Section 4
Molecular Vibrational Spectroscopy
(lectures 6-8 ish)

Previously:
- Quantum theory of atoms / molecules
- Quantum Mechanics
- Valence

Molecular Vibrational Spectroscopy
- Diatomic molecules (harmonic oscillator revision)
- Beyond the Harmonic Oscillator
- Rotational structure in vibrational spectra
- Polyatomic molecules: Normal modes
- Symmetry of normal modes
- Symmetry of vibrational levels
- Combination differences
- Combination bands
Molecular Energy Levels

Different electronic states (electronic arrangements)

\[ \Delta E_{\text{el}} \]

\[ \Delta E_{\text{vib}} \]

\[ \Delta E_{\text{rot}} \]

*i.e., typically* \( \Delta E_{\text{el}} \gg \Delta E_{\text{vib}} \gg \Delta E_{\text{rot}} \)

\[ \Delta E \approx 2 \times 10^4 – 10^5 \text{ cm}^{-1} \]

Transitions at \( \lambda \approx 500 – 100 \text{ nm} \) Vis – UV

\[ 10^2 – 5 \times 10^3 \text{ cm}^{-1} \]

\[ 100 \mu m – 2 \mu m \text{ infrared} \]

Rotational
\[ 3 – 300 \text{ GHz} \]
\[ (0.1 – 10 \text{ cm}^{-1}) \]

\[ 10 \text{ cm} – 1 \text{ mm} \text{ microwave} \]
4.1 Vibrational Energy Levels: The Harmonic oscillator

Obeys Hooke’s Law, \( F = -k_F x \)

Where \( k_F \) is the Force constant \((Nm^{-1})\) and \( x \) the displacement from equilibrium

\[ \therefore \text{The potential energy,} \]

\[ V(x) = -\int_{0}^{x} Fdx = \frac{k_F x^2}{2} \]

Classical frequency of oscillation:

\[ \nu_{vib} = \frac{1}{2\pi} \sqrt{\frac{k_F}{\mu}} \]
4.2 Harmonic Oscillator Eigenvalues

Eigenvalues:
The vibrational terms

\[ G_v = \left( v + \frac{1}{2} \right) \omega_e \]
\[ \frac{\omega_e}{\text{cm}^{-1}} = \frac{V_{\text{vib}}}{\tilde{c}} = \frac{1}{2\pi\tilde{c}} \sqrt{\frac{k_F}{\mu}} \]

\( v \) is the vibrational quantum number = 0, 1, 2, ...
\( \omega_e \) the vibrational constant (in cm\(^{-1}\)),
\( k_F \) is the Force Constant,
\( \mu \) is the reduced mass

Equally spaced non-degenerate energy levels

n.b., existence of zero point energy

\( G_0 = \frac{\omega_e}{2} \neq 0 \)
no classical analogue and arises due to Heisenberg Uncertainty

For HCl (\(^1\Sigma^+)\): \( k_F = 510 \text{ Nm}^{-1} \) \( \omega_e = 2990.9 \text{ cm}^{-1} \) vibrational frequency \( \sim 9 \times 10^{13} \text{ Hz} \)
CO: \( k_F = 1902 \text{ Nm}^{-1} \) \( \omega_e = 2169.8 \text{ cm}^{-1} \) vibrational frequency \( \sim 6.5 \times 10^{13} \text{ Hz} \)
4.2 Harmonic Oscillator Wavefunctions

The eigenfunctions of the Harmonic Oscillator are products of Hermite polynomials and Gaussian functions:

\[ \psi_v(x) = N_v H_v(y) \exp \left( -\frac{y^2}{2} \right) \quad y = x. \left( \frac{mk}{\hbar} \right)^{\frac{1}{4}} \]

<table>
<thead>
<tr>
<th>( v )</th>
<th>( H_v(y) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>2y</td>
</tr>
<tr>
<td>2</td>
<td>4y^2 - 2</td>
</tr>
<tr>
<td>3</td>
<td>8y^3 - 12y</td>
</tr>
<tr>
<td>4</td>
<td>16y^4 - 48y^2 + 12</td>
</tr>
<tr>
<td>5</td>
<td>32y^5 - 160y^3 + 120y</td>
</tr>
<tr>
<td>6</td>
<td>64y^6 - 480y^4 + 720y^2 - 120</td>
</tr>
</tbody>
</table>

