Molecular Spectroscopy 1. rotational & vibrational spectra

Reading: Atkins, Ch. 13 (7판 Ch. 16)

Molecular spectroscopy vs. Atomic spectroscopy

- electronic transition (Ch.14) +
- Rotational, vibrational

\[ E_{\text{elec}} >> E_{\text{vib}} >> E_{\text{rot}} \]
Energy of electromagnetic field: oscillating electric & magnetic disturbance

\[ E = h\nu = h\frac{c}{\lambda} \]

- \( h \): Planck constant \((6.6 \times 10^{-34} \text{ Js})\)
- \( c \): speed of light \((3 \times 10^8 \text{ m/s})\)
- \( \lambda \): wavelength \((\text{distance between the neighboring peaks of wave})\)
  \[ 1 \text{ Å} = 0.1 \text{ nm} = 10^{-10} \text{ m} \]
- \( \nu \): frequency \((\text{Hz} = 1 \text{ s}^{-1})\); number of times per second
  \[ \lambda\nu = c \]
- \( \lambda\nu \): wavenumber \((\text{cm}^{-1}, \text{reciprocal cm})\)
  \( \nu\)-bar = \( \nu/c = 1/\lambda \)
- \( \nu\)-bar \(1 \text{ eV} \sim 8066 \text{ cm}^{-1}\)

\[ \text{파장} (\lambda, \text{nm}) = \frac{1240}{\text{band gap energy (eV)}} \]
Electromagnetic spectrum
Experimental spectroscopy: absorption or emission
\[ E_2 - E_1 = h\nu \]

- Absorption spectroscopy

- Emission spectroscopy
**Source of radiation**
- far IR: mercury arc
- IR: Nernst glower (ZrO$_2$ + Y$_2$O$_3$)
- Visible: Tungsten lamp
- UV: H$_2$, D$_2$ or Xe lamp
- laser
- synchrotron radiation

**Dispersing element: separating the frequencies of the radiation**
- Prism, diffraction grating, monochromator
**Detectors**: radiation → electric current
- photomultiplier tube (PMT), diode (Si, Ge..), charge-coupled device (CCD)...

**Sample**: cell/window materials
- UV/visible: quartz, glass..
- IR: NaCl, KBr

- **Raman spectroscopy**

  Lower frequency: Stokes radiation
  Higher frequency: anti-Stokes radiation
  No frequency change: Rayleigh radiation

  Why Laser in Raman?: quite small frequency shift (monochromator needed)
  low scattered intensity
Intenistency of spectral lines

\[ I_0 \quad \text{incident intensity} \quad \rightarrow \quad I \quad \text{transmitted intensity} \]

- Transmittance \( T = \frac{I}{I_0} \)

- Beer-Lambert law \( I = I_0 10^{-\varepsilon [J]/l} \)

\([J]\): molar concentration, \( l\): length,

\( \varepsilon\): molar absorption coefficient

(Extinction coefficient), \( \text{Lmol}^{-1} \text{cm}^{-1} \)

or \( \text{cm}^2\text{mol}^{-1} \)

- Absorbance, \( A = \log[I_0/I], \text{ or } A = -\log T \) (at a given wavenumber)

\[ A = \varepsilon [J]/l \quad \text{“optical density”} \]
Absorption intensities

Population at equilibrium \( \frac{N_i}{N} \propto e^{-E_i/kT} \) at \( T \) (K) \( kT \approx 200 \text{ cm}^{-1} \) at room temperature

\[ \frac{N_1}{N_0} = e^{-(E_1-E_0)/kT} \]

\( E_2 \) e.g.) at room \( T \), \( E_1 - E_0 = 200 \text{ cm}^{-1} \) \( \rightarrow \) \( \frac{N_1}{N_0} = e^{-1} \)

\( E_1 \)

\( E_1 - E_0 = 2000 \text{ cm}^{-1} \) \( \rightarrow \) \( \frac{N_1}{N_0} \approx 0 \)

\( E_0 \)

Rotation: \( E_{\text{rot}} = J(J+1) \frac{\hbar^2}{2I} \)

\[ \frac{N_j}{N_0} \propto (2J + 1)e^{-E_{\text{rot}}/kT} \]
\( B_{nm} \): Einstein coefficient of stimulated absorption (B)

