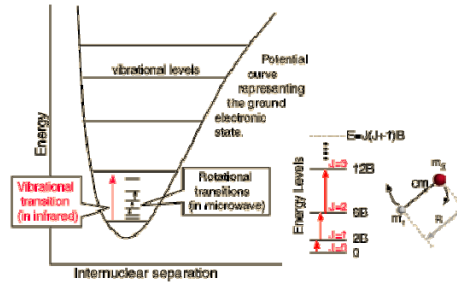


Quantitative Laser Diagnostics for Combustion Chemistry and Propulsion

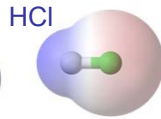
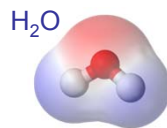
Lecture 2: Rotational and Vibrational Spectra

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

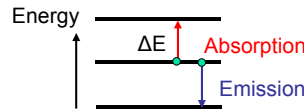


1. Light-matter interaction

- Possibilities of interaction
 - Permanent electric dipole moment
 - Rotation produces oscillating dipole (Emission/Absorption)

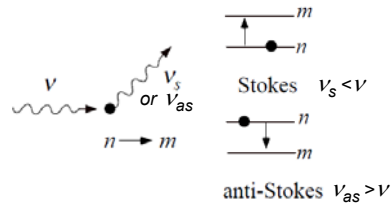
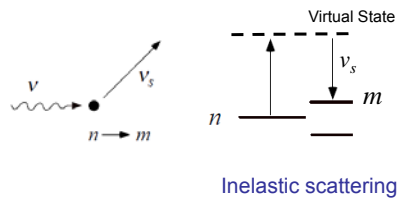


$\mu = qd$
What if Homonuclear?



- Induced polarization (Raman scattering)

- Elastic scattering (Rayleigh scattering)



1. Light-matter interaction

- Elements of spectra:
 - Line position
 - Line strength
 - Line shapes
- Spectral regions:
 - Rotation: Microwave Region (ΔJ)

Line position (λ) is determined by difference between **energy levels**

What determines the **energy levels**?

Quantum Mechanics!

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

$E_{\text{int}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}$

Are some molecules "Microwave inactive"? **YES, e.g., H₂, Cl₂, CO₂**

Time

3

1. Light-matter interaction

- Elements of spectra:
 - Line position
 - Line strength
 - Line shapes
- Spectral regions:
 - Rotation: Microwave Region (ΔJ)
 - Vibration: Infrared Region ($\Delta v, J$)

Heteronuclear case is IR-active

Are some vibrations "Infra-red inactive"? **Yes, e.g., symmetric stretch of CO₂**

$E_{\text{int}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}$

Time

4

1. Light-matter interaction

- Elements of spectra:
 - Line position
 - Line strength
 - Line shapes
- Spectral regions:
 - Rotation: Microwave Region (ΔJ)
 - Vibration: Infrared Region ($\Delta v, J$)
 - Electronic: UV & Visible Region ($\Delta \Lambda, v, J$)

$$E_{\text{int}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}$$

Photon ↑

C - O

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1. Light-matter interaction

- Regions of the spectrum

	Change of spin		Change of orientation	Change of configuration	Change of electron distribution		Change of nuclear configuration
	Radiofrequency		Microwave	Infra-red	Visible & Ultra-violet	X-ray	γ-ray
	Nuclear magnetic resonance	Electron spin resonance					
Wavenumber [cm ⁻¹]	10 ⁻²	1	100	10 ⁴	10 ⁶	10 ⁸	
Wavelength	10m	100cm	1cm	100μm	1μm	10nm	100pm
Frequency [Hz]	3x10 ⁶	3x10 ⁸	3x10 ¹⁰	3x10 ¹²	3x10 ¹⁴	3x10 ¹⁶	3x10 ¹⁸
Energy [J/mole]	10 ⁻³	10 ⁻¹	10	10 ³	10 ⁵	10 ⁷	10 ⁹

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1. Light-matter interaction

- Summary

$$E_{\text{int}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}$$

$\Delta E_{\text{rot}} < \Delta E_{\text{vib}} < \Delta E_{\text{elec}}$

- Energy levels are discrete
- Optically allowed transitions may occur only in certain cases
- Absorption/emission spectra are discrete