Note:
- Penetration into classically forbidden regions
- Probability distributions become more classical at high \( v \)
4.3 Harmonic Oscillator Selection Rules (preamble)

\[
\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2
\]

simplifies in scaled coordinates and units to become

\[
\hat{H} = -\frac{1}{2} \frac{d^2}{dq^2} + \frac{1}{2} q^2
\]

\(q\) is a vibrational coordinate

\[\psi_0 = \exp\left(-\frac{q^2}{2}\right)\]

is the lowest energy eigenfunction:

\[\hat{H}\psi_0 = \frac{1}{2} \psi_0\]

We can obtain all other eigenfunctions using the ladder operators:

\[\hat{Q}^+ = \sqrt{\frac{1}{2}} \left(q - \frac{d}{dq}\right)\]

\[\hat{Q} = \sqrt{\frac{1}{2}} \left(q + \frac{d}{dq}\right)\]

With the properties:

\[\hat{Q}^+ \psi_v \Rightarrow \psi_{v+1}\]

\[\hat{Q} \psi_v \Rightarrow \psi_{v-1}\]

and

\[\hat{Q}^+ + \hat{Q} = \sqrt{2} q\]

Finally, of course all vibrational eigenfunctions are orthonormal

\[\int_{-\infty}^{+\infty} \psi_v \psi_{v'} dq = \delta_{v,v'} = \begin{cases} 1 & \text{if } v' = v \\ 0 & \text{if } v' \neq v \end{cases}\]
4.3 Harmonic Oscillator Selection Rules

Consider the Transition Dipole Moment for a $v - v'$ transition

$$ R_{v'v} = \int_{-\infty}^{\infty} \psi_v^* \hat{\mu} \psi_{v'} dq $$

where $\hat{\mu} = \sum_i -e \hat{r}_i$

We can expand the dipole moment operator about $q = 0$:

$$ \hat{\mu} = \hat{\mu}_{q=0} + \left( \frac{d\hat{\mu}}{dq} \right)_{q=0} q + \frac{1}{2} \left( \frac{d^2 \hat{\mu}}{dq^2} \right)_{q=0} q^2 + ... $$

Consider each term in the TDM in turn:

$$ R_{v'v} = \int_{-\infty}^{\infty} \psi_v^* \hat{\mu}_{q=0} \psi_{v'} dq = \hat{\mu}_{q=0} \int_{-\infty}^{\infty} \psi_v^* \psi_{v'} dq $$

Hence this term is identically zero for any vibrational transition.
4.3 Harmonic Oscillator Selection Rules

\[ \hat{\mu} = \hat{\mu}_{q=0} + \left( \frac{d\hat{\mu}}{dq} \right)_{q=0} q + \ldots \]

For an allowed transition \((R_{vv'} \neq 0)\) we require:

\[ R_{vv'} = \left( \frac{d\hat{\mu}}{dq} \right)_{q=0} \int_{-\infty}^{\infty} \psi^{*}_v q \psi_v \, dq \neq 0 \]

1. \( \left( \frac{d\hat{\mu}}{dq} \right)_{q=0} \neq 0 \)
   i.e., a dipole moment that changes during the vibration
   
   **Gross selection rule**

2. \( \int_{-\infty}^{\infty} \psi^{*}_v q \psi_v \, dq \neq 0 \)
   
   \( \int_{-\infty}^{\infty} \psi^{*}_v q \psi_v \, dq = \frac{1}{\sqrt{2}} \int_{-\infty}^{\infty} \psi^{*}_v (\hat{Q}^+ + \hat{Q}) \psi_v \, dq \)

   i.e., \( \int_{-\infty}^{\infty} \psi^{*}_v \hat{Q}^+ \psi_v \, dq \neq 0 \) or \( \int_{-\infty}^{\infty} \psi^{*}_v \hat{Q} \psi_v \, dq \neq 0 \)

   \[ v' = v + 1 \]
   \[ v' = v - 1 \]
   
   i.e., \( \Delta v = \pm 1 \)

   **Specific selection rule**
4.4 The (very simple) spectrum of a harmonic oscillator

Vibrational Terms: \( \tilde{G}_v = (v + \frac{1}{2}) \omega_e \)

Selection Rule: \( \Delta v = \pm 1 \)