\( B_{mn} \): Einstein coefficient of stimulated emission (B') \( E_m, N_m \)

\( A_{mn} \): Einstein coefficient of spontaneous emission (A)

**Spontaneous emission:**
\[ -\frac{dN_m}{dt} = +A_{mn}N_m \]

\( \rho(\nu_{mn}) \):
\( \rho \) : density of radiation \( E_n, N_n \)

**Stimulated emission:**
\[ -\frac{dN_m}{dt} = +B_{mn}N_m\rho(\nu_{mn}) \]

**Stimulated absorption:**
\[ \frac{dN_n}{dt} = -\frac{dN_m}{dt} = B_{nm}N_n\rho(\nu_{mn}) \]

At equilibrium:
\[ \text{rate} \uparrow = \text{rate} \downarrow \]

\[ B_{nm}N_n\rho(\nu_{mn}) = A_{mn}N_m + B_{mn}N_m\rho(\nu_{mn}) \]

\[ \frac{N_m}{N_n} = \frac{B_{nm}N_n\rho(\nu_{mn})}{[A_{mn}N_m + B_{mn}N_m\rho(\nu_{mn})]} = e^{-\frac{(E_m - E_n)}{kT}} = e^{-\frac{h\nu_{mn}}{kT}} \]
\[ \rho (v_{mn}) = \frac{A_{mn}}{B_{nm} e^{-\frac{h v_{mn} }{kT}} - B_{mn}} \quad (1) \]

Planck’s law
\[ \rho (v_{mn}) = \left( 8 \pi \hbar v^3/c^3 \right) \left( \frac{1}{e^{-h v_{mn}/kT} - B_{mn}} \right) \quad (2) \]

(1) = (2) \quad B_{mn} = B_{nm} = B

\[ \frac{A}{B} = \frac{A_{mn}}{B_{mn}} = 8 \pi \hbar v^3/c^3 \]

\[ v \uparrow \rightarrow A \uparrow \text{(spontaneous emission)} \rightarrow \text{laser} \]

Lower frequency (rotational & vibrational transitions) \( \rightarrow \) A can be ignored
**Selection rules:** transition is forbidden or allowed?

transition dipole moment \( \mu_{fi} \)

\[
\mu_{fi} = \langle f_f | \hat{\mu} | f_i \rangle = \int \psi_f^* \hat{\mu} \psi_i \, dz
\]

\( \hat{\mu} \): electric dipole moment operator

\( \mu_{fi} \neq 0 \Rightarrow " \text{transition allowed}" \) : selection rule

Stimulated absorption (or emission)

\[
\beta = \frac{|\mu_{fi}|^2}{6 \epsilon_0 c h} \Rightarrow \text{intensity of transition} \propto |\mu_{fi}|^2
\]

- Electronic transition: \( \Delta l = \pm 1 \) (angular momentum \( \ell \), \( \pi \))

\[
\begin{align*}
1s & \rightarrow 2s \\
\text{(x)} & \rightarrow 2s \\
1s & \rightarrow 2p \\
\text{(o)} & \rightarrow 2p
\end{align*}
\]
rotation

N≡N (x)
(No dipole moment)

C=O (o)

Vibration

\[ \leftrightarrow \]

\[ \equiv \equiv \]

\[ \equiv \equiv \] (bending)

\[ \equiv \equiv \] (o)

\[ \equiv \equiv \] (o)

\[ \equiv \equiv \] (x)
Linewidths

Why? 1. experimental conditions, 2. Inherent limitations
→ To achieve high resolution, we need to know how to minimize these contributions

- Inherent limitations: Doppler broadening & lifetime broadening

(a) Doppler broadening

- Doppler effect: radiation is shifted in frequency when the source is moving towards or away from the observer

\[
\nu_{\text{receding}} = \nu \left( \frac{1 - \frac{v}{c}}{1 + \frac{v}{c}} \right)^{1/2}, \quad \nu_{\text{approaching}} = \nu \left( \frac{1 + \frac{v}{c}}{1 - \frac{v}{c}} \right)^{1/2}
\]
For nonrelativistic speeds ($v_x \ll c$)

\[ \frac{\nu}{1 + \frac{v_x}{c}} \quad \text{and} \quad \frac{\nu}{1 - \frac{v_x}{c}} \]

