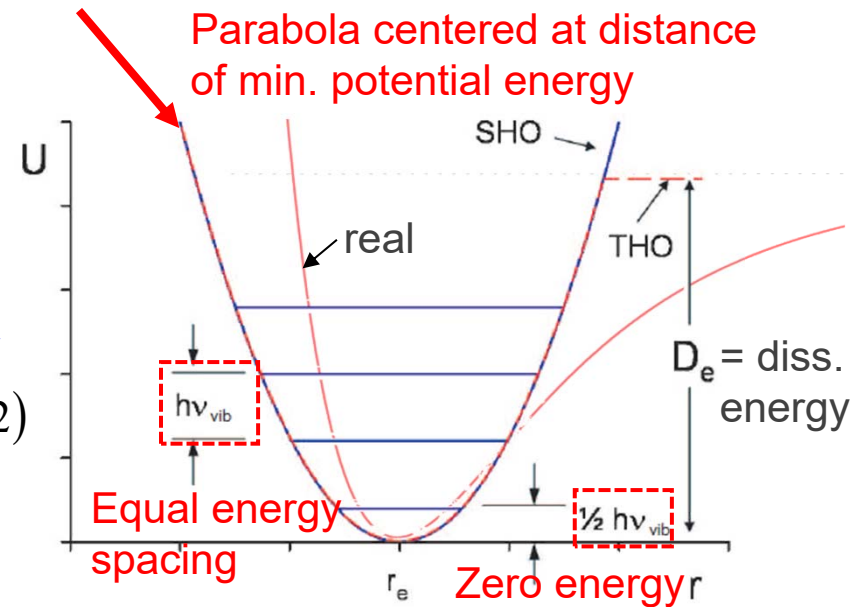
■ Simple Harmonic Oscillator (SHO)

Classical mechanics

- Force $= k_s(r - r_e)$ - Linear force law / Hooke's law
- Fundamental Freq. $\nu_{vib} = \frac{1}{2\pi} \sqrt{k_s / \mu}$ $\omega_e, cm^{-1} = \nu / c$
- Potential Energy $U = \frac{1}{2} k(r - r_e)^2$

Quantum mechanics

- v = vib. quantum no.
 $= 0, 1, 2, 3, \dots$
- Vibration energy $G = U/hc$
 $G(v), cm^{-1} = (\omega_e = \nu_{vib} / c)(v + 1/2)$
- Selection Rules:
 $\Delta v = v' - v'' = 1$ only!



4.1. Diatomic Molecules

Anharmonic Oscillator (AHO)

SHO

$$G(v), \text{cm}^{-1} = \omega_e (v + 1/2)$$



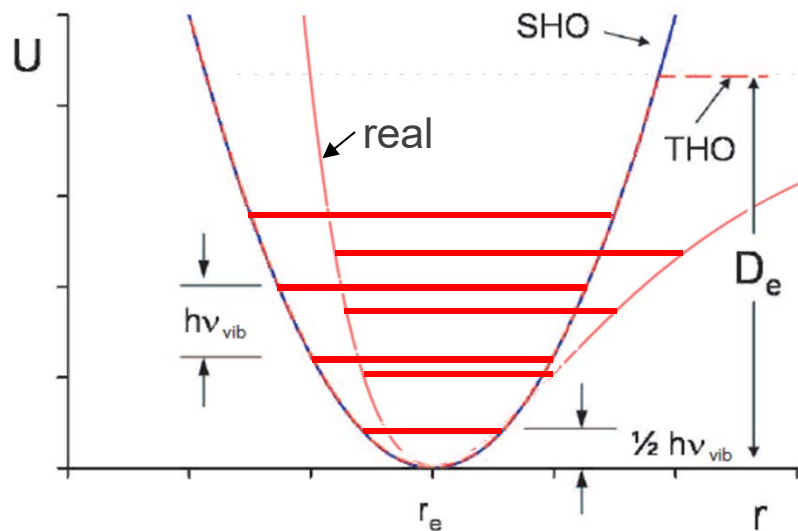
AHO

$$G(v), \text{cm}^{-1} = \omega_e (v + 1/2) - \underbrace{\omega_e x_e (v + 1/2)^2}_{\text{1st anharmonic correction}} + \dots + H.O.T.$$

Decreases energy spacing



1st anharmonic correction



$\Delta v = +1$	"Fundamental" Band (e.g., $1 \leftarrow 0, 2 \leftarrow 1$)	$\bar{\nu}_{1 \leftarrow 0} = G(1) - G(0)$ $= \omega_e (1 - 2x_e)$ $\bar{\nu}_{2 \leftarrow 1} = \omega_e (1 - 4x_e)$
$\Delta v = +2$	1 st Overtone (e.g., $2 \leftarrow 0, 3 \leftarrow 1$)	$\bar{\nu}_{2 \leftarrow 0} = 2\omega_e (1 - 3x_e)$
$\Delta v = +3$	2 nd Overtone (e.g., $3 \leftarrow 0, 4 \leftarrow 1$)	$\bar{\nu}_{3 \leftarrow 0} = 3\omega_e (1 - 4x_e)$

In addition, breakdown in selection rules

4.1. Diatomic Molecules

Vibrational Partition Function

$$Q_{vib} = \left[1 - \exp\left(\frac{-hc\omega_e}{kT}\right) \right]^{-1} \exp\left(\frac{-hc\omega_e}{2kT}\right)$$