Transitions at: \( \tilde{v} = \tilde{G}_{v+1} - \tilde{G}_v = \omega_e \)

i.e., only one line in the spectrum

\[ n.b. \text{ In absorption, only see transitions from } v = 0 \text{ since, except at very high } T, \text{ this is the only level populated: } \]

\[ e.g., \text{ if } \omega_e = 1000 \text{ cm}^{-1}, T = 300 \text{ K} \]

\[ \frac{n_{v=1}}{n_{v=0}} = \frac{g_1}{g_0} \exp \left\{ -\frac{\hbar \tilde{c} \omega_e}{kT} \right\} = 0.008 \]
4.5 Anharmonicity

But, of course, molecular bonds are not harmonic oscillators

- We can break bonds (pull them apart)
- We can identify (finite) dissociation energy for doing so
- As we stretch a bond the bond itself gets weaker (the restoring force is reduced)
4.5 Accounting for anharmonicity: The Morse Oscillator

Morse Potential:

\[ V(R) = D_e \left[ 1 - \exp\left(-\beta \left(R - R_e\right) \right) \right]^2 \]

SHO a good approx. at small x (low v)
4.5 Accounting for anharmonicity: The Morse Oscillator

**Morse Potential:**

\[ V(R) = D_e \left[ 1 - \exp\left(-\beta(R - R_e)\right) \right]^2 \]

**Energy Eigenvalues:**

\[ \tilde{G}_v = (v + \frac{1}{2}) \omega_e - (v + \frac{1}{2})^2 \omega_e x_e \]

\[ v = 0, 1, 2, 3, \ldots, v_{\text{max}} \]

\( x_e \) is the (dimensionless) anharmonicity constant:

\[ x_e = \frac{\omega_e}{4 D_e} \]

**Specific Selection rule:**

\[ \Delta v = \pm 1, (\pm 2, \pm 3, \text{ weaker}) \]

**Transitions:**

- Fundamental \((0 \rightarrow 1)\) \[ \tilde{v} = \omega_e - 2 \omega_e x_e \]
- 1\textsuperscript{st} overtone \((0 \rightarrow 2)\) \[ \tilde{v} = 2 \omega_e - 6 \omega_e x_e \]

\( n.b., \) the experimental dissociation energy, \( D_0 = D_e - \text{ZPE} \)

**HCl (\( ^1\Sigma^+ \)):** \( \omega_e = 2990.9 \text{ cm}^{-1}, \omega_e x_e = 52.8 \text{ cm}^{-1}, (x_e = 0.018), D_e = 35486 \text{ cm}^{-1}, D_0 = 34092 \text{ cm}^{-1} \)
4.6 Rotational fine structure: I. Diatomics

Associated with a vibrational transition, we observe rotational transitions:

Combined vibration-rotation terms: \( \tilde{S}(v,J) = \tilde{G}(v) + \tilde{F}(J) \)

\[ i.e., E_{\text{tot}} = E_{\text{vib}} + E_{\text{rot}} \]

E.g., or an anharmonic rigid rotor:

\[ \tilde{S}(v,J) = (v + \frac{1}{2}) \omega_e - (v + \frac{1}{2})^2 \omega_e x_e + \tilde{\omega}_v J(J+1) \]

Transitions: \( \tilde{\nu} = \tilde{S}(v',J') - \tilde{S}(v'',J'') \)

Subject to combined selection rules:

Recall rotational selection rule \( \Delta J = \pm 1 \):

All \( \Delta J = +1 \) transitions give rise to an \( R \)-branch and the \( \Delta J = -1 \) transitions comprise a \( P \)-branch.
4.7 Rotation Vibration Spectra

\[
\tilde{v}_R(J'') = \omega_e - 2\omega_e x_e \\
+ \tilde{B}_1 (J'' + 1)(J'' + 2) - \tilde{B}_0 J''(J'' + 1)
\]

\[
\tilde{v}_P(J'') = \omega_e - 2\omega_e x_e \\
+ \tilde{B}_1 (J'' - 1)(J'') - \tilde{B}_0 J''(J'' + 1)
\]

Assuming: \[\tilde{B}_1 = \tilde{B}_0 = \tilde{B}\]

Spacing in each branch = \(2\tilde{B}\)

Central gap = \(R(0) - P(1) = 4\tilde{B}\)

\[\omega_0 = \omega_e - 2\omega_e x_e\]

*Q-branch (\(\Delta J=0\)) absent unless additional angular momentum present (e.g., NO \(^2\Pi\)) or a degenerate bending mode is involved (see polyatomics later)
e.g., in the fundamental band of HCl

note offset of H\textsuperscript{35}Cl and H\textsuperscript{37}Cl lines due to different reduced mass (and hence different \(\omega_e\) and \(B\) constants)

Also, note bunching of the lines in the \(R\)-branch
4.8 Vibrational dependence of rotational constants

How good is the assumption \( \tilde{B}_1 = \tilde{B}_0 \)?

\[
\tilde{B} \propto \frac{1}{\mu R^2}
\]

but what exactly do we mean by \( 1/R^2 \) in a vibrating molecule?