(red shift)

Consider \n
\[ \lambda = \lambda_0 \left( 1 - \frac{v_x}{c} \right) \]

\[ \chi \text{ shift } \chi = \frac{\lambda - \lambda_0}{\lambda_0} = \frac{v_x}{c} \]

\[ v_x \sim v_x' + dv_x \]

probability \n
\[ f(v_x)dv_x = Ne^{-\frac{1}{2}mv_x^2/kT}dv_x \]

\[ = Ne^{-\frac{1}{2}mc^2x^2/kT}cdx = \int f(x)dx = N'e^{-\frac{1}{2}mc^2x^2/kT}dx \]
\[ x = \frac{\lambda - \lambda_0}{\lambda_0} \]

Full width at half-height point

\[ \frac{1}{2} mc^2 x^2 / kT = -\ln \frac{1}{2} = \ln 2 \]

\[ x = \pm \left( \frac{2kT \lambda_0^2}{mc^2} \right)^{1/2} \]

\[ \Delta \lambda = \lambda_0 (x_+ - x_-) = \frac{2\lambda_0}{c} \left( \frac{2kT \lambda_0^2}{mc} \right)^{1/2} \]

\( T \uparrow \rightarrow \) more broad: cold sample is better sharpness
(b) lifetime broadening: quantum mechanical effect

System that is changing with time → impossible to specify the energy level exactly

\[ \frac{\Delta E}{\Delta \tau} \approx \frac{\hbar}{\tau}, \ \therefore \text{lifetime} \]

Uncertainty broadening

Factors influencing the lifetime of excited states

→ Spontaneous emission (coefficient \( A \propto \nu^3 \)), stimulated emission, collision, deactivation (pressure broadening)

\[ E = h\nu = hc\overline{\nu}, \ \ \Delta E = hc \langle \Delta \overline{\nu} \rangle \]

Lifetime: \( \tau (\text{sec}) \)

\[ hc \langle \Delta \overline{\nu} \rangle \cdot \tau \approx \hbar \]

\[ \overline{\nu} \approx \frac{\hbar}{hc \tau} = \frac{1}{2\pi c \tau} = \frac{5 \times 10^{-12} \text{ cm}^{-1}}{\tau (\text{sec})} = \frac{5.3}{\tau (\text{ps})} \]
τ ↓ (shorter lifetime) → broader spectral lines
→ working at low pressure (collisional linewidth)
   low frequency transitions → small linewidth

\[ \text{rate} = \frac{dN_2}{dt} = -kN_2, \quad \int \frac{dN_2}{N_2} = -\int k dt \]

\[
\begin{align*}
\frac{N_2(t)}{N_2(0)} &= e^{-kt}, \quad N_2(t) = N_2(0) e^{-kt} \\
N_2(t) &= N_2(0) e^{-kt}
\end{align*}
\]

\[ \tau = \frac{dt}{dN} = \frac{dt}{dN/N_2} = \frac{dt}{k dt} = \frac{1}{k} \]

spontaneous emission \[ \xi_1 = \frac{1}{k_1} \quad \frac{dN_2}{dt} = -(k_1 + k_2) N_2 \]

stimulated " \[ \xi_2 = \frac{k_2}{k_3} \quad \frac{1}{\xi_2} = k_1 + k_2 + k_3 \ldots = \frac{1}{\xi_1 + \xi_2 + \xi_3 + \ldots} \]

\[ \zeta \text{ of electronic transitions} \ll \zeta \text{ of rotation, vibration} \]

\[ \downarrow \text{higher natural line width} \]
Pure rotation spectra: microwave region

Moment of inertia

I: moment of inertia

\[ I = \sum m_i r_i^2 \]

where \( r_i \) is the perpendicular distance of the atom \( i \) from the axis of rotation