Or choose reference (zero) energy at $v=0$, so $G(v) = \omega_e v$

then $\Rightarrow Q_{vib} = \left[1 - \exp\left(\frac{-hc\omega_e}{kT}\right) \right]^{-1}$

The same zero energy must be used in specifying molecular energies E_i for level i and in evaluating the associated partition function

Vibrational Temperature

$$\theta_{vib} [K] = \left(\frac{hc}{k} \right) \omega_e$$

$$\frac{N_{vib}}{N} = \frac{g_{vib} \exp(-v\theta_{vib}/T)}{Q_{vib}}$$

$$= \exp\left(-\frac{v\theta_{vib}}{T}\right) \left[1 - \exp\left(-\frac{\theta_{vib}}{T}\right) \right]$$

where $g_{vib} = 1$

Species	θ_{vib} [K]	θ_{rot} [K]
O ₂	2270	2.1
N ₂	3390	2.9
NO	2740	2.5
Cl ₂	808	0.351



4.1. Diatomic Molecules

- Some typical values (Banwell, p.63, Table 3.1)

Gas	Molecular Weight	Vibration ω_e [cm ⁻¹]	Anharmonicity constant x_e	Force constant k_s [dynes/cm]	Internuclear distance r_e [Å]	Dissociation energy D_{eq} [eV]
CO	28	2170	0.006	19×10^5	1.13	11.6
NO	30	1904	0.007	16×10^5	1.15	6.5
H ₂ [†]	2	4395	0.027	16×10^5	1.15	6.5
Br ₂ [†]	160	320	0.003	2.5×10^5	2.28	1.8

- [†] Not IR-active, use Raman spectroscopy!
- $\omega_e \propto \sqrt{k/\mu} \leftarrow \mu = m/2$ for homonuclear molecules
- $D_e \approx \omega_e / 4x_e \leftarrow$ large k , large D
- Weak, long bond \rightarrow loose spring constant \rightarrow low frequency



4.1. Diatomic Molecules

- Some useful conversions

- Energy $1 \text{ cal} = 4.1868 \text{ J}$

- $1 \text{ cm}^{-1} = 2.8575 \text{ cal/mole}$

- $1 \text{ eV} = 8065.54 \text{ cm}^{-1} = 23.0605 \text{ kcal/mole} = 1.60219 \times 10^{-19} \text{ J}$

- Force $1 \text{ N} = 10^5 \text{ dynes}$

- Length $1 \text{ \AA} = 0.1 \text{ nm}$

How many HO levels in a molecule? (Consider CO)

$$D_o = 256 \text{ kcal}$$

N = no. of HO levels

$$= \frac{256 \text{ kcal/mole}}{(2.86 \text{ cal/mole cm}^{-1})(2170 \text{ cm}^{-1})} \cong \underline{41}$$



Actual number is GREATER

as AHO shrinks level spacing

4.2. Vib-Rot spectra – simple model

- Born-Oppenheimer Approximation
 - Vibration and Rotation are regarded as **independent**
→ Vibrating rigid rotor

Energy: $T(v, J) = RR + SHO = F(J) + G(v)$
 $= BJ(J+1) + \omega_e(v + 1/2)$

Selection Rules: $\Delta v = +1$
 $\Delta J = \pm 1$



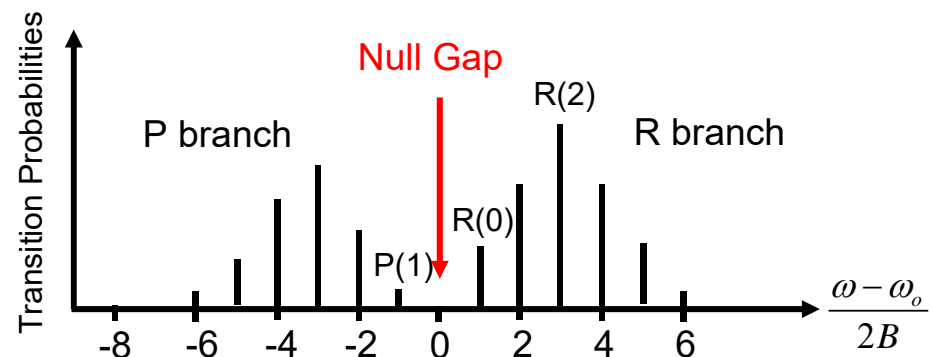
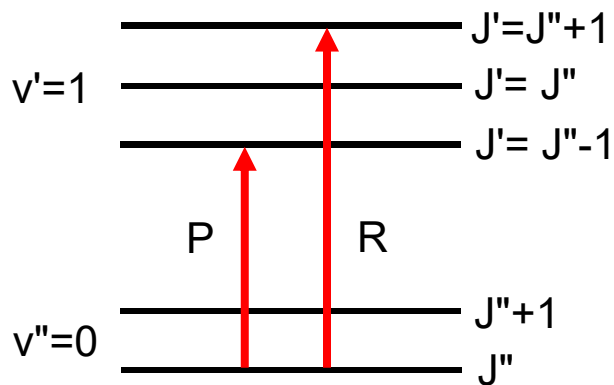
Two Branches: P ($\Delta J = -1$)
 R ($\Delta J = +1$)

$$\Delta J = J' - J''$$

Line Positions: $\bar{\nu} = T' - T'' = T(v', J') - T(v'', J'')$

Aside: Nomenclature for “branches”

■ Branch	O	P	Q	R	S
■ ΔJ	-2	-1	0	+1	+2



4.2. Vib-Rot spectra – simple model

- R-branch

- $R(J''), cm^{-1} = \underbrace{[G(v') - G(v'')]}_{\omega_o} + B(J''+1)(J''+2) - BJ''(J''+1)$

