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)

- Induced polarization (Raman scattering)

- Elastic scattering (Rayleigh scattering)

\[ \mu = q \mathbf{d} \]

What if Homonuclear?

\[ \Delta E \]

Absorption

Emission

Inelastic scattering

Stokes \( \nu_s < \nu \)

anti-Stokes \( \nu_{as} > \nu \)
1. Light-matter interaction

- Elements of spectra:
  - Line position
  - Line strength
  - Line shapes

- Internal Energy:
  \[ E_{\text{int}} = E_{\text{elec}}(n) + E_{\text{vib}}(v) + E_{\text{rot}}(J) \]

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

- Rotation: Microwave Region (\( \Delta J \))

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

Are some molecules "Microwave inactive"?
YES, e.g., \( H_2, Cl_2, CO_2 \)

**Diagram:**
- Energy levels for microwave region
- Microwave vs IR/Vis
- Electric dipole moment orientation
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 \((\Delta J)\)

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

Are some vibrations “Infra-red inactive”? Yes, e.g., symmetric stretch of CO\(_2\)
1. Light-matter interaction

Summary

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

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

\[ \Delta E_{\text{rot}} < \Delta E_{\text{vib}} < \Delta E_{\text{elec}} \]

Current interest

- **Rotation**
  - Rigid Rotor
  - Simple Harmonic Oscillator

- **Vibration**
  - Non-rigid Rotor
  - Anharmonic Oscillator
2. Rigid-Rotor model of diatomic molecule

- Rigid Rotor

![Diagram of Rigid Rotor](image)

- Axes of rotation
- Center of mass $C$
- $r_1$, $r_2$
- $m_1$, $m_2$
- $r_1 + r_2 = r_e \sim 10^{-8}\text{cm}$
- $C$: $r_1 m_1 = r_2 m_2$

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

- Rotational Energy
  \[ E_{\text{rot}} = \frac{1}{2} I \omega_{\text{rot}}^2 = \frac{1}{2I} (I \omega_{\text{rot}})^2 = \frac{1}{2I} J(J+1) \hbar^2 = J(J+1) \frac{\hbar^2}{8 \pi^2 I} \]
  Convention is to denote rot. energy as \( F(J), \text{cm}^{-1} \)

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

- Quantum Mechanics
  Value of \( \omega_{\text{rot}} \) is quantized
  \[ I \omega_{\text{rot}} = \sqrt{J(J+1)} (\hbar = \hbar / 2\pi) \]
  Rot. quantum number = 0, 1, 2, …
  \( \therefore \) \( E_{\text{rot}} \) is quantized!

So energy, cm\(^{-1} \) = (energy, \( J \))/\( hc \)
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

\[
\propto \int \psi_m \mu \psi_n^* d\tau \rightarrow \Delta J = \pm 1
\]

**Selection Rules** for rotational transitions

\[
\Delta J = J' - J'' = +1
\]

Recall:

\[
F(J) = BJ(J + 1)
\]

e.g., \[
\nu_{J=1 \rightarrow J=0} = F(J = 1) - F(J = 0) = 2B - 0 = 2B
\]
2. Rigid-Rotor model of diatomic molecule

Absorption spectrum

Remember that: \( F(J) = B(J + 1) \)

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

<table>
<thead>
<tr>
<th>J</th>
<th>F</th>
<th>1st diff = ( \bar{\nu} )</th>
<th>2nd diff = spacing</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>2B</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2B</td>
<td>4B</td>
<td>2B</td>
</tr>
<tr>
<td>2</td>
<td>6B</td>
<td>6B</td>
<td>2B</td>
</tr>
<tr>
<td>3</td>
<td>12B</td>
<td>8B</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>20B</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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
2. Rigid-Rotor model of diatomic molecule

Absorption spectrum

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

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

Note:
1. Uniform spacing (easy to identify/interpret)
2. \( B_{CO} \sim 2 \text{cm}^{-1} \)  \( \lambda_{J'' = 0} = 1/\sqrt{\nu} = 1/4 \text{cm} = 2.5 \text{mm} \) (microwave/mm waves)
3. \( \nu_{\text{rot},J=1} = c/\lambda = 3 \times 10^{10}/.25 \text{ Hz} = 1.2 \times 10^{11} \text{Hz} \) (microwave)
2. Rigid-Rotor model of diatomic molecule

- Usefulness of rotational spectra

Measured spectra $\rightarrow$ Physical characteristics of molecule

Line spacing $= 2B$

$B = \frac{h}{8\pi^2 Ic}$

$I = \mu r_e^2$

$\rightarrow r_e$ Accurately!