We actually mean \( <1/R^2> \)

\(<1/R^2> \) decreases with \( \nu \) and therefore:

\[
\tilde{B}_0 > \tilde{B}_1 > \tilde{B}_{\nu>1}
\]

\[
\tilde{B}_\nu = \tilde{B}_e - \alpha (\nu + \frac{1}{2})
\]

Under high resolution we can determine the rotational constant in each vibrational level using a method of combination differences.
4.9 Combination Differences

Use transitions with common upper or lower levels to determine rotational constants for each vibrational level:

\[ \tilde{v}_R(J) - \tilde{v}_P(J) = 2\tilde{B}_1 (2J + 1) \]

\[ \rightarrow \tilde{B}_1 \]

**Example:** R(J) and P(J) originate at \( v = 0, J; \)

Likewise the difference of R(J-1) and P(J+1), which both terminate at \( v = 1, J, \) gives:

\[ \tilde{v}_R(J - 1) - \tilde{v}_P(J + 1) = 2\tilde{B}_0 (2J + 1) \]

\[ \rightarrow \tilde{B}_0 \]
4.10 Band heads in Vibrational Spectra

Consider the R-branch in a linear molecule:

\[
\nu_R(J'') = \omega_e - 2\omega_e x_e + (\tilde{B}_1 + \tilde{B}_0)(J'' + 1) + (\tilde{B}_1 - \tilde{B}_0)(J'' + 1)^2
\]

At high enough \( J \) the wavenumber separation of adjacent transitions can change sign. This leads to a bandhead in R-branch:

![Graph showing vibrational spectra with bands labeled P and R.](image)
4.11 Beyond Diatomics: Normal Modes in Polyatomic Molecules

Diatomics have only one vibrational mode.

In polyatomics we define Normal Modes as independent, harmonic vibrations which:

1. leave the centre of mass unmoved;
2. involve all atoms moving in phase (coherent motion);
3. transform as an irreducible representation of the molecular point group

I. Number of Normal Modes:

$N$ isolated atoms have $3N$ degrees of freedom ($x$, $y$, $z$ translations for each)

$N$ atoms in a molecule have $3N$ degrees of freedom arranged amongst translations, vibrations and rotations:

<table>
<thead>
<tr>
<th>Molecule:</th>
<th>Linear</th>
<th>Non-linear</th>
</tr>
</thead>
<tbody>
<tr>
<td>no. translations =</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>no. rotations =</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>\therefore no. vibrations =</td>
<td>$3N-5$</td>
<td>$3N-6$</td>
</tr>
</tbody>
</table>
4.12 Visualising normal modes

**H$_2$O**

- **Symmetric stretch**
  - $v_1$ (3652 cm$^{-1}$)

- **Bend**
  - $v_2$ (1595 cm$^{-1}$)

- **Asymmetric stretch**
  - $v_3$ (3756 cm$^{-1}$)

**CO$_2$**

- **Symmetric stretch**
  - $v_1$ (1388 cm$^{-1}$)

- **Asymmetric stretch**
  - $v_3$ (2349 cm$^{-1}$)

- **Degenerate Bend**
  - $v_2$ (667 cm$^{-1}$)
4.13 Symmetry of normal mode vibrations

*A normal mode must transform as an irreducible representation of the point group of the molecule.*

Once we can picture the mode itself this is usually easy:

e.g., water, \( C_{2v} \)

<table>
<thead>
<tr>
<th>( C_{2v} )</th>
<th>( E )</th>
<th>( C_2 )</th>
<th>( \sigma^{xz} )</th>
<th>( \sigma^{yz} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

**Mode 1**

*Symmetric stretch*

\( \nu_1 \) (3652 cm\(^{-1}\))

**Mode 2**

*Bend*

\( \nu_2 \) (1595 cm\(^{-1}\))

**Mode 3**

*Asymmetric stretch*

\( \nu_3 \) (3756 cm\(^{-1}\))
4.14 Symmetry of normal modes: Linear molecules ($D_{\infty h}$, $C_{\infty v}$)

**CO$_2$**  $D_{\infty h}$

**HCN**  $C_{\infty v}$

**acetylene**  $D_{\infty h}$
As well as the normal modes, the vibrational wavefunctions have distinct symmetry which can be useful in determining selection rules. These are different for different \( \nu \) levels.

