VIBRATION-ROTATION SPECTRA

SUMMARY
Every vibrational energy level has a rotational energy level structure built on it. The rotational part is exactly as in the previous section, but centrifugal distortion can be ignored. For one vibration (e.g. a diatomic), energies \(G(v)\) are expressed as:

\[
G(v) = (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2\omega_e x_e + (\text{possible higher terms})
\]

A simple harmonic oscillator (SHO) has only the first term. \(\omega_e\) and \(\omega_e x_e\) are the frequency and anharmonicity for infinitesimal vibration amplitude at the bottom of the potential well.

Selection Rules:
1. For IR, the vibration must cause a change in dipole moment.
2. For Raman, the vibration must change the polarisability.
3. In centro-symmetric molecules, no vibration can be both IR and Raman active.
4. In both IR and Raman, \(\Delta v = \pm 1\) transitions are by far the strongest. This rule is not strict, because:
   a) a transition dipole can come from higher powers of the vibration coordinate extension, even for SHO.
   b) Anharmonicity removes the symmetry of the vibration wavefunctions. So \(\Delta v = \pm 2, \pm 3\ldots\) transitions are seen weakly.
5. The selection rules for rotational fine structure are \(\Delta J = \pm 1\) for IR and \(\Delta J = 0, \pm 2\) for Raman, if no other angular momentum is present. If another angular momentum is present then \(\Delta J = 0, \pm 1\) for IR and \(\Delta J = 0, \pm 1, \pm 2\) for Raman.

Line Positions:
For \(\Delta v = 1\), the vibrational origins (\(\Delta J = 0\)) are at \(\Delta G(v) = \omega_e - 2v\omega_e x_e\), where \(v\) is the quantum number of the upper state. Successive origins differ by \(2\omega_e x_e\).

IR rotational structure may have P,Q and R branches for \(\Delta J = -1,0,+1\) respectively. The B values are different in each vibrational level, written \(B_0, B_1, \text{ etc.}\). Because they are only slightly different, the P and R branches have a line spacing of about \(2B_{av}\), but there is a double-sized gap of about \(4B_{av}\) at the band origin. Lines close up in the R branch and spread out in P.

Remember that when observing different isotopes (e.g. HCl), the correct ratio (for this example it would be 3:1) is NOT seen, because transmittance is on a logarithmic scale.

The B values are smaller for higher vibration levels, because on average the bonds get extended:

\[
B_v = B_e - (v + \frac{1}{2})\alpha
\]

From B values in two levels \(\alpha\) can be found (\(B_1 - B_0 = \alpha\)). \(B_e\) is the (theoretical) rotational constant at the bottom of the potential well and gives the equilibrium bond length.

Formally, \(B_e = h/(8\pi^2\mu c)\) where \(I = \mu r_e^2\).
For Raman, with \(\Delta J = 0, \pm 2\), the structure is analogous.

Intensities:
For the rotational part, populations are as given in the last section. Vibrational energies are \(>kT\), so normally only \(v=0\) is strongly populated. The weak transitions starting from \(v=1\) etc. are called hot bands.
Vibrational Energy Levels

Energy of a molecular vibration depends on internuclear distance. Harmonic Oscillator + Quantum Mechanics gives:

\[ E = (v + \frac{1}{2}) \hbar \nu \]

A real diatomic curve diverges at higher energies:

\[ E \]

This is anharmonicity. Convergence of energy levels. This is described well by:

\[ E = (v + \frac{1}{2}) \hbar \nu - (v + \frac{1}{2})^2 x_0 \nu + (v + \frac{1}{2})^3 y_0 \hbar \nu \]

\( x_0 \) – small anharmonicity correction term. Further terms are even smaller, usually neglected.

\[ v = \frac{1}{2 \pi} \left( \frac{1}{\mu} \right)^{1/2} \]

Isotopically related molecules (e.g. \( \text{H}_2 \) and \( \text{D}_2 \)) have identical potential energy curves. Independent of mass. \( k \) is thus the same, so can predict energy level spacings. Spacing smaller for the heavier isotopes. Dissociation Energies are thus different \( \Rightarrow \) smaller ZPE for heavier atoms. \( \text{C-H} \) easier to break than \( \text{C-D} \).

