Molecular Spectroscopy 1. rotational & vibrational spectra

Reading: Atkins, Ch. 13 (7판 Ch. 16)

Molecular spectroscopy	vs.	Atomic spectroscopy
electronic transition (Ch.14) + Rotational, vibrational		electronic transition

$E_{elec} >> E_{vib} >> E_{rot}$

Energy of electromagnetic field: oscillating electric & magnetic disturbance

$$E = h\nu = h\, c/\lambda$$

h; Planck constant (6.6 x 10^{-34} Js)

speed of light (c); 3 x 10^{8} m/s,

wavelength (λ); distance between the neighboring peaks of wave,

$$1\ \text{Å} = 0.1\ \text{nm} = 10^{-10}\ \text{m}$$

frequency (ν, Hz = 1 s^{-1}); number of times per second

$$\lambda\nu = c$$

wavenumber (cm^{-1}, reciprocal cm), ν-bar = $\nu/c = 1/\lambda$

cf) 1 eV ~ 8066 cm^{-1}

파장(λ, nm) = 1240/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_2O_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

- photomutiplier tube (PMT), diode (Si, Ge..), charge-coupled device (CCD)..

Sample: cell/window materials

-UV/visible: quartz, glass..

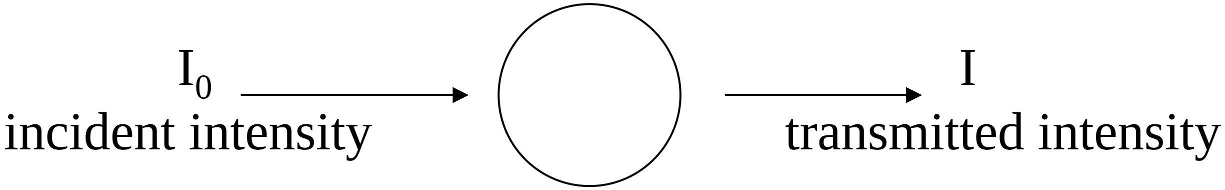
- IR: NaCl, KBr

- **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

Intensity of spectral lines



I_0 incident intensity

I transmitted intensity

- Transmittance $T = I/I_0$

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

[J]: molar concentration, *l*: length,

ε: molar absorption coefficient

(extinction coefficient), $\mathrm{L mol^{-1}\,cm^{-1}}$

or $\mathrm{cm^2 mol^{-1}}$

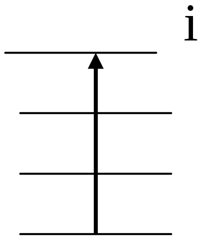
- Absorbance, $A = \log[I_0/I]$, or $A = -\log T$ (at a given wavenumber)

$A = \varepsilon[J]l$ "optical density"

Absorption intensities

Population at equilibrium $N_i/N \propto e^{-Ei/kT}$ at T (K)

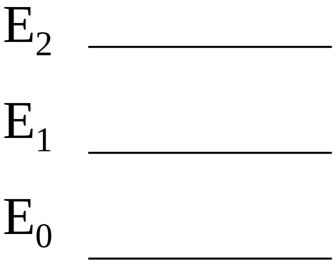
$kT \sim 200$ cm^{-1} at room temperature



$$I \propto \text{population} \propto e^{-Ei/kT}$$

$$N_0/N = Ae^{-E0/kT},\ \ N_1/N = Ae^{-E1/kT}$$

$$\rightarrow\ N_1/N_0 = e^{-(E1-E0)/kT}$$



e.g.) at room T, $E_1 - E_0 = 200$ c m^{-1} → $N_1/N_0 = e^{-1}$

$E_1 - E_0 = 2000$ c m^{-1} → $N_1/N_0 \sim 0$

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

$$N_J/N_0 \propto (2J + 1)e^{-Erot/kT}$$

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: $-dN_m/dt = +A_{mn}N_m$

B_{nm} B_{mn} A_{mn}

Stimulated emission: $-dN_m/dt = +B_{mn}N_m\rho(\nu_{mn})$

ρ : density of radiation E_n, N_n

Stimulated absorption: $dN_n/dt = -dN_m/dt = B_{nm}N_n\,\rho(\nu_{mn})$

At equilinrium   rate ↑ = rate ↓

$$B_{nm}N_n\,\rho(\nu_{mn}) = A_{mn}N_m + B_{mn}N_m\rho(\nu_{mn})$$

$$N_m/N_n = B_{nm}N_n\,\rho(\nu_{mn})\,/[A_{mn}N_m + B_{mn}N_m\rho(\nu_{mn})] = e^{-(Em - En)/kT} = e^{-h\nu mn/kT}$$