I. Ground levels (\( \nu = 0 \) levels)

As we have seen, \( \psi_0 \) has the form

\[
\psi_0 = \exp\left(-\frac{q^2}{2}\right)
\]

The sign of \( \Psi_0 \) is independent of the sign of \( q \):

\[\rightarrow \text{It follows that } \Psi_0 \text{ transforms as the totally symmetric irreducible representation of the relevant point group}\]

\[i.e., \quad A_1 \text{ in } C_{2v} \]
\[\Sigma_g^+ \text{ in } D_{\infty h} \]
\[\Sigma^+ \text{ in } C_{\infty v} \]
II. First excited vibrational levels ($v = 1$ levels)

$$\psi_1 \propto \hat{Q}^+ \psi_0 = \frac{1}{\sqrt{2}} \left( q - \frac{d}{dq} \right) \exp \left( \frac{-q^2}{2} \right) = \sqrt{2} q \exp \left( \frac{-q^2}{2} \right)$$

$\psi_1$ has the same symmetry as the normal coordinate $q$

$\rightarrow$ $\psi_1$ transforms as the same symmetry as the normal mode

So, in the case of water:

<table>
<thead>
<tr>
<th>Normal mode</th>
<th>$\psi_0$</th>
<th>$\psi_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode 1</td>
<td>$A_1$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>Mode 2</td>
<td>$A_1$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>Mode 3</td>
<td>$B_2$</td>
<td>$A_1$</td>
</tr>
</tbody>
</table>

$v_1$ (3652 cm$^{-1}$)  
$v_2$ (1595 cm$^{-1}$)  
$v_3$ (3756 cm$^{-1}$)
III. Higher vibrational levels

For non-degenerate modes:

$$\psi_2 = \hat{Q}^+ \psi_1 \propto q^2 \rightarrow \text{transforms as tot. symmetry IR}$$

$$\psi_3 = \hat{Q}^+ \psi_2 \propto q + q^3 \rightarrow \text{transforms as same symmetry as the normal mode}$$

(degenerate modes, $E$, $T$, etc., are more complex)
4.16 Vibrational Selection Rules in Polyatomic Molecules

As normal modes are *harmonic*, the selection rules are:

- The dipole moment must change during the vibration
- $\Delta n_i = \pm 1$

For polyatomics it can be hard to see if the former is true. Clearly though it relates to the transition dipole moment,

$$R_{v, v'} = \int_{-\infty}^{\infty} \psi_{v'}^* \hat{\mu} \psi_v \, dq$$  

a vector with x, y, z components of:

$$R_{v, v'}^x = \int_{-\infty}^{\infty} \psi_{v'}^* \hat{\mu}_x \psi_v \, dx$$  
$$R_{v, v'}^y = \int_{-\infty}^{\infty} \psi_{v'}^* \hat{\mu}_y \psi_v \, dy$$  
$$R_{v, v'}^z = \int_{-\infty}^{\infty} \psi_{v'}^* \hat{\mu}_z \psi_v \, dz$$

Each of these is a *scalar* and thus in order for $R_{v, v'} \neq 0$ at least one of these components must transform as the totally symmetric IR.

*i.e.*, see if any of the direct products

$$\Gamma_{v'} \otimes \Gamma_{\mu_x} \otimes \Gamma_v$$  
$$\Gamma_{v'} \otimes \Gamma_{\mu_y} \otimes \Gamma_v$$  
$$\Gamma_{v'} \otimes \Gamma_{\mu_z} \otimes \Gamma_v$$

transform as the totally symmetric irrep.
4.16 Example of Vibrational Selection Rules

Consider the fundamental (0→1) band in mode 3 ($B_2$) of H$_2$O ($C_{2v}$):

\[
\begin{array}{c|cccc}
C_{2v} & E & C_2^z & \sigma^{xz} & \sigma^{yz} \\
\hline
A_1 & 1 & 1 & 1 & 1 \\
A_2 & 1 & 1 & -1 & -1 \\
B_1 & 1 & -1 & 1 & -1 \\
B_2 & 1 & -1 & -1 & 1 \\
\end{array}
\]

\(\psi_0\) transforms as the totally symmetric IR, i.e., \(A_1\)