Diatomics:

\[ \omega_u = \frac{\omega_e}{\sqrt{2}} = (v + \frac{1}{2}) \omega_e - (v + \frac{1}{2})^2 \omega_e x_0 \]

\[ \omega_e = \frac{1}{2 \pi c \nu} \text{ vib. freq at } \neq, \text{ in cm}^{-1} (\nu \text{ in kg}) \]

\[ x_0 = \text{anharmonicity constant} \]

\[ \text{ZPE } \Rightarrow \quad v = 0 \]

Harmonic Oscillator Potential:

\[ V(R) = \frac{1}{2} k (R - R_e)^2. \]

Morse Potential:

\[ V(R) = D \left[ 1 - e^{a(R-R_e)} \right]^2. \]

\[ a = 2 \pi c \omega_a (\mu/2D_e)^{1/2}. \]

Dissociation Energy:

\[ \frac{dG(v)}{dv} = 0 \text{ at } v = 0 \]

\[ D_o = D_e - \text{ZPE} \]

Polyatomics:

Quanta in normal modes – \( A, B, C \ldots \) : \( v_A, v_B, v_C \ldots \)
Degeneracy \( d_A, d_B, d_C \ldots \)

Ignoring Anharmonicity:

\[ C_u(v_n, v_s \ldots) = (v_n + \frac{d_A}{2}) \omega_a^2 + (v_s + \frac{d_B}{2}) \omega_b^3 + \ldots \quad / \text{cm}^{-1} \]

No simple relationship between bond force constants and vibrational frequencies of normal modes.
Vibration-Rotation Energy Levels

Diatomics:
\[ F(v, J) = G(v) + F(J) \]

B varies with vibrational level as:
\[ B_v = B_e - \alpha (v + \frac{1}{2}) \]
\[ B_e = \frac{h}{8\pi^2 c \mu_{re}^2} \]

Symmetric Top Polyatomics –
\[ F(v_A, v_B, \ldots; J; K) = G(v_A, v_B, \ldots) + F(J, K) \]
\[ B_v = \frac{h}{8\pi^2 c \mu (\langle 1/r^2 \rangle_v)} \]

Variation due to:
- Anharmonicity
- Intrinsic property of \( \langle 1/r^2 \rangle \)

Infrared Spectroscopy – Vibration-Rotation

Diatomics –
Vibrational Changes:
\[
\chi_e(R) = \mu(R_e) + \frac{\partial \mu}{\partial R} \delta(R - R_e) + \frac{1}{2} \frac{\partial^2 \mu}{\partial R^2} \delta(R - R_e)^2 + \ldots
\]

Only first 2 terms =
\[
\int \chi_e(R) \mu(R) \chi_e(R) \, dR = 0
\]
\[
\int \chi_e(R) \mu(R) \chi_e(R) \, dR + \frac{\partial \mu}{\partial R} \int \chi_e(R) \delta(R - R_e) \, dR = 0 \quad \text{unless} \quad \chi_e = \chi_0 \]
Second Term ≠ 0 if \( \frac{\partial \mu}{\partial R} \neq 0 \)

For real molecules, anharmonicity \( \Delta v = \pm 2, \pm 3 \ldots \)
Allowed, but weak.
Also, dipole moment change ≠ 0, so heteronuclear only.

Populations –
\[ N_v/N_0 = e^{G(v)hc/kT} \]
Hence for most diatomics, only see absorption from \( v = 0 \) (for room-temp).

Vibrational Transition Energies –
\[ G(v+1) - G(v) = \omega_e - 2(v+1) \omega_e x_e \]
For \( v = 0 \), \( \omega_e - 2\omega_e x_e \approx \omega_0 \)
This \( \omega_0 \) is the Fundamental vibrational frequency.
First Overtone, \( G(2) - G(0) = 2\omega_e - 6\omega_e x_e \)
Note, \( D_e = \omega_e^2 / 4\omega_e x_e \)
Rotational Changes – \( \Delta J = \pm 1 \)
R-branch:
\[ v^R(J) = F(v+1,J+1) - F(v,J) = v_0 + (B_0 + B_1)(J+1) + (B_1 - B_0)(J+1)^2 \]