$\omega_o = \nu_o$ = Rotationless transition wavenumber

$= \omega_e$ (SHO)

$= \omega_e(1 - 2x_e)$ (AHO, $1 \leftarrow 0$)

$= \omega_e(1 - 4x_e)$ (AHO, $2 \leftarrow 1$)

$= \dots$

$$R(J'') = \omega_o + 2B(J''+1)$$



Note: spacing = $2B$, same as RR spectra

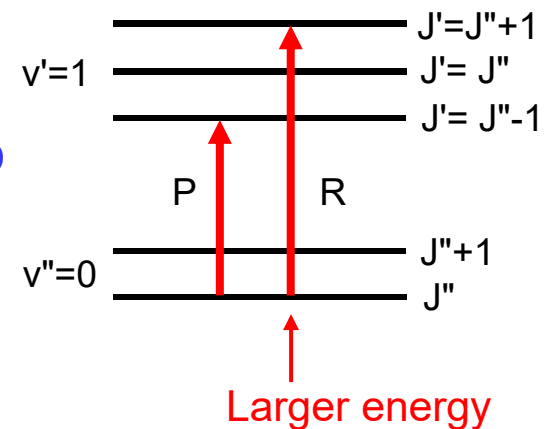
- P-branch

- $P(J'') = \omega_o - 2BJ''$



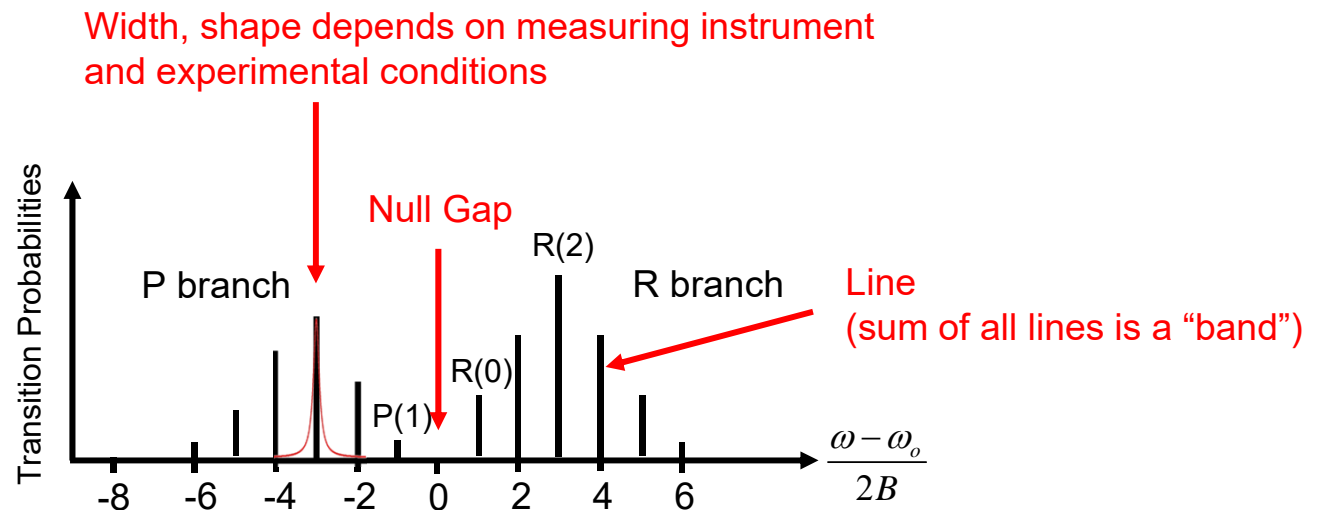
Note: $\omega_o = f(\nu'')$ for AHO

- P-R Branch peak separation $\Delta \bar{\nu} = \sqrt{\frac{8BkT}{hc}}$



4.2. Vib-Rot spectra – simple model

- Absorption spectrum (for molecule in $v'' = 0$)



- Height of line \propto amount of absorption $\propto N_J/N$
- “Equal probability” approximation – independent of J (as with RR)

What if we remove RR limit? \rightarrow Improved treatment

4.3. Vib-Rot spectra – improved model

- Breakdown of Born-Oppenheimer Approximation
 - Allows non-rigid rotation, anharmonic vibration, vib-rot interaction

$$\begin{aligned}
 T(v, J) &= G(v) + F(v, J) \\
 &= \underbrace{\omega_e(v + 1/2)}_{\text{SHO}} - \underbrace{\omega_e x_e(v + 1/2)^2}_{\text{Anharm. corr.}} + \underbrace{B_v J(J+1)}_{\text{RR}(v)} - \underbrace{D_v J^2(J+1)^2}_{\text{Cent. dist. term}}
 \end{aligned}$$