Current interest

➔ Rotation	Rigid Rotor	Non-rigid Rotor
Vibration	Simple Harmonic Oscillator	Anharmonic Oscillator

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2. Rigid-Rotor model of diatomic molecule

- Rigid Rotor

Center of mass **C**

$\sim 10^{-13}\text{cm}$
C: $r_1 m_1 = r_2 m_2$
 $r_1 + r_2 = r_e \sim 10^{-8}\text{cm}$

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

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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

- Rotational Energy

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

Convention to denote rot. energy

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

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu} \quad \therefore \epsilon_J = \frac{E_{rot}}{hc}$$

- Quantum Mechanics

Value of ω_{rot} is quantized

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



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

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2. Rigid-Rotor model of diatomic molecule

- Absorption spectrum

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

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

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: $F(J) = B J(J+1)$

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

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2. Rigid-Rotor model of diatomic molecule

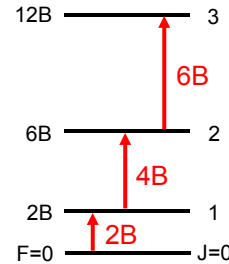
- Absorption spectrum

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

$\bar{\nu}_{J' \leftarrow J''}, \text{cm}^{-1} = 2B(J''+1)$ Let's look at absorption spectrum

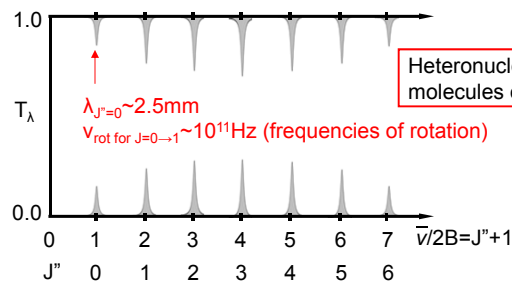
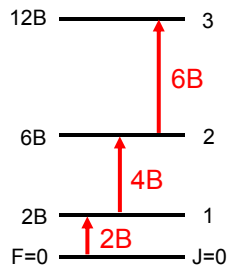
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2. Rigid-Rotor model of diatomic molecule

- Absorption 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:
- Uniform spacing (easy to identify/interpret)
 - $B_{\text{CO}} \sim 2 \text{cm}^{-1} \Rightarrow \lambda_{J''=0} = 1/\bar{\nu} = 1/4 \text{cm} = 2.5 \text{mm}$ (microwave/mm waves)
 - $\nu_{\text{rot}, J=1} = c/\lambda = 3 \times 10^{10} / .25 \text{ Hz} = 1.2 \times 10^{11} \text{ Hz}$ (microwave)

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2. Rigid-Rotor model of diatomic molecule

- Usefulness of rotational spectra

Measured spectra \rightarrow Physical characteristics of molecule

$$\text{Line spacing} = 2B \rightarrow B = \frac{h}{8\pi^2 Ic} \rightarrow I = \mu r_e^2 \rightarrow r_e \text{ Accurately!}$$

Example: CO

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

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

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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

\uparrow Degeneracy is a QM result associated w/ possible directions of ang. Mom. vector

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

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

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

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

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

CO: $\sigma=1 \rightarrow$ microwave active!
 N₂: $\sigma=2 \rightarrow$ microwave inactive!

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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: occur where the population is at a local maximum

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

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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

E.g.,

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

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

→ Agrees w/ 0.02% of other determinations

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3. Non-Rigid Rotation

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

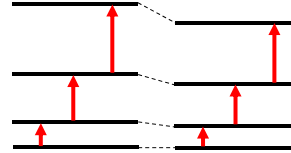
- Vibrational stretching $r(v)$

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

- Centrifugal distortion $r(J)$

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

Effects shrink line spacings/energies



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

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

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

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

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3. Non-Rigid Rotation

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

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:

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

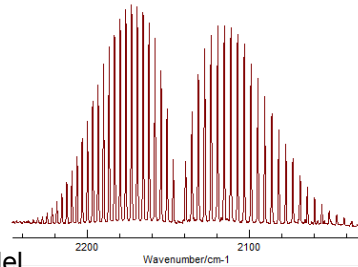
- Herzberg, Vol. I

e denotes "evaluated at equilibrium inter-nuclear separation" r_e

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4. Vibration-Rotation Spectra (IR)