P-branch:
\[ v^P(J) = F(v+1,J-1) - F(v,J) = v_0 - (B_1 + B_0)J + (B_1 - B_0)J^2 \]

\[ v(J+1) - v^P(J) = -(B_1 + B_0) + (B_1 - B_0)(2J+1) \]

Isotope Effects –
\[ \omega_e \propto \frac{1}{\sqrt{\mu}} \]
\[ \omega_b \propto \frac{1}{\mu} \]

Combination Differences –
In IR vib-rot spectra.

\[ \dot{v}^R(J) - \dot{v}^R(J+2) = 4B_0(J+1)(J+\frac{3}{2})^{-3} \]
\[ \approx 4B_0(J+\frac{3}{2}) \quad \text{(ignoring centrifugal)} \]

\[ \dot{v}^P(J) - \dot{v}^P(J+2) = 4B_1(J+1)(J+\frac{1}{2})^{-3} \]
\[ \approx 4B_1(J+\frac{1}{2}) \quad \text{(ignoring centrifugal)} \]

Normal Modes in polyatomic molecules. Combined motion of several atoms.
Bond vibrations not independent.

What are Normal Modes?
The vibratory motions in a polyatomic molecule can be analysed as a sum of “normal modes”, component vibrations in which all atoms move at the same frequency with sinusoidal displacements.

Normal modes are SHO, independent, and orthogonal – model valid for low quantum numbers only.

N – number of atoms:

- Linear –
  \[ 3N - 5 \text{ normal modes of vibration.} \]
e.g. \( CO_2 \):

\[
\begin{align*}
\text{IR active} & \quad \text{IR inactive} \\
v_1 & \quad v_2 \\
\text{O-C=O} & \quad \text{O-C=O} \\
\text{Stretch} & \quad \text{Bend} \\
G(v_1, v_2, v_3) &= (v_1 + \frac{1}{2})\omega_1 + (v_2 + \frac{1}{2})\omega_2 + (v_3 + \frac{1}{2})\omega_3 \\
&= \text{(ignoring anharmonicity)}
\end{align*}
\]

Infrared Selection Rules –
Dipole moment must change on vibration.
\( \Delta J = \pm 1 \) for parallel vibrations (change parallel to linear molecule xis).
\( \Delta J = 0, \pm 1 \) for perpendicular vibrations (change perpendicular to axis – bending).
Q-branch –
\[ G(v_2=1, J) - G(v_2=0, J) = (B_1-B_0)J(J+1) + v_0. \]

\( B_1 - B_0 \) small – transitions pile up.
Transition allowed because of double degeneracy.

**Symmetry of Rotational Wavefunction – parity**
Designate levels wrt space-fixed inversion.

\[ + \leftrightarrow - \quad \text{allowed} \]
\[ + \leftrightarrow + / - \leftrightarrow - \quad \text{disallowed} \]

**Overtone and Combination Bands (Linear)**
Overtone – change of vibrational quantum number by > 1 in one mode.
Combination Band – excitation of 2 different vibrational modes simultaneously.
Example, CO_2

Selection Rules for Overtones and Combinations:
\( v_1 \) – g symmetry.
\( v_2 \) – u for odd quanta, g for even.
\( v_3 \) – u for odd, g for even.
\( (0,0,0) \) – g.
Selection Rule – g ↔ u.

**Vibrational Spectroscopy of Non-Linear Polyatomics**
3N – 6 normal modes of vibration.
Characterise by irreducible representations of the molecular symmetry group, e.g.

\[ (a_1, a_1, a_1) \rightarrow (a_1, 5, 5) \]
\[ (a_2, a_2, a_2) \rightarrow (a_1, 5, 5) \]
\[ (a_3, a_1, 0) \rightarrow (5, 5, 5) \]
\[ (a_3, 0, 0) \rightarrow (5, 5, 0) \]
\[ (0, a_3, 0) \rightarrow (5, 5, 0) \]

Those displayed above \( \rightarrow \) no dipole change. IR inactive.