→ depending on molecular structure:
masses & molecular geometry

→ rotational spectroscopy:
information about bond lengths & bond angles
Linear molecules: zero I around the internuclear axis

e.g., I of H$_2$O around axis
Rigid rotors
Spherical rotors: 3 equal I (e.g., CH₄, SiH₄, SF₆)
Symmetric rotors: 2 equal I (e.g., NH₃, CH₃Cl, CH₃CN)
Linear rotors: 1 zero I (1 about the molecule axis) (CO₂, HCl, OCS, HCCH)
Asymmetric rotors: three different I (H₂O, H₂CO, CH₃OH)

Rotational energy levels

E = J²/2I,  J: magnitude of the angular momentum (J(J + 1)ℏ², J = 0, 1, 2,…)

For a, b, c axes, E = Eₐ + Eₕ + Eₖ = Jₐ²/2Iₐ + Jₕ²/2Iₕ + Jₖ²/2Iₖ
(a) Spherical rotors
3 equal I (e.g., CH₄, SiH₄, SF₆)

\[ E = \frac{(J_a^2 + J_b^2 + J_c^2)}{2I} = \frac{J^2}{2I} \]

\[ E_J = \frac{(J(J + 1)\hbar^2}{2I}, \quad J = 0, 1, 2, \ldots \]

Rotational constant of the molecule, B

\[ \hbar c B = \frac{\hbar^2}{2I} \quad \text{so} \quad B = \frac{\hbar}{4\pi c I} \]

→ \[ E_J = \hbar c B(J + 1), \quad J = 0, 1, 2, \ldots \]

→ wavenumber term, \( F(J) = B(J + 1) \)

\( F(J) \): rotational term

\( F(J) - F(J - 1) = 2BJ \)

\[ I \uparrow \rightarrow B \downarrow \]

Large molecules: closely spaced rotational energy levels

e.g., CCl₄, \( I = 4.85 \times 10^{-45} \text{ kgm}^2 \)

→ \( B = 0.0577 \text{ cm}^{-1} \)
(b) Symmetric rotors
2 equal I & 1 different I (e.g., CH₃Cl, NH₃, C₆H₆):
principle axis (Iₜ) & other two (Iₙ)
If $\rightarrow$ oblate (like pancake or C₆H₆)
If $\rightarrow$ prolate (like cigar, CH₃Cl)

$$E = \frac{(J_b^2 + J_c^2)}{2I_n} + \frac{J_a^2}{2I_t}$$

$$J^2 = J_a^2 + J_b^2 + J_c^2$$

$$E = \frac{(J^2 - J_a^2)}{2I_n} + \frac{J_a^2}{2I_t} = \frac{J^2}{2I_n} + (\frac{1}{2I_t} - \frac{1}{2I_n})J_a^2$$

Quantum mechanics

$$J^2 = (J(J + 1)\hbar^2, \quad J = 0, 1, 2....$$

$$J_a = K\hbar, \quad K = 0, \pm 1, \ldots \pm J$$

$$E_{J,K} = J(J + 1)\hbar^2/2I_n + K^2\hbar^2/2(1/I_t - 1/I_n)$$

$$F(J, K) = BJ(J + 1) + (A - B)K^2$$

With $A = \hbar / 4\pi c I_t$ and $B = \hbar / 4\pi c I_n$

$K = 0$, $E$ depends only on $I_n$
$K = \pm J$, $F(J, K) = BJ + AJ^2$ e.g., 16.2
(c) Linear rotors
K = 0

\[ E = J(J + 1)\hbar^2/2I \]  \hspace{1em} J = 0, 1, 2, \ldots
\[ F(J, K) = BJ(J + 1) \]

(d) Degeneracies and the Stark effect
E of symmetric rotor depends on J & K
J, K \rightarrow M_j quantized, M_j = 0, \pm 1, \ldots, \pm J
\rightarrow (2J + 1) degeneracy

Symmetric rotor:
K \neq 0; 2(2J +1)-fold degenerate (J, K, respectively)
K = 0, (2J+1)-fold degenerate

Linear rotor (K = 0): 2J+1 fold degenerate
Spherical rotor: 2J+1 fold degenerate

Stark effect: splitting of states by an electric field
Electric field, $E$

\[ E(J, M_J) = \hbar c B J (J + 1) + a(J, M_J) \mu^2 E^2 \]

where

\[ a(J, M_J) = \frac{[J(J + 1) - 3M_J^2]}{[2\hbar c B J (J + 1)(2J - 1)(2J + 3)]} \]