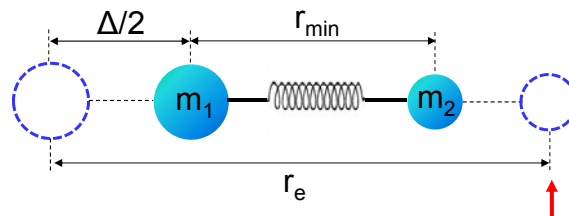
1. Diatomic Molecules
 - Simple Harmonic Oscillator (SHO)
 - Anharmonic Oscillator (AHO)
2. Vibration-Rotation spectra – Simple model
 - R-branch / P-branch
 - Absorption spectrum
3. Vibration-Rotation spectra – Improved model
4. Combustion Gas Spectra
 - Example Applications



Vibration-Rotation spectrum of CO
(from FTIR)

4.1. Diatomic Molecules

- Simple Harmonic Oscillator (SHO)



Molecule at instance of greatest compression

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

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

4.1. Diatomic Molecules

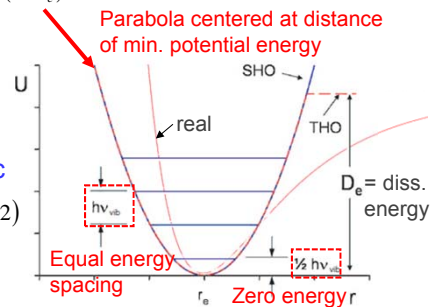
- Simple Harmonic Oscillator (SHO)

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, ...
- 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!



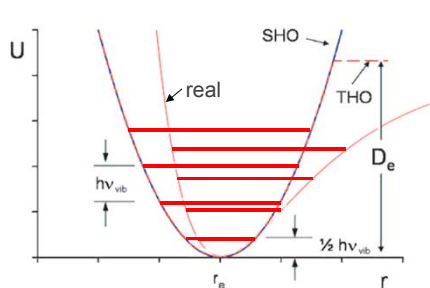
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4.1. Diatomic Molecules

- Anharmonic Oscillator (AHO)

SHO $G(v), cm^{-1} = \omega_e(v + 1/2)$ \rightarrow AHO $G(v), cm^{-1} = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \dots + H.O.T.$

Decreases energy spacing \leftarrow 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

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4.1. Diatomic Molecules

- Vibrational Partition Function

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

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

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

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

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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 x 10 ⁵	1.13	11.6
NO	30	1904	0.007	16 x 10 ⁵	1.15	6.5
H ₂ [†]	2	4395	0.027	16 x 10 ⁵	1.15	6.5
Br ₂ [†]	160	320	0.003	2.5 x 10 ⁵	2.28	1.8

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

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4.1. Diatomic Molecules

- Some useful conversions

- Energy
 - 1 cal = 4.1868 J
 - 1 cm⁻¹ = 2.8575 cal/mole
 - 1 eV = 8065.54 cm⁻¹ = 23.0605 kcal/mole = 1.60219 × 10⁻¹⁹ J
- Force
 - 1 N = 10⁵ dynes
- Length
 - 1 Å = 0.1 nm

How many HO levels? (Consider CO)

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

N = no. of HO levels

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

➡ Actual number is GREATER

as AHO shrinks level spacing

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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 ($\Delta J = +1$)

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

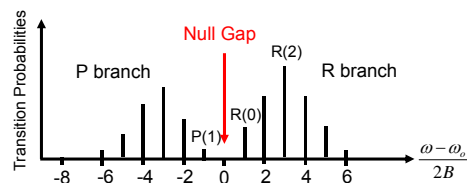
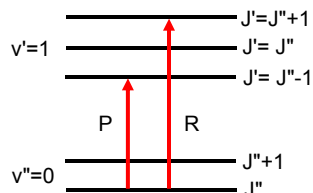
$$\Delta J = J' - J''$$

P ($\Delta J = -1$)

R ($\Delta J = +1$)