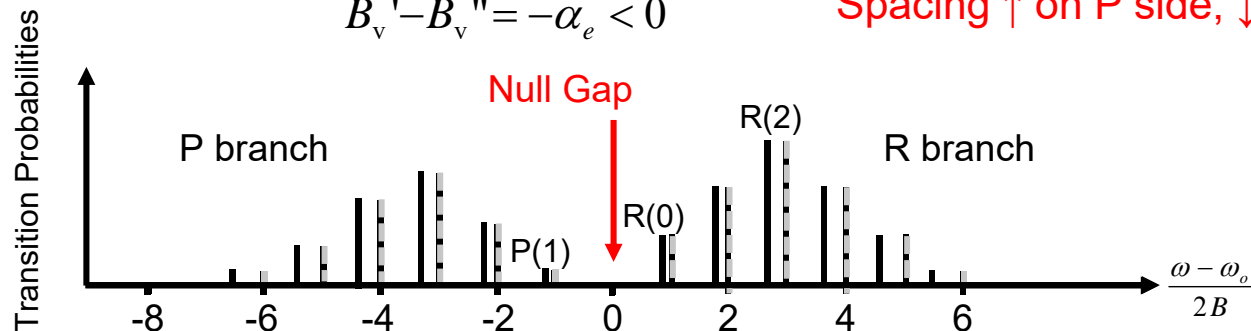
B(v)

- **R-branch** $R(v'', J'') = \omega_o(v'') + 2B_v' + (3B_v' - B_v'')J'' + (B_v' - B_v'')J''^2$
- **P-branch** $P(v'', J'') = \omega_o(v'') - (B_v' + B_v'')J'' + (B_v' - B_v'')J''^2$

$$B_v = B_e - \alpha_e(v + 1/2) \quad \left\{ \begin{array}{l} B_v' = B_e' - \alpha_e(v' + 1/2) \\ B_v'' = B_e'' - \alpha_e(v'' + 1/2) \end{array} \right. \quad \Rightarrow \quad B_v' < B_v''$$

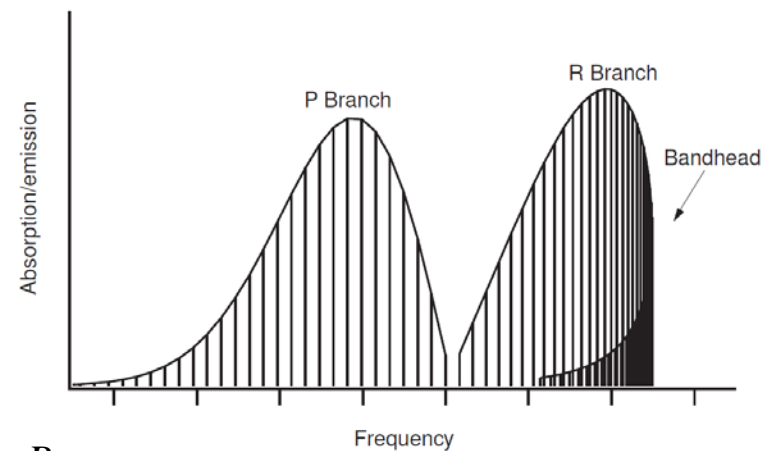
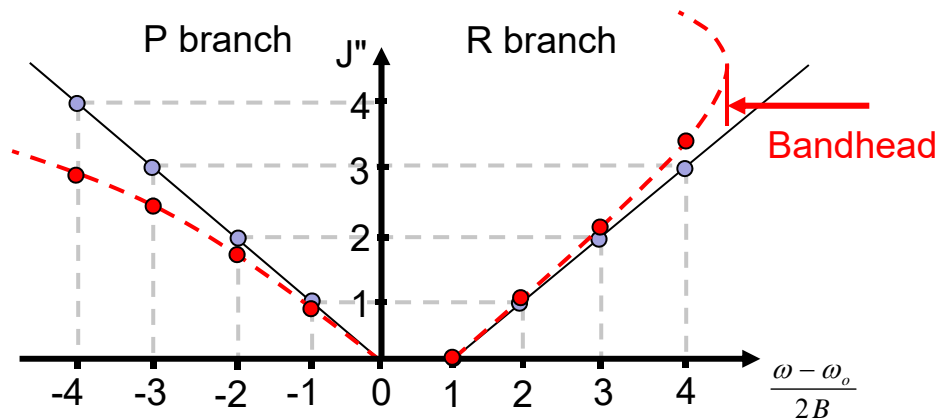
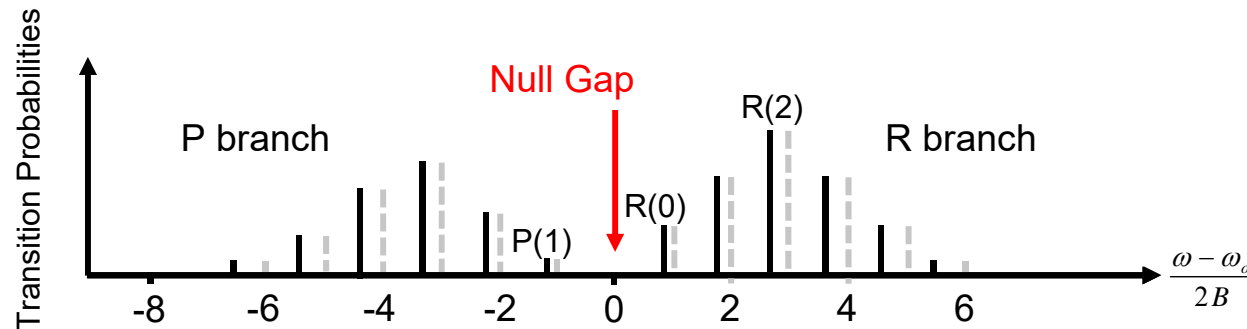
$$B_v' - B_v'' = -\alpha_e < 0$$