**Vibrational Selection Rules:**
\[ \langle \psi_i | \mu | \psi_f \rangle \] - totally symmetric.
\( \rightarrow \) must contain \( A_1 \) for allowed transition.
\( \Gamma_{y} \) - transforms as x, y, z.
\( \Gamma_{y'} \) - normally totally symmetric for Ground Level (\( a_{1g} \)).
\( \Gamma_{y'} \) - must transform as x, y or z.
For \( D_{4h} \), \( a_{2u} \) and \( e_u \) modes active (those with x, y, z in character table).

**Rotational Structure in IR Spectra of Polyatomics – Symmetric Top**

Selection Rules:
Parallel (allowed by z) –
\[ \Delta K = 0 \]
\[ \Delta J = \pm 1 \] for \( K = 0 \), \( \Delta J = 0, \pm 1 \) for \( K \neq 0 \)
Perpendicular (allowed by $x, y$) –
\[ \Delta K = \pm 1 \quad \Delta J = 0, \pm 1 \]

**Overtones and Combination Bands (Polyatomics)**
Consider direct product for excited modes. Overtone allowed if product transforms as $x, y, z$.
e.g. $D_{4h} - b_{1g} \times b_{2u} = a_{2u}$ (allowed).

**Hot Bands**
Intensity of transitions from vibrationally excited states increases as $T$ increases.

**Group Frequencies**
Bond vibrations strongly coupled if similar intrinsic frequencies. Some bonds almost completely
decoupled $\Rightarrow$ Group Frequency.

**Tunnelling and Inversion**
When more than one minimum in PE surface $\Rightarrow$ overlap of vibrational wavefunctions possible $\Rightarrow$
tunnelling, e.g. $\text{NH}_3$:

\[ \pm \text{linear combinations have slightly different energies.} \]
Overlap increases nearer top of the well, hence tunnelling splitting increases.
Tunnelling Splitting Frequency = rate constant for inversion.

Small splittings in other bands also observed due to anharmonic effects, e.g. excitation of other $v_i$
stretching mode causes slight change in bonding potential $\Rightarrow$ different tunnelling frequency.

**Broadening in Spectra**
a) Lifetime broadening – “natural linewidth”.
b) Pressure broadening (collisions)
c) Doppler Effect (effective frequency observed by molecule)
d) Power (saturation) broadening.
e) Unresolved underlying structure.
f) Instrumental resolution.

**Lifetime Broadening** – if the probability of a system existing in a particular state decays as:
\[ |\psi|^2 \approx |\psi|^2 e^{-t/\tau} \]
This gives rise to an energy uncertainty.
\[ \tau \delta E \approx \hbar. \]
$\delta E$ is the full width at half maximum height.
\[ \tau \delta v = 1/2\pi c \]

**Raman Spectroscopy**
Monochromatic light, wavenumber $v_o$ (visible).
Measure spectrum of scattered light.
Raman Effect. Inelastic Scattering:
- \( v' > v_L \) – Anti-Stokes
- \( v' < v_L \) – Stokes
Conservation of Energy: \( h v' - h v_L = \Delta E \).

**Quantum Picture of Raman**

The “absorption” and “emission” are instantaneous and simultaneous – no transfer of population. “virtual” state – off-resonant, transient, polarisation induced.

Both pure rotational and vib-rot changes are observed:

**Classical description of Raman**
Molecule rotating at frequency \( \omega' \) – polarisability oscillates with frequency \( 2\omega' \) → oscillating dipole radiates.

**Gross Selection Rules for Raman:**
**Rotational** – molecule must have anisotropic polarisability.

\[ \Delta J = 0, \pm 2 \] (rotational and vibrational)

Rotational –
\[ \Delta J = 0 \] (Rayleigh)
\[ \Delta J = \pm 2 \] Stokes / Anti-Stokes

\[ F(J+2) - F(J) = B[(J+2)(J+3) - J(J+1)] = (4J+6)B \]

So Stokes lines at \( v_L - (4J+6)B \)
\[ J = 0, 1, ... \]

\[ F(J-2) - F(J) = (4J-2)B \]

So Anti-Stokes lines at \( v_L + (4J-2)B \)
\[ J = 2, 3, ... \]

Resolution is not normally sufficiently high to include centrifugal distortion.