Aside: Nomenclature for "branches"

Branch	O	P	Q	R	S
ΔJ	-2	-1	0	+1	+2



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4.2. Vib-Rot spectra – simple model

- R-branch

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

$$\begin{aligned} \omega_0 = \nu_0 &= \text{Rotationless transition wavenumber} \\ &= \omega_e \text{ (SHO)} \\ &= \omega_e(1 - 2x_e) \text{ (AHO, } 1 \leftarrow 0) \\ &= \omega_e(1 - 4x_e) \text{ (AHO, } 2 \leftarrow 1) \\ &= \dots \end{aligned}$$

$$R(J'') = \omega_0 + 2B(J''+1)$$

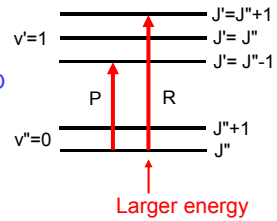
➡ Note: spacing = 2B, same as RR spectra

- P-branch

- $P(J'') = \omega_0 - 2BJ''$

➡ Note: $\omega_0 = f(\nu'')$ for AHO

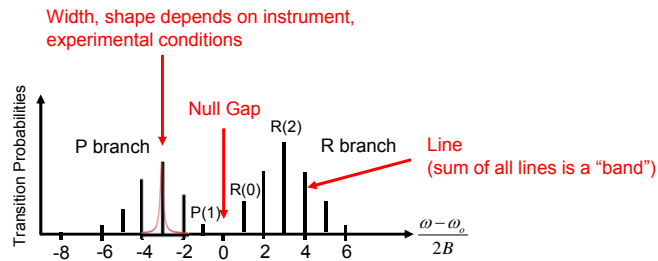
- P-R Branch peak separation $\Delta \bar{\nu} = \sqrt{\frac{8BkT}{hc}}$



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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

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4.3. Vib-Rot spectra – improved model

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

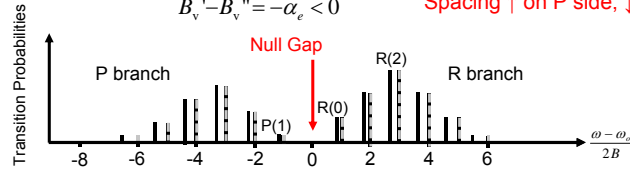
$$T(v, J) = G(v) + F(v, J)$$

$$= \underbrace{\omega_e(v+1/2)}_{\text{SHO}} - \underbrace{\omega_e x_e(v+1/2)^2}_{\text{Anharm. corr.}} + \underbrace{B_v J(J+1)}_{\text{RR}(v)} - \underbrace{D_v J^2(J+1)^2}_{\text{Cent. dist. term}}$$

- R-branch $R(v'', J'') = \omega_0(v'') + 2B_{v'} + (3B_{v'} - B_{v''})J'' + (B_{v'} - B_{v''})J''^2$
- P-branch $P(v'', J'') = \omega_0(v'') - (B_{v'} + B_{v''})J'' + (B_{v'} - B_{v''})J''^2$

$$B_v = B_e - \alpha_e(v+1/2) \begin{cases} B_{v'} = B_e - \alpha_e(v'+1/2) \\ B_{v''} = B_e - \alpha_e(v''+1/2) \end{cases} \Rightarrow B_{v'} < B_{v''}$$

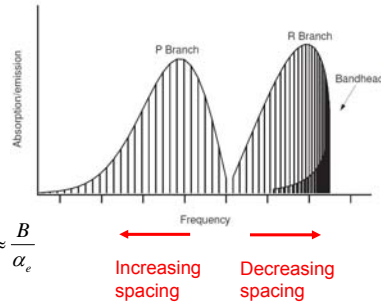
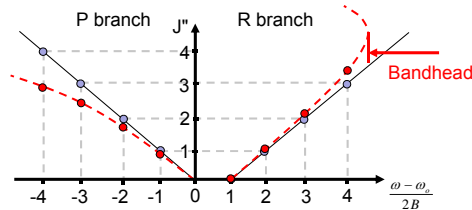
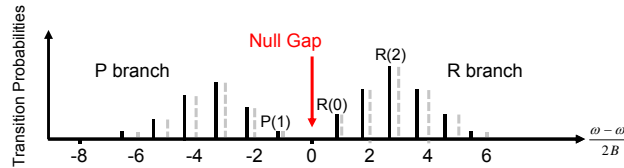
$$B_{v'} - B_{v''} = -\alpha_e < 0 \quad \text{Spacing } \uparrow \text{ on P side, } \downarrow \text{ on R side}$$