$\mu$: permanent electric dipole moment

(e) Centrifugal distortion
Rigid rotor by centrifugal force: change $I$
Diatom molecule

\[ F(J) = B J (J + 1) - D_J J^2 (J + 1)^2 \]

$D_J$: centrifugal distortion const

\[ D_J = 4B^3/\sqrt{\nu}^2 \]
Rotational transitions
B of small molecules $\rightarrow$ 0.1 ~ 10 cm$^{-1}$ (microwave region)

(a) Rotational selection rules
Gross selection rule: $\mu \neq 0$ (permanent electric dipole moment)
$\rightarrow$ for pure rotational spectrum, it must be polar
Homonuclear diatomic molecules,
symmetrical linear molecule (CO$_2$),
spherical rotor $\rightarrow$ rotationally inactive

Specific rotational selection rules: transition dipole moment between rotational states
For linear molecule: $\Delta J = \pm 1$, $\Delta M_J = 0$, $\pm 1$
($\Delta J = -1$: emission, $\Delta J = +1$: absorption)
$\rightarrow$ conservation of angular momentum
when a photon, a spin-1 particle, is emitted or absorbed

Symmetric rotors: $\Delta K = 0$, $\Delta J = \pm 1$
(principal axis: no change)
\[ F(J, K) = BJ(J + 1) + (A - B)K^2 \]

Absorption: \( J \rightarrow J + 1; \quad \bar{\nu} = 2B(J + 1), \quad J = 0, 1, 2 \ldots \)
\( \rightarrow 2B, 4B, 6B, \ldots \)
Separation: 2B

e.g., 16.3

Intensity of rotational spectrum
I is proportional to \( N_J \): population at equilibrium
\[ N_J = N_g \exp(-E_J/kT) / \sum g_J \exp(-E_J/kT) \]
\( g_J \): degeneracy of level \( J \)

Linear molecule: \( g_J = 2J + 1 \)
\[ E_J = hCBJ(J + 1) \]
\[ N_J = N(2J + 1) \exp(-hCBJ(J + 1)/kT) \]
\[ J_{max} \rightarrow N_J/dJ = 2 \exp(-hCB(J + 1)/kT) - [hCB(2J + 1)^2/kT] \exp(-hCB(J + 1)/kT) \]
\[ = [2 - hCB(2J + 1)^2/kT] \exp(-hCB(J + 1)/kT) \]
\[ J_{max} \sim (kT/2hcB)^{1/2} - \frac{1}{2} \]
e.g., typical molecule at room T, \( kT \sim 1000hcB \rightarrow J_{max} \sim 22 \)
Rotational Raman spectra
Selection rule: must be anisotropically polarizable

Raman effect: inelastic light scattering

\[ h\nu_0 \rightarrow h\nu \]

\[ \nu_\text{Stokes} < \nu_\text{incident} \Rightarrow \text{entire spectrum range is very small} \]

\[ \nu_\text{anti-Stokes} \rightarrow \nu_\text{incident} \Rightarrow \text{incident light must be highly monochromatic (e.g. laser)} \]
anisotropically (비정방성) polarizable?

\[ \text{H}_2 \]

Induced dipole moment,  \( \mu = \alpha E \)
\( \alpha \): polarizability

Atom: isotropically polarizable

Spherical rotor: isotropically polarizable (정방성)
→ \( \text{CH}_4, \text{SF}_6 \): rotationally Raman inactive, rotationally (microwave) inactive

Nonspherical rotors: anisotropically polarizable (depend on the direction of \( E \))
→ diatomics, linear molecules, symmetric rotors
→ rotationally Raman active
e.g., homonuclear diatomic:
rotational inactive, but rotationally Raman active
Selection rule
Gross selection rule: anisotropic $\alpha$
Specific selection rule  linear rotors: $\Delta J = 0, \pm 2$
Symmetric rotors: $\Delta J = 0, \pm 1, \pm 2; \Delta K = 0$
$\Delta J = 0$: no shift of the scattered photon’s frequency (Rayleigh line)