Example: CO

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

$10^{-6} \text{ Å} = 10^{-16} \text{ m}$
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:

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

\[
E_J = \frac{\hbar c F(J)}{k} = \left(\frac{\hbar c}{k}\right) B J (J+1) = \theta_r J (J+1)
\]

Partition function:

\[
Q_{rot} = \frac{1}{\sigma} \frac{kT}{\hbar c B} = \frac{1}{\sigma} \frac{T}{\theta_r}
\]

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

Define rotational T:

\[
\theta_r [K] = \left(\frac{\hbar c}{k}\right) B
\]

CO: \(\sigma=1\) → microwave active!
N\(_2\): \(\sigma=2\) → microwave inactive!
2. Rigid-Rotor model of diatomic molecule

- Intensities of spectral lines

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

<table>
<thead>
<tr>
<th>Species</th>
<th>$\theta_{rot} [K]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>2.1</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2.9</td>
</tr>
<tr>
<td>NO</td>
<td>2.5</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>0.351</td>
</tr>
</tbody>
</table>

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

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

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

$h/c = 1.44 K / cm^{-1}$
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:

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

\[ (m_{^{12}C} = 12.00) \]

Agrees 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 $r(J)$
    \[ J \uparrow \quad r \uparrow \quad B \downarrow \]

**Result:**
\[ F_v(J) = B_v J(J+1) - D_v J^2 (J+1)^2 \]
\[ \bar{v}_{J'\leftarrow J'',v} = 2 B_v (J''+1) - 4 D_v (J''+1)^3 \]

**Notes:**
1. $D$ 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; $D = \frac{4B^3}{\omega^2_e} \ll B$

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

     $\to$ 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 $\beta_e / D_e \sim 0.001$
- $D_e \approx 5.8 \times 10^{-6} \left( ^2\Pi_{1/2} \right)$
- $\beta_e \approx 0.0014 D_e \sim 8 \times 10^{-9} \text{cm}^{-1}$
- $\omega_e = 1904.03 \left( ^2\Pi_{1/2} \right); 1903.68 \left( ^2\Pi_{3/2} \right)$
- $\omega_e x_e = 13.97 \text{cm}^{-1}$

**Aside:**

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

$e$ denotes “evaluated at equilibrium inter-nuclear separation” $r_e$
4. Vibration-Rotation Spectra (IR)

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
4.1. Diatomic Molecules

- Simple Harmonic Oscillator (SHO)

Molecule at instance of greatest compression

As usual, we begin w. classical mechanics + incorporate QM only as needed
4.1. Diatomic Molecules

- Simple Harmonic Oscillator (SHO)

**Classical mechanics**

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

**Quantum mechanics**

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

Parabola centered at distance of min. potential energy
Equal energy spacing
Zero energy
4.1. Diatomic Molecules

- Anharmonic Oscillator (AHO)

\[
\begin{align*}
G(v), \text{cm}^{-1} &= \omega_e (v + 1/2) \\
G(v), \text{cm}^{-1} &= \omega_e (v + 1/2) - \omega_0 x_e (v + 1/2)^2 + \ldots + H.O.T.
\end{align*}
\]

Decreases energy spacing

1st anharmonic correction

In addition, breakdown in selection rules
4.1. Diatomic Molecules

- Vibrational Partition Function

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

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

\[ G(v) = \omega_e v \]

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

- Vibrational Temperature

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

\[ \begin{align*}
  \frac{N_{vib}}{N} &= g_{vib} \exp\left(-v\theta_{vib} / T\right) \\
  &= \frac{Q_{vib}}{\exp\left(-\frac{v\theta_{vib}}{T}\right)} \left[ 1 - \exp\left(-\frac{\theta_{vib}}{T}\right) \right] \\
  &= \exp\left(-\frac{v\theta_{vib}}{T}\right) \left[ 1 - \exp\left(-\frac{\theta_{vib}}{T}\right) \right]
\end{align*} \]

where \( g_{vib} = 1 \)

<table>
<thead>
<tr>
<th>Species</th>
<th>( \theta_{vib} [K] )</th>
<th>( \theta_{rot} [K] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_2)</td>
<td>2270</td>
<td>2.1</td>
</tr>
<tr>
<td>N(_2)</td>
<td>3390</td>
<td>2.9</td>
</tr>
<tr>
<td>NO</td>
<td>2740</td>
<td>2.5</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>808</td>
<td>0.351</td>
</tr>
</tbody>
</table>
### 4.1. Diatomic Molecules