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4.3. Vib-Rot spectra – improved model

- Bandhead



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

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

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4.3. Vib-Rot spectra – improved model

- Finding key parameters: $B_e, \alpha_e, \omega_e, x_e$

- 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

$$\begin{aligned} \omega &= \omega_e + (B' + B'')m + (B' - B'')m^2 \\ m &= J + 1 \text{ in R-branch} \\ m &= -J \text{ in P-branch} \end{aligned}$$

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

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4.3. Vib-Rot spectra – improved model

- Finding key parameters: $B_e, \alpha_e, \omega_e, x_e$

- 3rd Approach: Use the “method of common states”

\leftarrow Common upper-state
 \leftarrow Common lower-state

In general $F(J) = BJ(J+1)$
 $\Delta E = F(J+1) - F(J-1)$
 $= R(J-1) - P(J-1)$
 $= B''(J+1)(J+2) - B''(J-1)J$
 $\therefore \Delta E = B''(4J+2) \Rightarrow B''$

$\Delta E = F(J+1) - F(J-1)$
 $= B'(J+1)(J+2) - B'(J-1)J$
 $\therefore \Delta E = B'(4J+2) \Rightarrow B'$

B_e, α

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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 $^{13}\text{C}^{16}\text{O}$

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

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

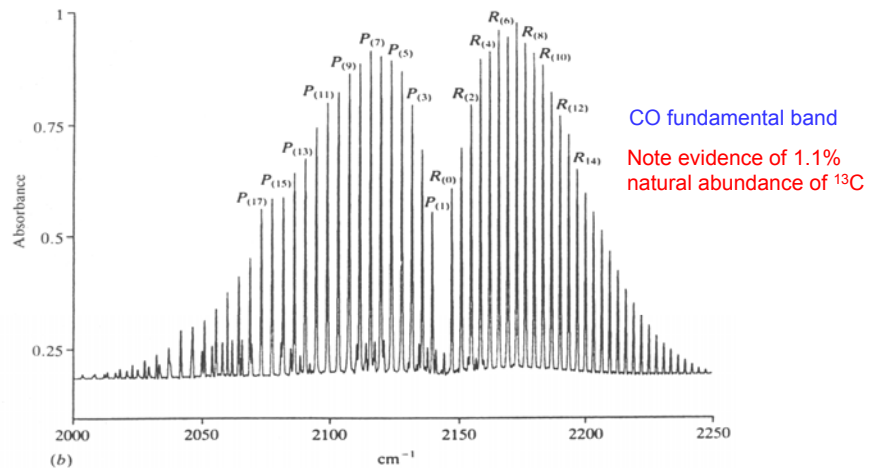
$$\blacksquare \quad \omega_e^{^{13}\text{C}^{16}\text{O}} = \frac{\omega_e^{^{12}\text{C}^{16}\text{O}}}{\sqrt{1.046}}$$

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

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4.3. Vib-Rot spectra – improved model

- Isotopic effects



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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 H³⁵Cl and H³⁷Cl

- $[H^{35}Cl] \cong 3[H^{37}Cl]$

- $\mu_{37} / \mu_{35} = \frac{37.1/38}{35.1/36} \cong 1.0015$

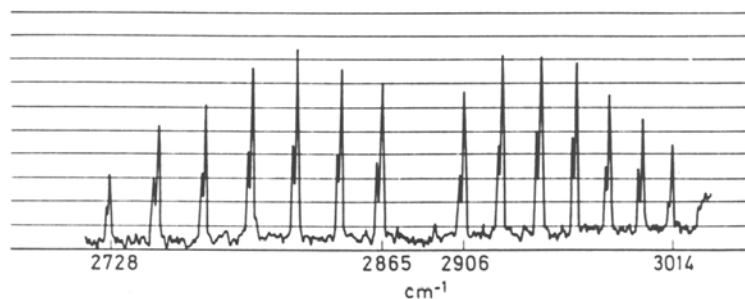
➡ Shift in ω_e is $.00075\omega_e = 2.2\text{cm}^{-1} \rightarrow \text{Small!}$