c.f. Why $\Delta J = \pm 2$?
i) $\mu_{\text{ind}} = \alpha E(t) = \alpha E \cos \omega_i t$, $\omega_i$: angular frequency of incident photon
If molecule is rotating at a circular frequency $\omega_R$
$\rightarrow \alpha = \alpha_0 + \Delta \alpha \cos 2\omega_R t$, where $\Delta \alpha = \alpha_{II} - \alpha_{\perp}$, $\alpha$ from $\alpha_0 + \Delta \alpha$ to $\alpha_0 - \Delta \alpha$ as the molecule rotates $\rightarrow$ “2”; 1 revolution, polarizability twice
\[ \mu_{\text{ind}} = (\alpha_0 + \Delta \alpha \cos 2\omega_R t) \times (E \cos \omega_i t) = \alpha_0 E \cos \omega_i t + E \Delta \alpha \cos 2\omega_R t \cos \omega_i t = \alpha_0 E \cos \omega_i t + \frac{1}{2} E \Delta \alpha [\cos (\omega_i + 2\omega_R) t + \cos (\omega_i - 2\omega_R) t] \]

\(\omega_i\), incident frequency  \(\omega_i \pm 2\omega_R\)
Rayleigh radiation  shifted Raman lines

ii) Raman → 2 photons involved (spin-1 particle) → max. changes in angular momentum quantum number = ±2

Raman spectrum of a linear rotor: \(\Delta J = \pm 2\)
\(\Delta J = +2, J \rightarrow J + 2\), Stokes lines
\[ \tilde{\nu}(J \rightarrow J + 2) = \tilde{\nu}_i - [B(J + 2)(J + 3) - BJ(J + 1)] = \tilde{\nu}_i - 2B(2J + 3), J = 0, 1, 2, \ldots \]
Stokes lines: -6B, -10B, -14B,…

\(\Delta J = -2, J \rightarrow J - 2\), Anti-Stokes lines
\[ \tilde{\nu}(J \rightarrow J - 2) = \tilde{\nu}_i + 2B(2J - 1), J = 2, 3, 4, \ldots \]
e.g., 16.4
The vibrations of diatomic molecules

Molecular vibrations

Diatomic molecule

$H_2$

Harmonic oscillator, $V = \frac{1}{2}kx^2$, $x = R - R_e$

$-\left(\frac{\hbar^2}{2\mu}\right)\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi$

$\mu = m_{\text{eff}} = \frac{m_1m_2}{m_1 + m_2}$: reduced or effective mass

$E_v = (v + \frac{1}{2})\hbar\omega$, $v = 0, 1, 2…$

$\omega = \sqrt{\left(\frac{k}{\mu}\right)}$, $\omega = 2\pi v \rightarrow v = \frac{1}{2\pi}\sqrt{\left(\frac{k}{\mu}\right)}$

Vibrational term, $G(v) = (v + \frac{1}{2})\nu$, $E_v = \hbar c G(v)$

$\nu = \frac{1}{2\pi c}\sqrt{\left(\frac{k}{\mu}\right)}$

Homonuclear diatomic molecule, $m_1 = m_2$, $\mu = 1/2m$
Selection rule
Gross selection rule: dipole moment $\mu \neq 0$
(dipole moment must change) $\rightarrow$ infrared active
Specific vibrational selection rule
\( \Delta v = +1: \text{absorption}, \Delta v = -1: \text{emission} \)
\( \Delta G_{v+1/2} = G(v + 1) - G(v) = \overline{\nu} \)

At room T, \( kT/\hbar c = 200 \text{ cm}^{-1} \) → IR > 200 cm\(^{-1}\)

Anharmonicity
True potential energy?
\( V(x) = V(0) + (dV/dx)_0 x + \frac{1}{2}(d^2V/dx^2)_0 x^2 + \ldots \)

One approach to anharmonicity
Morse potential energy
\( V = \hbar c D_e [1 - e^{-a(R - R_e)}]^2 \)
\( a = [m_{\text{eff}} \omega^2/2\hbar c D_e]^{1/2} \), \( D_e \): depth of the potential minimum
H = T + V, HΨ = EΨ
→ E_v = (v + ½)hν - (v + ½)^2x_e hν + (v + ½)^3y_e hν + ...
x_e = ħa^2/2μω = ν/4D_e: anharmonicity constant