Spacing ↑ on P side, ↓ on R side



4.3. Vib-Rot spectra – improved model

■ Bandhead



$$\frac{dR(J)}{dJ} = \underbrace{(3B' - B'')}_{2B' - \alpha_e} + 2 \underbrace{(B' - B'')}_{-\alpha_e} J'' = 0 \quad \Rightarrow \quad J''_{\text{bandhead}} \approx \frac{2B' - \alpha_e}{2\alpha_e} \approx \frac{B}{\alpha_e}$$

E.g., CO $\frac{B}{\alpha_e} \approx \frac{1.9}{0.018} \approx 106 \rightarrow$ not often observed

4.3. Vib-Rot spectra – improved model

- Finding key parameters: B_e , α_e , ω_e , x_e

- 1st Approach:

Use measured band origin data for the fundamental and first overtone, i.e., $\Delta G_{1 \leftarrow 0}$, $\Delta G_{2 \leftarrow 0}$, to get ω_e , x_e

$$\begin{aligned} \Delta G_{1 \leftarrow 0} &= G(1) - G(0) = \omega_e(1 - 2x_e) \\ \Delta G_{2 \leftarrow 0} &= G(2) - G(0) = 2\omega_e(1 - 3x_e) \end{aligned} \Rightarrow \omega_e, x_e$$

- 2nd Approach:

Fit rotational transitions to the line spacing equation to get B_e and α

$$\omega = \omega_o + (B' + B'')m + (B' - B'')m^2$$

$$m = J + 1 \text{ in R - branch}$$

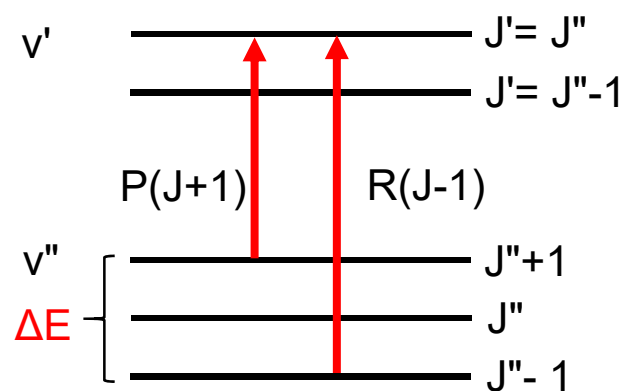
$$m = -J \text{ in P - branch}$$

$$\begin{aligned} B' &= B_e - \alpha_e (v' + 1/2) \\ B'' &= B_e - \alpha_e (v'' + 1/2) \end{aligned}$$

$$\Rightarrow B', B'' \Rightarrow B_e, \alpha$$

4.3. Vib-Rot spectra – improved model

- Finding key parameters: B_e , α_e , ω_e , x_e
 - 3rd Approach: Use the “method of common states”

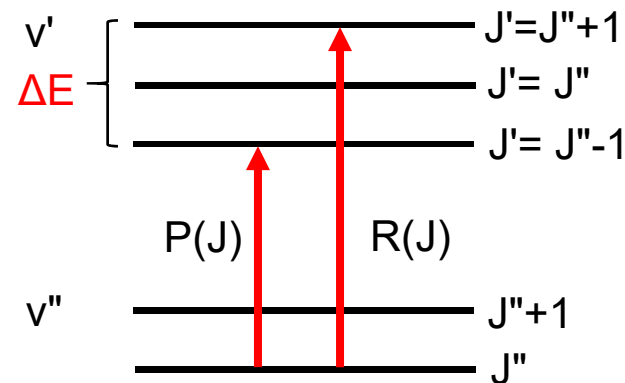


← Common upper-state

In general $F(J) = BJ(J+1)$

$$\begin{aligned}\Delta E &= F(J+1) - F(J-1) \\ &= R(J-1) - P(J-1) \\ &= B''(J+1)(J+2) - B''(J-1)J\end{aligned}$$

$$\therefore \Delta E = B''(4J+2) \Rightarrow B''$$



$$\begin{aligned}\Delta E &= F(J+1) - F(J-1) \\ &= B'(J+1)(J+2) - B'(J-1)J\end{aligned}$$

$$\therefore \Delta E = B'(4J+2) \Rightarrow B'$$

← Common lower-state

B_e, α

4.3. Vib-Rot spectra – improved model

- Isotopic effects

$$B \propto \frac{1}{I} \propto \frac{1}{\mu} \rightarrow \text{Line spacing changes as } \mu \text{ changes}$$

$$\omega_e \propto \sqrt{\frac{k_s}{\mu}} \propto \sqrt{\frac{1}{\mu}} \rightarrow \text{Band origin changes as } \mu \text{ changes}$$

1st Example: CO Isotope $^{13}\text{C}^{16}\text{O}$

$$\frac{\mu_{^{13}\text{C}^{16}\text{O}}}{\mu_{^{12}\text{C}^{16}\text{O}}} = 1.046 \quad \blacksquare \quad B_{^{13}\text{C}^{16}\text{O}} = \frac{B_{^{12}\text{C}^{16}\text{O}}}{1.046}$$