$$\rho(\nu_{mn}) = A_{mn}/(B_{nm}e^{-h\nu mn/kT} – B_{mn} \qquad (1)$$

Planck’s law

$$\rho(\nu_{mn}) = (8\pi h\nu^3/c^3)(1/e^{-h\nu mn/kT} – B_{mn}) \qquad (2)$$

(1) = (2) $B_{mn} = B_{nm} = B$

$A/B = A_{mn}/B_{mn} = 8\pi h\nu^3/c^3$

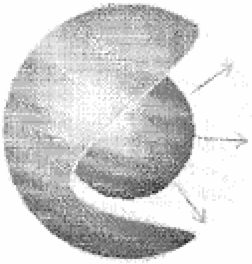
ν ↑ → A ↑ (spontaneous emission) → laser

Lower frequency (rotational & vibrational transitions) → A can be ignored

Selection rules: transition is forbidden or allowed?

transition dipole moment (μ_{fi})

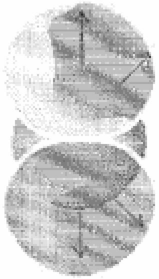
$$\mu_{fi} = \langle f_f | \hat{\mu} | f_i \rangle = \int \psi_f^* \hat{\mu} \psi_i \, d\tau$$



(a)

$\hat{\mu}$: electric dipole moment operator

$\mu_{fi} \neq 0 \Rightarrow$ " transition allowed " : selection rule



(b)

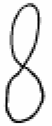
Stimulated absorption (& emission)

$$B = \frac{|\mu_{fi}|^2}{6 \varepsilon_0 \hbar^2} \Rightarrow \text{intensity of transition} \propto |\mu_{fi}|^2$$

- electronic transition : $\Delta l = \pm 1$ (angular momentum q. #)

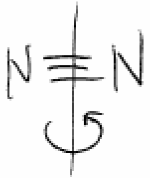
1s → 2s　　　　　1s → 2p

$\textcircled{1s} \rightarrow \textcircled{2s}$ (x)　　　$\textcircled{1s} \rightarrow$

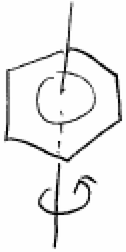


2p (o) (∵ transition dipole moment)

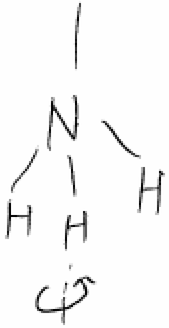
- rotation



(x)

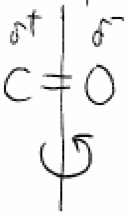


(x)



(x)

(no dipole moment)

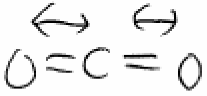


(o)

- Vibration

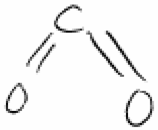
(o)

CO_2



(x)

(o)



(bending) (o)

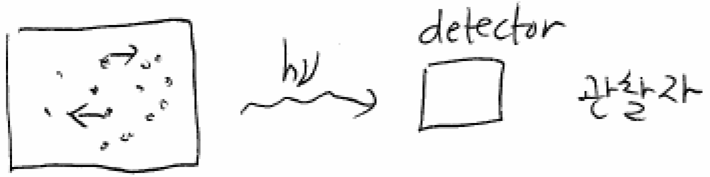
Linewidths

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

- Inherent limitations: <u>Doppler broadening & lifetime broadening</u>

(a) Doppler broadening

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



speed v_x (speed of source)

$$\nu_{receding} = \nu\left(\frac{1-v_x/c}{1+v_x/c}\right)^{1/2}, \quad \nu_{approaching} = \nu\left(\frac{1+v_x/c}{1-v_x/c}\right)^{1/2}$$