G(v) = (v + ½)ν - (v + ½)^2x_e ν, v = 0, 1, 2,...,v_max

Wavenumbers of transitions with Δv = +1
ΔG_{v+1/2} = G(v + 1) - G(v) =  ν - 2(v + 1)x_e ν + ...
(or ΔE (v → v + 1) = hν - 2(v + 1)x_e hν..)
→ when x_e ≠ 0, the transitions move to lower wavenumbers as v increases

Mainly Δv = ±1 (fundamental frequency), however, anharmonicity allows additional weak lines corresponding Δv = ±2, ±3,... ("overtones")

1st overtone, G(v + 2) - G(v) = 2ν - 2(2v + 3)x_e ν + ...

Selection rule is derived from harmonic oscillator, for an anharmonic oscillator, all values of Δv are allowed, but transitions with Δv > 1 are weak if the anharmonicity is slight
Vibration-rotation spectra
Each line of high-resolution vib. Spectrum of heteronuclear diatomic molecular consists of large # of closely spaced lines ("band spectra") → rotational transition with vibrational transition

\[ E = E_{\text{vib}} + E_{\text{rot}} + E_{\text{ele}}, \quad E_{\text{ele}} > E_{\text{vib}} > E_{\text{rot}} \]

IR radiation → no electronic transition, vib. transition + rotational transition

Diatomic molecule
\[ E_{v,J} = (v + \frac{1}{2})h\nu + hcBJ(J + 1) \quad \text{H.O.} \]
\[ E_{v,J} = (v + \frac{1}{2})h\nu - (v + \frac{1}{2})2x_\nu h\nu + hcBJ(J + 1) \quad \text{Anharm.} \]

Vibration-rotation term
\[ S(v,J) = G(v) + F(J) \]
Selection rule $\mu \neq 0$

$\Delta v = \pm 1,$

$\Delta J = \pm 1, 0$ (total orbital ang. momentum about internuclear axis $\neq 0, \Lambda \neq 0$)

e.g., paramagnetic molecule, NO

$\Delta v = 1 \ (v \rightarrow v + 1)$

i) $\Delta J = -1, \Delta E = h\nu - 2B J,$

$\nu_p(J) = S(v+1, J-1) - S(v, J) = \nu - 2BJ$

$\rightarrow h\nu - 2B, h\nu - 4B, \ldots$ P-branch

ii) $\Delta J = 0, \Delta E = h\nu,$

$\nu_Q(J) = S(v+1, J) = \nu$ Q-branch

allowed: NO, forbidden: HCl

iii) $\Delta J = +1, \Delta E = h\nu + 2B(J + 1),$

$\nu_R(J) = S(v+1, J+1) - S(v, J) = \nu + 2B(J + 1)$ R-branch
Vibrational Raman spectra of diatomic molecule
Gross selection rule: polarizability should change as the molecule vibrates
Homonuclear and heteronuclear diatomic molecules → vibrational Raman active
Specific selection rule: $\Delta v = \pm 1$, $\Delta J = 0$, $\pm 2$
$\Delta v = +1$
i) $\Delta J = -2$, O-branch
ii) $\Delta J = 0$, Q-branch
iii) $\Delta J = +2$, S-branch
<table>
<thead>
<tr>
<th></th>
<th>$\tilde{v}_0$/cm$^{-1}$</th>
<th>$\theta_r$/K</th>
<th>$B$/cm$^{-1}$</th>
<th>$\theta_r$/K</th>
<th>$r$/pm</th>
<th>$k$/(N m$^{-1}$)</th>
<th>$D$/(kJ mol$^{-1}$)</th>
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<td>$^1$H$_2$</td>
<td>2321.8</td>
<td>3341</td>
<td>29.8</td>
<td>42.9</td>
<td>106</td>
<td>160</td>
<td>255.8</td>
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<td>4400.39</td>
<td>6332</td>
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<td>74.138</td>
<td>574.9</td>
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<td>$^2$H$_2$</td>
<td>3118.46</td>
<td>4487</td>
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<td>$^1$H$^{19}$F</td>
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<td>5955</td>
<td>20.956</td>
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<td>91.680</td>
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<td>564.4</td>
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<td>4304</td>
<td>10.593</td>
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<td>109.76</td>
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<td>2.08</td>
<td>120.75</td>
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<td>$^{35}$Cl$_2$</td>
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<td>3122</td>
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<tr>
<td>$^{79}$Br$^{81}$Br</td>
<td>323.2</td>
<td>465</td>
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<td>10.116</td>
<td>283.3</td>
<td>245.9</td>
<td>190.2</td>
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</table>