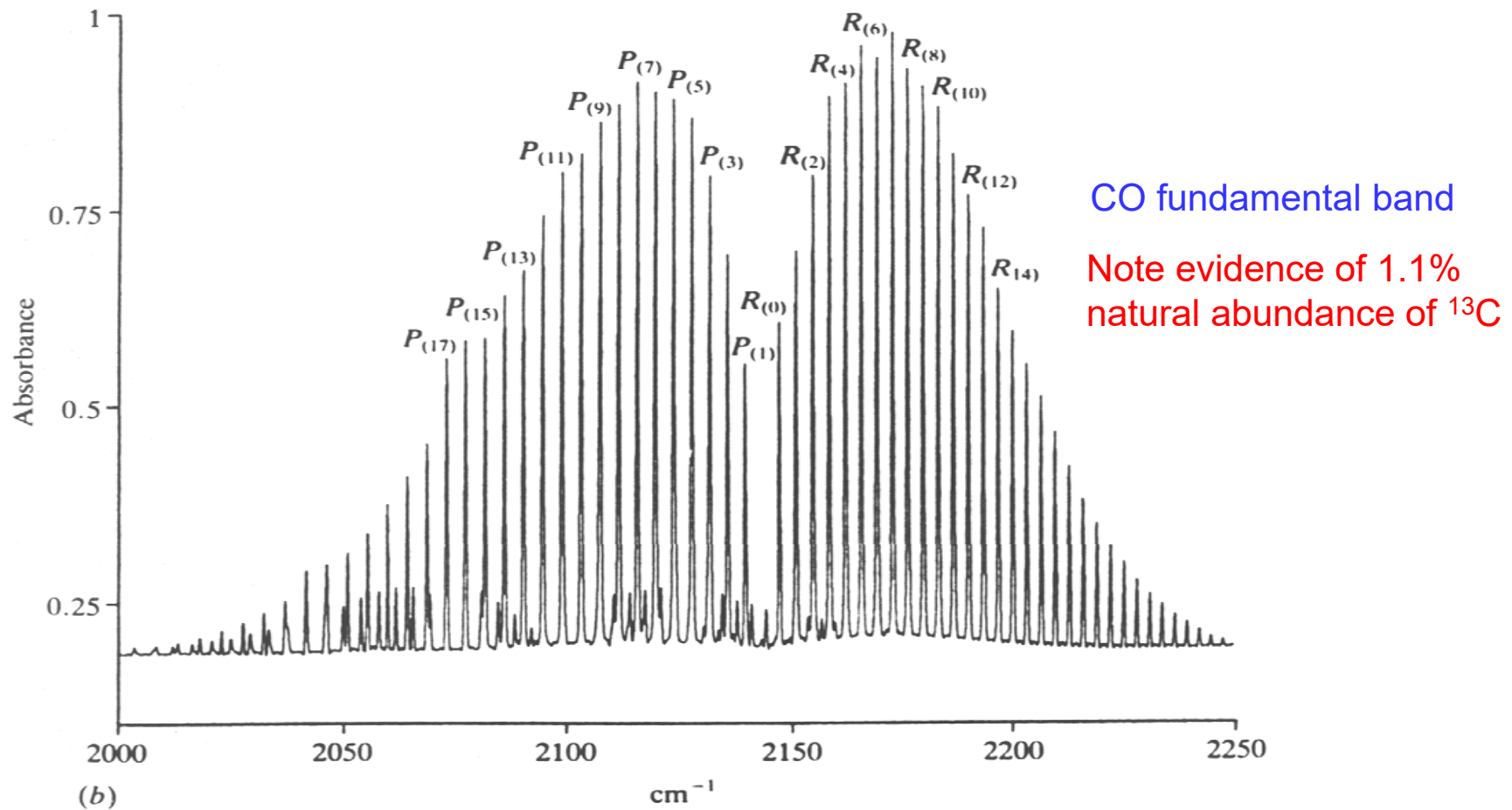
$$\Rightarrow \Delta(2B) = -0.046 \times 3.88 \approx -0.17 \text{ cm}^{-1}$$

$$\blacksquare \quad \omega_{e\ ^{13}\text{C}^{16}\text{O}} = \frac{\omega_{e\ ^{12}\text{C}^{16}\text{O}}}{\sqrt{1.046}}$$

$$\Rightarrow \Delta\omega_e = 0.046 \times 2200 / 2 \approx 50 \text{ cm}^{-1}$$

4.3. Vib-Rot spectra – improved model

- Isotopic effects





4.3. Vib-Rot spectra – improved model

- Isotopic effects

$$B \propto \frac{1}{I} \propto \frac{1}{\mu} \rightarrow \text{Line spacing changes as } \mu \text{ changes}$$

$$\omega_e \propto \sqrt{\frac{k_s}{\mu}} \propto \sqrt{\frac{1}{\mu}} \rightarrow \text{Band origin changes as } \mu \text{ changes}$$