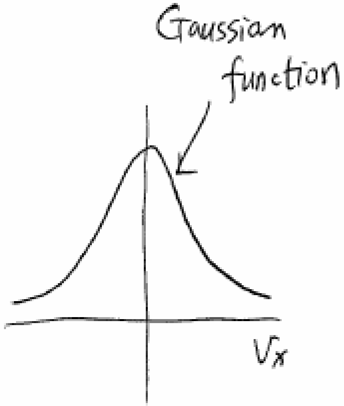
For nonrelativistic speeds ($v_x \ll c$)

$$\nu_{\text{receding}} \approx \frac{\nu}{1+v_x/c}, \quad \nu_{\text{approaching}} \approx \frac{\nu}{1-v_x/c}$$

(red shift)

Consider $\nu_{\text{approaching}} \approx \dfrac{\nu_0}{1-v_x/c} \xrightarrow[\nu=\frac{c}{\lambda}]{} \lambda = \lambda_0\left(1-\dfrac{v_x}{c}\right)$

% shift $\quad x = \dfrac{\lambda-\lambda_0}{\lambda_0} = \dfrac{v_x}{c}$

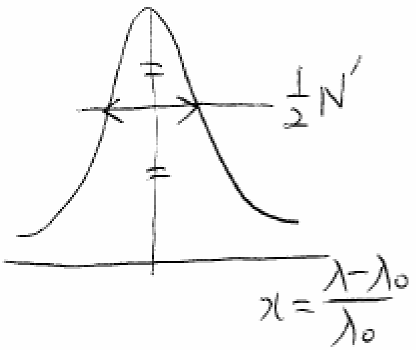


$v_x \sim v_x + dv_x$

probability $\quad f(v_x)dv_x = Ne^{-\frac{1}{2}mv_x^2/kT}\cdot dv_x$

$$= Ne^{-\frac{1}{2}mc^2x^2/kT}\cdot c\,dx =$$

$$= F(x)dx = N'e^{-\frac{1}{2}mc^2x^2/kT}\cdot dx$$

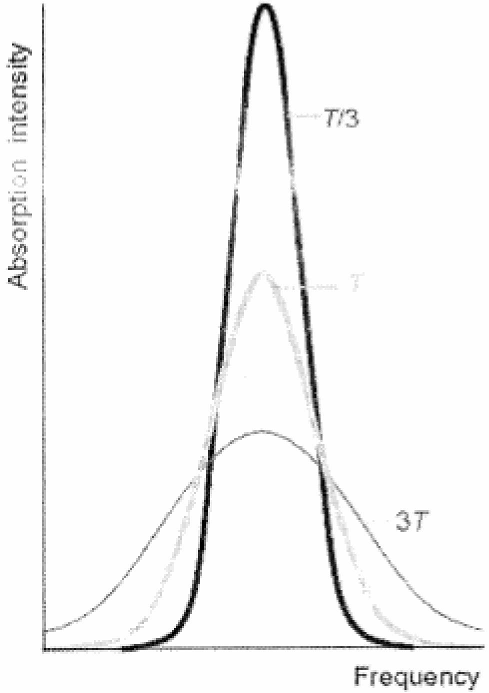


full width at half-height point

$$\frac{1}{2} m c^2 x^2 / kT = -\ln\frac{1}{2} = \ln 2$$

$$x_{\pm} = \pm\left(\frac{2kT\ln 2}{mc^2}\right)^{1/2}$$

$$\Delta\lambda = \lambda_0 (x_+ - x_-) = \frac{2\lambda_0}{c}\left(\frac{2kT\ln 2}{m}\right)^{1/2}$$



T ↑ → 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

$$\left(\because \begin{array}{l} \delta p_x \cdot \delta x \geq \frac{\hbar}{2} \\ \delta E \cdot \delta t \geq \frac{\hbar}{2} \end{array} \right)$$