**Vibrational** – polarisability change on vibration.

**Selection Rules** –
\[ \Delta v = 1, \Delta J = 0 \]

Rotational Structure –
**Q-branch**: \( \Delta v = 1, \Delta J = 0 \)

\[ F(v=1,J) - F(v=0,J) \]
\[ = v_0 + \left( B_1 - B_0 \right) J(J+1) \approx v_0 \] [displacement from \( v_L \) ]
\[ = \omega_o - 2\omega_x \]
S-branch: \( \Delta v = 1, \Delta J = +2 \)

\[
F(v=1, J+2) - F(v=0, J) = v_0 + B_1(J+2)(J+3) - B_0(J+1) = v_0 + (B_1+B_0)(2J+3) + (B_1-B_0)(J^2 + 3J + 3)
\]

O-branch: \( \Delta v = 1, \Delta J = -2 \)

\[
F(v=1, J-2) - F(v=0, J) = v_0 + B_1(J-1)(J-2) - B_0(J+1) = v_0 - (B_1+B_0)(2J-1) + (B_1-B_0)(J^2 - J + 1)
\]

**Rule of Mutual Exclusion – Polyatomic**

For molecules with centre of inversion symmetry (i): IR active modes are Raman inactive and vice versa. There may be some modes that are inactive in both.

**Transition Intensities and Group Theory**

Raman effect arises from interaction of the induced dipole moment of the molecule with the EM field.

For a diatomic in an E-field \( \varepsilon \) polarised in the z-direction, the component of the induced dipole in that direction:

\[
\mu_z = \alpha_x \varepsilon \sin^2 \Theta + \alpha_y \varepsilon \cos^2 \Theta
\]

2 parts of \( \mu_z \) transform in \( D_{\infty h} \) group in the same way as \( x^2 + y^2 \) and \( z^2 \) (\( A_{1g} \)).

Transition Moment (Raman) is of the form:

\[
<v'J' | \mu_z | v''J'' >
\]

For non-zero transition probability require:

- \( \Gamma_{v'} \), \( \Gamma_{\mu_z} \), \( \Gamma_{v''} \) transforms to \( A_{1g} \) (totally symmetric)

\( x^2, y^2, xy \) etc \( \rightarrow g \)

\( x, y, z \rightarrow u \)

(Hence mutual exclusion principle above).

**Effects of Nuclear Spin Statistics**

**Pauli Principle:**

- \( \Psi_{v''} \) is antisymmetric when exchange of equivalent **FERMIONS**
- \( \Psi_{v''} \) is symmetric when exchange of equivalent **BOSONS**

\[
\Psi = \Psi_{v''} \Psi_{v''} \Psi_{v''} \Psi_{v''} \Psi_{v''}
\]

- \( \Psi_{v''} \) is always

- \( \Psi_{v''} \) is usually \( \square \), but e.g. \( \text{CO}_2 \) (\( \square \))
- \( \Psi_{v''} \) is always \( \square \) in vib ground state
- \( \Psi_{v''} \) is always \( \square \) in diatomic
- \( \Psi_{v''} \) in polyatomic, may be \( \square \) for odd \# of \( \text{nuc}\)
- \( \text{e.g.: CO}_2 \) \( (v_i,v_i,v_i) \)
\[(0,0,0) \; (1,0,0) ; (0,0,1) \]

- \( \Psi_{v''} \) is symmetric for even \( J \)
- \( \Psi_{v''} \) is antisymmetric for odd \( J \)

Can thus stipulate \( \Psi_{\text{nuc}} \).
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Applications to Diatomics (homonuclear) and Linear Molecules

\[ \frac{1}{2} \left[ \alpha(1) \beta(2) + \alpha(2) \beta(1) \right] \]

\[ \frac{1}{2} \left[ \alpha(1) \beta(2) - \alpha(2) \beta(1) \right] \]

\[ \psi_{\text{nuc}} = \text{symmetric} \]

For rotational Raman:

\[ \psi_{\text{rot}} = \text{only} \]

For infrared: for (0,0,1).

\[ \psi_{\text{vib}} = \text{only} \]

\[ \psi_{\text{rot}} = \text{only} \]

Only odd J levels exist. Raman: 1 \rightarrow 3, 3 \rightarrow 5, ...