2nd Example: HCl Isotope H^{35}Cl and H^{37}Cl

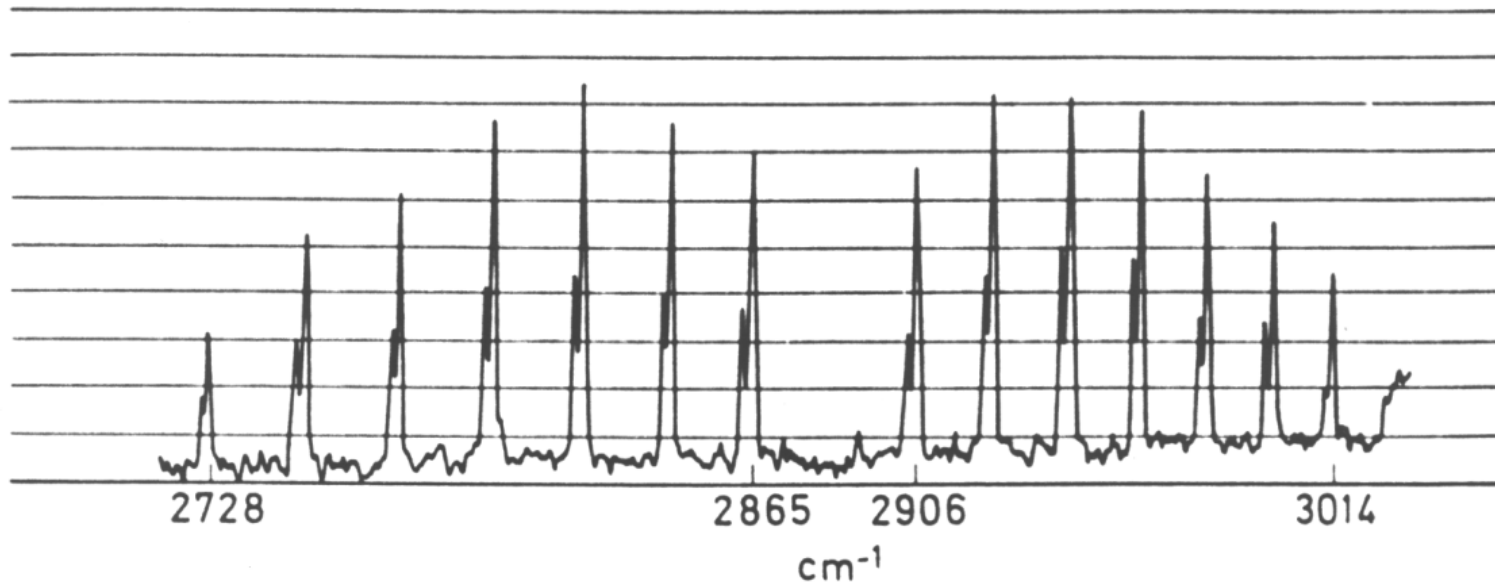
- $[H^{35}Cl] \cong 3[H^{37}Cl]$
- $\mu_{37} / \mu_{35} = \frac{37.1/38}{35.1/36} \cong 1.0015$

➡ Shift in ω_e is $.00075\omega_e = 2.2\text{cm}^{-1} \rightarrow \text{Small!}$

4.3. Vib-Rot spectra – improved model

- Isotopic effects

HCl fundamental band



Note isotropic splitting due to H³⁵Cl and H³⁷Cl

4.3. Vib-Rot spectra – improved model

- Hot bands

When are hot bands (bands involving excited states) important?

$$\frac{N_v}{N} = \frac{g \exp\left(-\frac{v\theta_v}{T}\right)}{Q_{vib}} = \exp\left(-\frac{v\theta_v}{T}\right) \left[1 - \exp\left(-\frac{\theta_v}{T}\right)\right]$$

E.g. $\theta_{v,CO} = 3000K$ $\frac{N_1}{N} = \begin{cases} e^{-10} \approx 0 & @300K \\ e^{-1}(1 - e^{-1}) \approx 0.23 & @3000K \end{cases}$



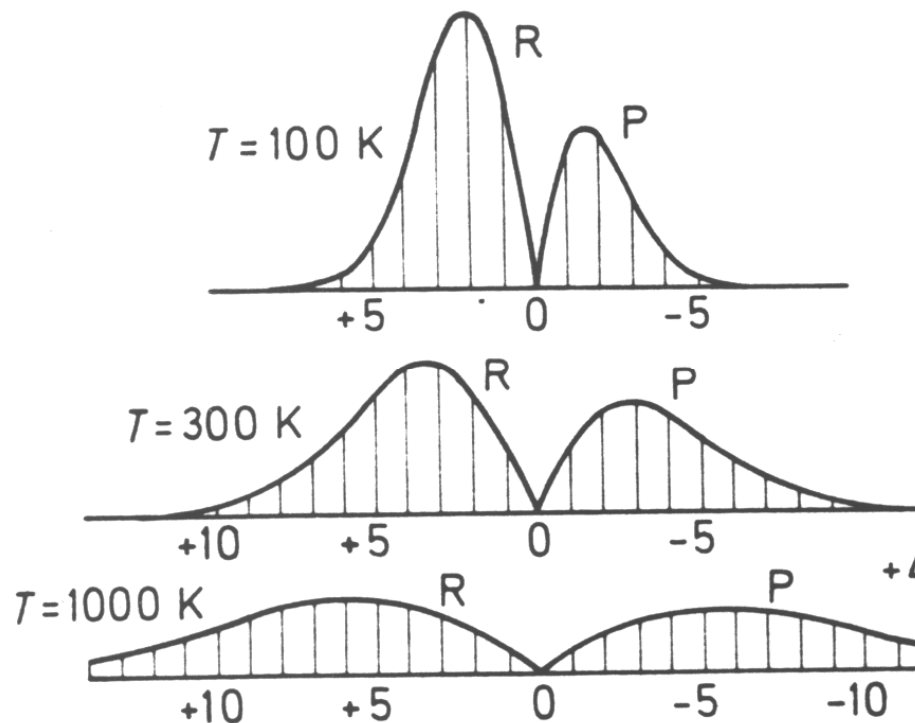
“Hot bands” become important when temperature is comparable to the characteristic vibrational temperature