Uncertainty broadening

$$\delta E \simeq \frac{\hbar}{\tau}, \quad \tau = \text{lifetime}$$

Factors influencing the lifetime of excited states

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

$$E = h\nu = hc\tilde{\nu}, \quad \delta E = hc(\delta\tilde{\nu})$$

lifetime : $\tau(\text{sec})$

$$hc(\delta\tilde{\nu}) \cdot \tau \approx \hbar$$

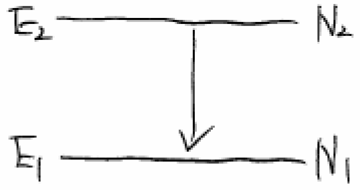
$$\delta\tilde{\nu} \simeq \frac{\hbar}{hc\tau} = \frac{1}{2\pi c\tau} = \frac{5 \times 10^{-12}\ \text{cm}^{-1}}{\tau(\text{sec})} = \frac{5.3\ \text{cm}^{-1}}{\tau(\text{ps})}$$

τ ↓ (shorter lifetime) → broader spectral lines

→ working at low pressure (collisional linewidth)

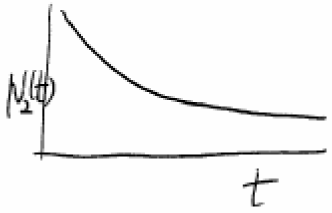
low frequency transitions → small linewidth

· lifetime vs. rate



$$\text{rate} = \frac{dN_2}{dt} = -\overset{\text{rate const}}{k}N_2 \ , \quad \int \frac{dN_2}{N_2} = -\int k\,dt$$

$$\frac{N_2(t)}{N_2(0)} = e^{-kt}, \quad N_2(t) = N_2(0)\,e^{-kt}$$



$$\tau : dt \rightarrow \frac{dN}{N}, \quad \tau = \frac{dt}{|dN_2/N_2|} = \frac{dt}{k\,dt} = \frac{1}{k}$$

$N_2 \xrightarrow{k_1} N_1$ spontaneous emission $\tau_1 = \frac{1}{k_1}$

$\xrightarrow{k_2} N_1$ stimulated " $\tau_2 = \frac{1}{k_2}$

$\xrightarrow{k_3} N_1$ collision activation $\tau_3 = \frac{1}{k_3}$

$$\frac{dN_2}{dt} = -(k_1+k_2+k_3)N_2$$

$$\frac{1}{\tau} = k_1+k_2+k_3\cdots = \frac{1}{\tau_1}+\frac{1}{\tau_2}+\frac{1}{\tau_3}+\cdots$$

τ of electronic transitions << τ of rotation, vibration

⇓

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 <u>bond lengths & bond angles</u>

Linear molecules: zero I around the internuclear axis

e.g., I of H_2O around axis

Rigid rotors

Spherical rotors: 3 equal I (e.g., CH_4, SiH_4, SF_6)
Symmetric rotors: 2 equal I (e.g., NH_3, CH_3Cl, CH_3CN)
Linear rotors: 1 zero I (1 about the molecule axis) (CO_2, HCl, OCS, HCCH)
Asymmetric rotors: three different I (H_2O, H_2CO, CH_3OH)

Rotational energy levels

$E = J^2/2I$,   J: magnitude of the angular momentum ($J(J + 1)\hbar^2$, $J = 0, 1, 2,\ldots$)

For a, b, c axes, $E = E_a + E_b + E_c = J_a{}^2/2I_a + J_b{}^2/2I_b + J_c{}^2/2I_c$

(a) Spherical rotors

3 equal I (e.g., CH_4, SiH_4, SF_6)

$$E = (J_a^2 + J_b^2 + J_c^2)/2I = J^2/2I$$

$$E_J = (J(J + 1)\hbar^2/2I, \quad J = 0, 1, 2,\ldots$$

Rotational constant of the molecule, B

$hcB = \hbar^2/2I$ so $B = \hbar/4\pi cI$

→ $E_J = hcBJ(J + 1)$, $J = 0,1,2,\ldots$

→ wavenumber term, $F(J) = BJ(J + 1)$

F(J): rotational term

$F(J) – F(J – 1) = 2BJ$

$I\uparrow \rightarrow B\downarrow$

Large molecules: closely spaced rotational energy levels

e.g., CCl_4, $I = 4.85 \times 10^{-45}$ kgm^2

→ $B = 0.0577$ cm^{-1}

(b) Symmetric rotors

2 equal I & 1 different I (e.g., CH_3Cl, NH_3, C_6H_6):

principle axis (I_{II}) & other two ($I_{\perp}$)