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

<table>
<thead>
<tr>
<th>Gas</th>
<th>Molecular Weight</th>
<th>Vibration $\omega_e$ [cm$^{-1}$]</th>
<th>Anharmonicity constant $x_e$</th>
<th>Force constant $k_s$ [dynes/cm]</th>
<th>Internuclear distance $r_e$ [Å]</th>
<th>Dissociation energy $D_{eq}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>28</td>
<td>2170</td>
<td>0.006</td>
<td>$19 \times 10^5$</td>
<td>1.13</td>
<td>11.6</td>
</tr>
<tr>
<td>NO</td>
<td>30</td>
<td>1904</td>
<td>0.007</td>
<td>$16 \times 10^5$</td>
<td>1.15</td>
<td>6.5</td>
</tr>
<tr>
<td>$\text{H}_2^+$</td>
<td>2</td>
<td>4395</td>
<td>0.027</td>
<td>$16 \times 10^5$</td>
<td>1.15</td>
<td>6.5</td>
</tr>
<tr>
<td>$\text{Br}_2^+$</td>
<td>160</td>
<td>320</td>
<td>0.003</td>
<td>$2.5 \times 10^5$</td>
<td>2.28</td>
<td>1.8</td>
</tr>
</tbody>
</table>

- $^+$ Not IR-active, use Raman spectroscopy!
- $\omega_e \propto \sqrt{k/\mu} \quad \mu = m/2$ for homonuclear molecules
- $D_e \approx \omega_e / 4x_e$ for 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** \( 1 \text{ Å} = 0.1 \text{ nm} \)

*How many HO levels? (Consider CO)*

\[
D_o = 256 \text{ kcal}
\]

**N = no. of HO levels**

\[
N = \frac{256 \text{ kcal/mole}}{(2.86 \text{ cal/mole cm}^{-1})(2170 \text{ cm}^{-1})} \approx 41
\]

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
    \[ \rightarrow \text{Vibrating rigid rotor} \]

Energy:
\[ T(v, J) = RR + \text{SHO} = F(J) + G(v) = BJ(J + 1) + \omega_e(v + 1/2) \]

Selection Rules:
\[ \Delta v = +1 \]
\[ \Delta J = \pm 1 \]

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

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

Aside: Nomenclature for “branches”
- Branch: O P Q R S
- \(\Delta J\): -2 -1 0 +1 +2

Transition Probabilities:
- P branch
- R(0) R(2)
- Null Gap
4.2. Vib-Rot spectra – simple model

- **R-branch**
  - \( R(J''), cm^{-1} = [G(v') - G(v'')] + B(J''+1)(J''+2) - BJ''(J''+1) \)
  - \( \omega_o = v_o = \text{Rotationless transition wavenumber} \)
  - \( = \omega_e \text{ (SHO)} \)
  - \( = \omega_e (1 - 2x_e)(\text{AHO}, 1 \leftrightarrow 0) \)
  - \( = \omega_e (1 - 4x_e)(\text{AHO}, 2 \leftrightarrow 1) \)
  - \( = ... \)
  - \( R(J'') = \omega_o + 2B(J''+1) \)  \( \rightarrow \) Note: spacing = 2B, same as RR spectra

- **P-branch**
  - \( P(J'') = \omega_o - 2BJ'' \)  \( \rightarrow \) Note: \( \omega_o = f(v'') \) for AHO

- **P-R Branch peak separation**
  - \( \Delta \bar{v} = \sqrt{\frac{8BkT}{hc}} \)
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?** → **Improved treatment**
4.3. Vib-Rot spectra – improved model

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

\[
T(v, J) = G(v) + F(v, J) = \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2 + B_v J (J + 1) - D_v J^2 (J + 1)^2
\]

- SHO
- Anharmonicity corr.
- Cent. dist. term

- R-branch
  \[
  R(v'', J'') = \omega_o (v'') + 2B_v' + (3B_v' - B_v'')J'' + (B_v' - B_v'')J''^2
  \]

- P-branch
  \[
  P(v'', J'') = \omega_o (v'') - (B_v' + B_v'')J'' + (B_v' - B_v'')J''^2
  \]

\[
B_v = B_e - \alpha_e (v + 1/2)
\]

- \( B_v' = B_e' - \alpha_e (v' + 1/2) \)
- \( B_v'' = B_e'' - \alpha_e (v'' + 1/2) \)

\[
B_v' - B_v'' = -\alpha_e < 0
\]

- Spacing ↑ on P side, ↓ on R side

Transition Probabilities

\[\frac{\omega - \omega_o}{2B}\]
4.3. Vib-Rot spectra – improved model

- Bandhead

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

E.g., CO \[\frac{B}{\alpha_e} \approx \frac{1.9}{0.018} \approx 106\] → not often observed
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., $\Delta G_{1\rightarrow0}$, $\Delta G_{2\rightarrow0}$, to get $\omega_e$, $x_e$
    