Gas	$\bar{\nu}_{0 \rightarrow 1} (cm^{-1})$	$N_1 / N_0 = e^{-hc\bar{\nu}/kT}$	
		300K	1000K
H ₂	4160.2	2.16×10^{-9}	2.51×10^{-3}
HCl	2885.9	9.77×10^{-7}	1.57×10^{-2}
N ₂	2330.7	1.40×10^{-5}	3.50×10^{-2}
CO	2143.2	3.43×10^{-4}	4.58×10^{-2}
O ₂	1556.4	5.74×10^{-4}	1.07×10^{-1}
S ₂	721.6	3.14×10^{-2}	3.54×10^{-1}
Cl ₂	566.9	6.92×10^{-2}	4.49×10^{-1}
I ₂	213.1	2.60×10^{-1}	7.36×10^{-1}

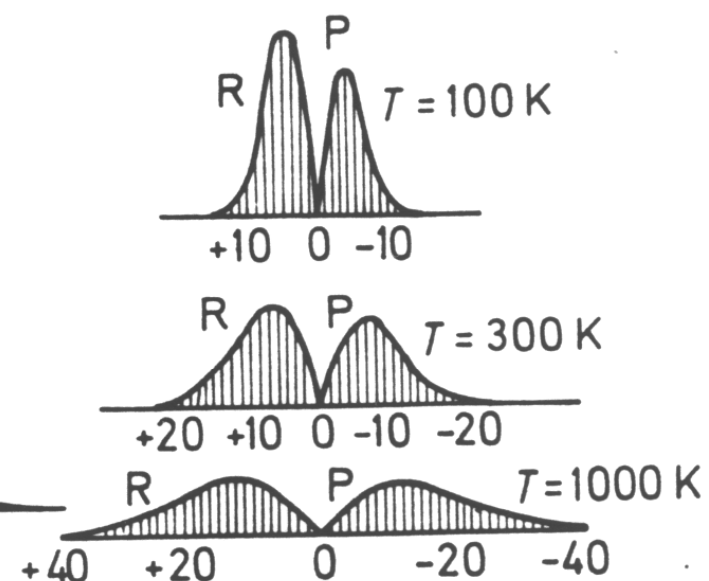
4.3. Vib-Rot spectra – improved model

- Examples of intensity distribution within the rotation-vibration band

$B = 10.44\text{cm}^{-1}$ (HCl)

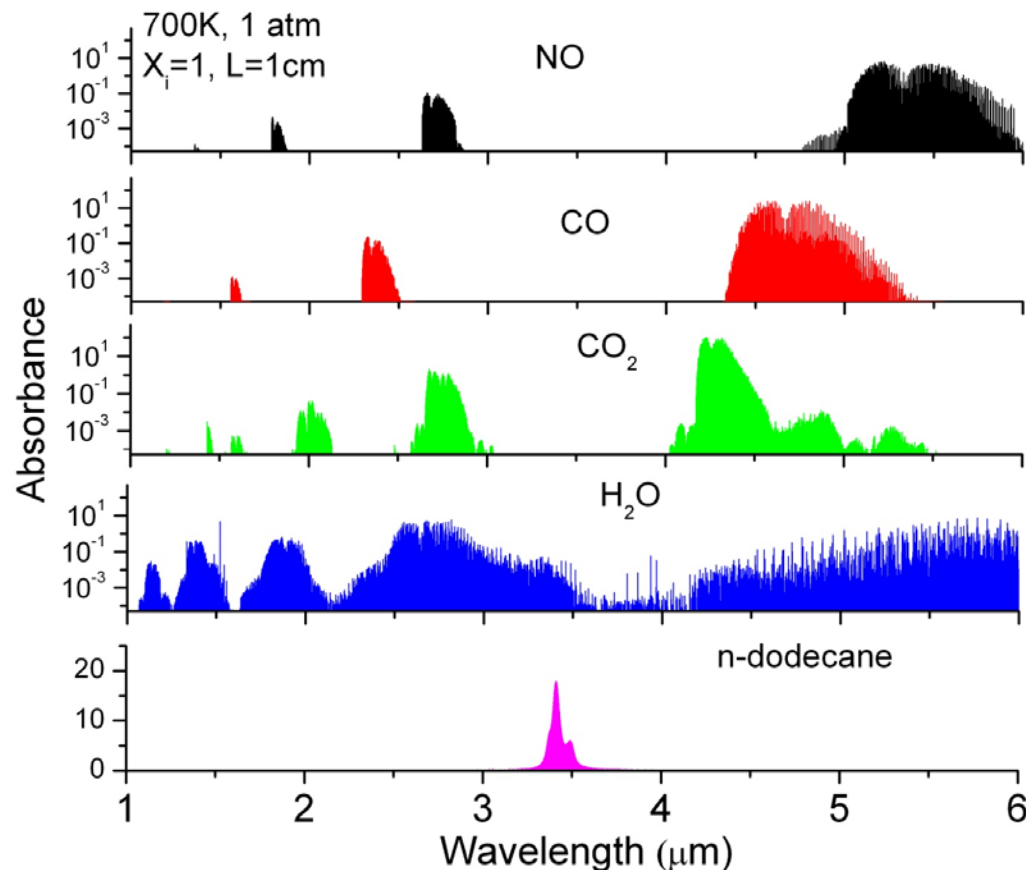


$B = 2\text{cm}^{-1}$ (CO)



4.4. Absorption Spectra for Combustion Gases

- TDL Sensors Provide Access to a Wide Range of Combustion Species/Applications



- Small species such as NO, CO, CO₂, and H₂O have discrete rotational transitions in the vibrational bands
- Larger molecules, e.g., hydrocarbon fuels, have blended spectral features



Next: Diatomic Molecular Spectra

- ❖ Electronic (Rovibronic) Spectra (UV, Visible)