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4.3. Vib-Rot spectra – improved model

- Isotopic effects

HCl fundamental band



Note isotopic splitting due to H³⁵Cl and H³⁷Cl

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

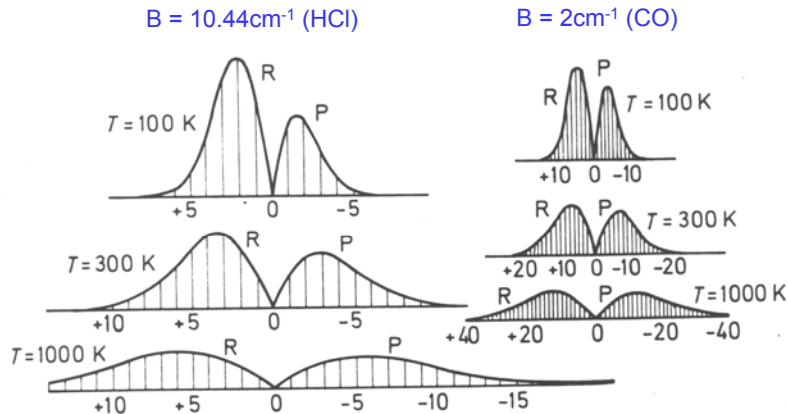
➔ "Hot bands" become important when temperature is comparable to the characteristic vibrational temperature

Gas	$\bar{\nu}_{0-1} (cm^{-1})$	$N_1 / N_0 = e^{-hc\bar{\nu}/kT}$	
		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}

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4.3. Vib-Rot spectra – improved model

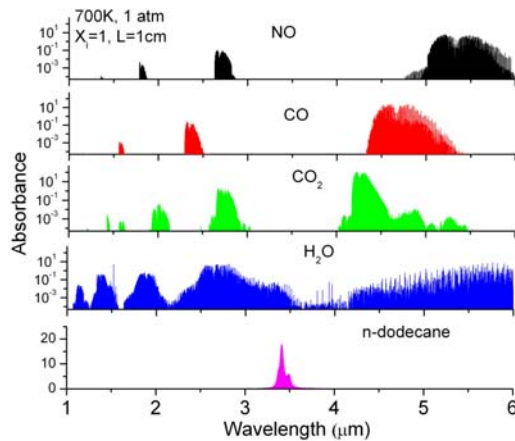
- Intensity distribution within the rotation-vibration band



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4.4. Absorption Spectra for Combustion Gases

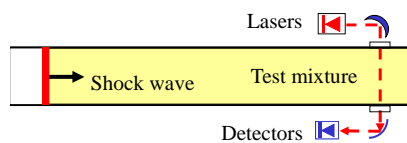
- TDL Sensors Provide Access to a Wide Range of Combustion Species/Applications



- 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
- Different strategies used to monitor discrete or blended absorption features using different strategies

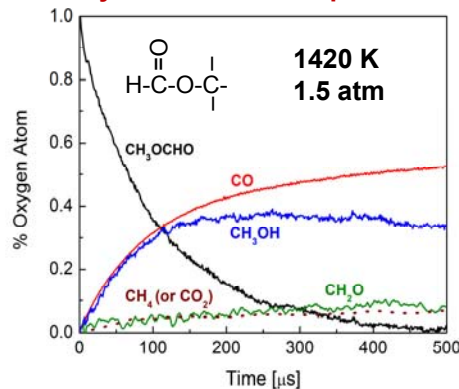
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4.5 Working Example of Absorption: First Multi-Species Sensing for Shock Tube Kinetics



- Multi-species time histories provide step-changing advantage for mechanism validation
- Chemistry progress monitored by quantitative laser absorption
- Multi-species strategy allows tracking of atomic species, e.g. O-atoms to determine key reaction rates

Oxygen Balance: Methyl Formate Decomposition





Next: Diatomic Molecular Spectra

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