    $\Delta G_{1\rightarrow0} = G(1) - G(0) = \omega_e (1 - 2x_e)$
    $\Delta G_{2\rightarrow0} = G(2) - G(0) = 2\omega_e (1 - 3x_e)$
    
    $\omega_e, x_e$
  
  - 2nd Approach:
    Fit rotational transitions to the line spacing equation to get $B_e$ and $\alpha$
    
    $\omega = \omega_o + (B'+B'')m + (B'-B'')m^2$
    
    $m = J + 1$ in R - branch
    $m = -J$ in P - branch
    
    $B' = B_e - \alpha_e (V' + 1/2)$
    $B'' = B_e - \alpha_e (V'' + 1/2)$
4.3. Vib-Rot spectra – improved model

- Finding key parameters: $B_e$, $\alpha_e$, $\omega_e$, $\chi_e$
- 3rd Approach: Use the “method of common states”

\[
\Delta E = F(J+1) - F(J-1) = R(J-1) - P(J-1) = B''(J+1)(J+2) - B''(J-1)J
\]

\[
\therefore \Delta E = B''(4J+2)
\]

\[
\Delta E = F(J+1) - F(J-1) = B'(J+1)(J+2) - B'(J-1)J
\]

\[
\therefore \Delta E = B'(4J+2)
\]

$B_e, \alpha_e$
4.3. Vib-Rot spectra – improved model

- Isotopic effects

\[ B \propto \frac{1}{I} \propto \frac{1}{\mu} \quad \rightarrow \text{Line spacing changes as } \mu \text{ changes} \]

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

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

\[ \frac{\mu_{^{13}\text{C}^{16}\text{O}}}{\mu_{^{12}\text{C}^{16}\text{O}}} = 1.046 \quad \rightarrow \quad B_{^{13}\text{C}^{16}\text{O}} = \frac{B_{^{13}\text{C}^{16}\text{O}}}{1.046} \]

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

\[ \omega_{e^{13}\text{C}^{16}\text{O}} = \frac{\omega_{e^{13}\text{C}^{16}\text{O}}}{\sqrt{1.046}} \]

\[ \Delta \omega_e = 0.046 \times 2200 / 2 \approx 50 \text{ cm}^{-1} \]
4.3. Vib-Rot spectra – improved model

- Isotopic effects

CO fundamental band

Note evidence of 1.1% natural abundance of $^{13}$C
4.3. Vib-Rot spectra – improved model

- Isotopic effects

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

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

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

- \([H^{35}\text{Cl}] \approx 3[H^{37}\text{Cl}]\)

- \(\mu_{37}/\mu_{35} = \frac{37.1/38}{35.1/36} \approx 1.0015\)

\(\text{Shift in } \omega_e \text{ is } 0.0075\omega_e=2.2\text{cm}^{-1} \rightarrow \text{Small!}\)
4.3. Vib-Rot spectra – improved model

- Isotopic effects

Note isotopic splitting due to H\textsuperscript{35}Cl and H\textsuperscript{37}Cl
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. \( \theta_{v,CO} = 3000K \)

\[ \frac{N_1}{N} = \begin{cases} 
  e^{-10} \approx 0 & \text{@ 300K} \\
  e^{-1} (1 - e^{-1}) \approx 0.23 & \text{@ 3000K} 
\end{cases} \]

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

<table>
<thead>
<tr>
<th>Gas</th>
<th>( \bar{\nu}_{0\to1} (cm^{-1}) )</th>
<th>( \frac{N_1}{N_0} = e^{-h\bar{\nu} / kT} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>300K</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>4160.2</td>
<td>2.16 \times 10^{-9}</td>
</tr>
<tr>
<td>( \text{HCl} )</td>
<td>2885.9</td>
<td>9.77 \times 10^{-7}</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>2330.7</td>
<td>1.40 \times 10^{-5}</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>2143.2</td>
<td>3.43 \times 10^{-4}</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>1556.4</td>
<td>5.74 \times 10^{-4}</td>
</tr>
<tr>
<td>( \text{S}_2 )</td>
<td>721.6</td>
<td>3.14 \times 10^{-2}</td>
</tr>
<tr>
<td>( \text{Cl}_2 )</td>
<td>566.9</td>
<td>6.92 \times 10^{-2}</td>
</tr>
<tr>
<td>( \text{I}_2 )</td>
<td>213.1</td>
<td>2.60 \times 10^{-1}</td>
</tr>
</tbody>
</table>
4.3. Vib-Rot spectra – improved model

- Examples of intensity distribution within the rotation-vibration band

\[ B = 10.44\text{cm}^{-1} \ (\text{HCl}) \quad B = 2\text{cm}^{-1} \ (\text{CO}) \]
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)