Data: AIP
The vibrations of polyatomic molecules

Diatomic molecule: one mode of vibration → bond stretch
Polyatomic molecules: several modes

\[ N \text{ atoms} \rightarrow \text{degree of freedom for vibration (p. 522, Justification 16.9)} \]

- linear: \( 3N - 5 \) (total: 3N, 3 translation, 2 rotation)
- nonlinear: \( 3N - 6 \) (total: 3N, 3 translation, 3 rotation)

CO\(_2\) (linear molecule), \( f_v = 3 \times 3 - 5 = 4 \) modes for vibration

Symmetric stretch, \( \nu_1 = 1388 \text{ cm}^{-1} \) (IR inactive)

Antisymmetric stretch, \( \nu_3 = 2349 \text{ cm}^{-1} \)

Bending, \( \nu_2 = 667 \text{ cm}^{-1} \) (degenerate)

\( \nu(\text{bending}) < \nu(\text{stretch}) \)

\[ G_p(v) = (v + \frac{1}{2})\bar{\nu}_q, \quad \bar{\nu}_q = (1/2\pi c)\sqrt{(k_q/m_q)} \]
\( H_2O, f_v = 3 \times 3 - 6 = 3 \) modes

Gross selection rule for IR: change of dipole moment
e.g., symmetric stretch of \( \text{CO}_2 \): no dipole moment change \( \rightarrow \) IR inactive
antisymmetric stretch, bending modes \( \rightarrow \) IR active

Specific selection rule \( \Delta v_q = \pm 1 \) in harmonic approximation

Molecules can be identified from characteristic frequencies and intensities
Table 16.3 Typical vibrational wavenumbers, $\tilde{\nu}/\text{cm}^{-1}$

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Wavenumber Range</th>
<th>Bond Type</th>
<th>Wavenumber Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H stretch</td>
<td>2850–2960</td>
<td>C–F stretch</td>
<td>1000–1400</td>
</tr>
<tr>
<td>C–H bend</td>
<td>1340–1465</td>
<td>C–Cl stretch</td>
<td>600–800</td>
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<td>C–C stretch, bend</td>
<td>700–1250</td>
<td>C–Br stretch</td>
<td>500–600</td>
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<tr>
<td>C≡C stretch</td>
<td>1620–1680</td>
<td>C–I stretch</td>
<td>500</td>
</tr>
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<td>C≡C stretch</td>
<td>2100–2260</td>
<td>CO$_3^{2-}$</td>
<td>1410–1450</td>
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<tr>
<td>O–H stretch</td>
<td>3590–3650</td>
<td>NO$_3^-$</td>
<td>1350–1420</td>
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<td>H-bonds</td>
<td>3200–3570</td>
<td>NO$_2^-$</td>
<td>1230–1250</td>
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<td>C≡O stretch</td>
<td>1640–1780</td>
<td>SO$_4^{2-}$</td>
<td>1080–1130</td>
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<td>C≡N stretch</td>
<td>2215–2275</td>
<td>Silicates</td>
<td>900–1100</td>
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<tr>
<td>N–H stretch</td>
<td>3200–3500</td>
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<td></td>
</tr>
</tbody>
</table>

Vibrational Raman spectra of polyatomic molecules

Vibrational modes are Raman active if changing polarizability e.g., symmetric stretch of CO$_2$: Raman active

Exclusion rule: if the molecule has a centre of symmetry, then no modes can be both IR and Raman active

Depolarization ratio, $\rho$

The ratio of intensities of the scattered light with polarization perpendicular and parallel to the plane of polarization of the incident radiation

$$\rho = \frac{I_\perp}{I_\parallel}$$

Measuring $\rho$: polarizing filter

If emergent light is not polarized: $\rho \sim 1$

$\rho \geq 0.75$: depolarized, $\rho < 0$: polarized