\(\psi_1\) transforms as the normal mode, i.e., \(B_2\)

The components of \(\hat{\mu}\) transform, in \(C_{2v}\) as:

\(\Gamma_{\mu_x} = B_1\)

\(\hat{\mu}\) transforms as \(x, y, z\)

read IRs from character table:

\(\Gamma_{\mu_y} = B_2\)

\(\Gamma_{\mu_z} = A_1\)

The components \(\Gamma_y \otimes \Gamma_{\hat{\mu}_{x,y,z}} \otimes \Gamma_y\) become

\(\mu_x : B_2 \otimes B_1 \otimes A_1 = B_2 \otimes B_1 = A_2\)

\(\mu_x : B_2 \otimes B_2 \otimes A_1 = B_2 \otimes B_2 = A_1\)

\(\mu_x : B_2 \otimes A_1 \otimes A_1 = B_2 \otimes A_1 = B_2\)

The \(y\)-component transforms as \(A_1\), so the transition is “dipole-allowed with transition dipole along \(y\)".
4.17 General Vibrational Selection Rules

The *fundamental* transition is allowed provided the symmetry of the normal mode (and thus $\nu = 1$) is the same as $x$, $y$, or $z$. In this case the mode is *infra-red active*.

If the transition moment is *parallel* to the symmetry ($z$-) axis the mode is called a *parallel mode*.
If the transition moment is *perpendicular* to the symmetry axis the mode is called a *perpendicular mode*.
4.18 Combination Bands

Just as anharmonicity permits changes in vibrational quantum number $\Delta v > \pm 1$, it also allows for simultaneous changes in more than one normal mode.

Such transitions all break the harmonic oscillator selection rule but we can again use symmetry to determine if such combination bands are allowed:

e.g., Consider the $v_1=0, v_3=0 \rightarrow v_1=1, v_3=1$ combination band in H$_2$O (i.e., simultaneous excitation of both symmetric and asymmetric stretches) $v=0$ transforms as $A_1$ symmetry.
$v_1=1$ level transforms as $A_1$,
$v_3=1$ level transforms as $B_2$.
Hence, the $v_1=1, v_3=1$ level transforms as $A_1 \otimes B_2 = B_2$

$$B_2 \otimes \Gamma_{\mu_r} \otimes A_1 = B_2 \otimes B_2 \otimes A_1 = A_1$$

The transition is symmetry allowed with transition dipole along $y$.
(Despite breaking the harmonic oscillator selection rule)
4.19 Rotational Fine Structure

1. Linear Molecules

<table>
<thead>
<tr>
<th>point group</th>
<th>IR of active mode</th>
<th>IR of ( v = 0 )</th>
<th>IR of ( v = 1 )</th>
<th>type of transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{\infty} )</td>
<td>( \Sigma^+ )</td>
<td>( \Sigma^+ )</td>
<td>( \Sigma^+ )</td>
<td>parallel</td>
</tr>
<tr>
<td></td>
<td>( \Pi )</td>
<td>( \Sigma^+ )</td>
<td>( \Pi )</td>
<td>perpendicular</td>
</tr>
<tr>
<td>( D_{coh} )</td>
<td>( \Sigma^u )</td>
<td>( \Sigma^g )</td>
<td>( \Sigma^u )</td>
<td>parallel</td>
</tr>
<tr>
<td></td>
<td>( \Pi_u )</td>
<td>( \Sigma^g )</td>
<td>( \Pi_u )</td>
<td>perpendicular</td>
</tr>
</tbody>
</table>

2 types of bands:

- \( \Sigma - \Sigma \) (parallel bands)
  \( \Delta J = \pm 1 \) (P, R, branches)

- \( \Sigma - \Pi \) (perpendicular bands)
  \( \Delta J = 0, \pm 1 \) (Q, P, R branches)

\[ Q(J) = \bar{v}_{el-vib} + (B' - B'')J(J + 1) \]

Q-branch \((\Delta J=0)\) arises from the additional angular momentum from the degenerate bending mode.

\( \Sigma^+ - \Sigma^+ \) infrared band in HCN
(asymmetric stretch fundamental)

\( \Pi_u - \Sigma^+_g \) overtone band in HC≡CH
2. Symmetric tops

A. Parallel transitions:
\[ \Delta J = 0, \pm 1 \quad \Delta K = 0 \]

B. Perpendicular transitions:
\[ \Delta J = 0, \pm 1 \quad \Delta K = \pm 1 \]