If → oblate (like pancake or C_6H_6)

If → prolate (like cigar, CH_3Cl)

$$E = (J_b^2 + J_c^2)/2I_{\perp} + J_a^2/2I_{II}$$

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

$$E = (J^2 - J_a^2)/2I_{\perp} + J_a^2/2I_{II} = J^2/2I_{\perp} + (1/2I_{II} - 1/2I_{\perp})J_a^2$$

Quantum mechanics

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

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

$$E_{J,K} = J(J + 1)\hbar^2/2I_{\perp} + K^2\hbar^2/2(1/I_{II} - 1/I_{\perp})$$

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

With $A = \hbar/4\pi c I_{II}$ and $B = \hbar/4\pi c I_{\perp}$

$K = 0$, E depends only on $I_{\perp}$

$K = \pm J$, $F(J, K) = BJ + AJ^2$ e.g., 16.2

(c) Linear rotors

$K = 0$

$$E = J(J + 1)\hbar^2/2I \quad J = 0.\ 1, 2\ldots.$$

$$F(J, K) = BJ(J + 1)$$

(d) Degeneracies and the Stark effect

E of symmetric rotor depends on J & K

J, K → M_J quantized, $M_J = 0, \pm 1, \ldots, \pm J$

→ (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

$$E(J, M_J) = hcBJ(J + 1) + a(J, M_J)\mu^2 E^2$$

where $a(J, M_J) = [J(J + 1) - 3M_J^2]/[2hcBJ(J + 1)(2J - 1)(2J + 3)]$

μ: permanent electric dipole moment

(e) Centrifugal distortion

Rigid rotor by centrifugal force: change I

Diatomic molecule

$F(J) = BJ(J + 1) - D_J J^2(J + 1)^2$

D_J: centrifugal distortion const

$$D_J = 4B^3/\bar{\nu}^2$$

Rotational transitions

B of small molecules → 0.1 ~ 10 cm^{-1} (microwave region)

(a) Rotational selection rules

Gross selection rule: $\mu \neq 0$ (permanent electric dipole moment)

→ for pure rotational spectrum, it must be *polar*

Homonuclear diatomic molecules,

symmetrical linear molecule (CO_2),

spherical rotor → 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)

→ 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: $J \rightarrow J + 1$; $\bar{\nu} = 2B(J + 1)$, $\quad J = 0, 1, 2\ldots$

$\rightarrow 2B, 4B, 6B,\ldots$

Separation: 2B

e.g., 16.3

Intensity of rotational spectrum

I is proportional to N_J: population at equilibrium

$$N_J = Ng_J\exp(-E_J/kT)/\sum g_J\exp(-E_J/kT)$$

g_J: degeneracy of level J

Linear molecule: $g_J = 2J + 1$

$$E_J = hcBJ(J + 1)$$

$N_J \quad N(2J + 1)\exp(-hcBJ(J + 1)/kT)$

$J_{max} \rightarrow N_J/dJ = 2\exp(-hcBJ(J + 1)/kT) - [hcB(2J + 1)^2/kT]\exp(-hcBJ(J + 1)/kT)$

$$= [2 - hcB(2J + 1)^2/kT]\exp(-hcBJ(J + 1)/kT)$$

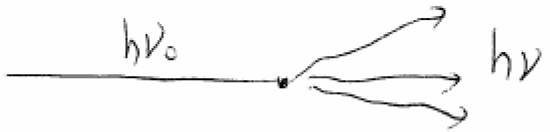
$J_{max} \sim (kT/2hcB)^{1/2} - \frac{1}{2}$

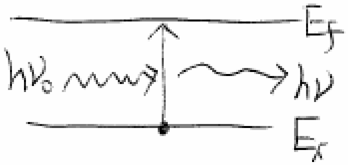
e.g., typical molecule at room T, $kT \sim 1000hcB \rightarrow J_{max} \sim 22$

Rotational Raman spectra

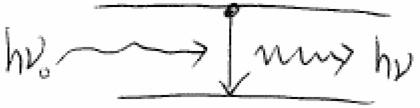
Selection rule: must be anisotropically polarizable

Raman effect: inelastic light scattering

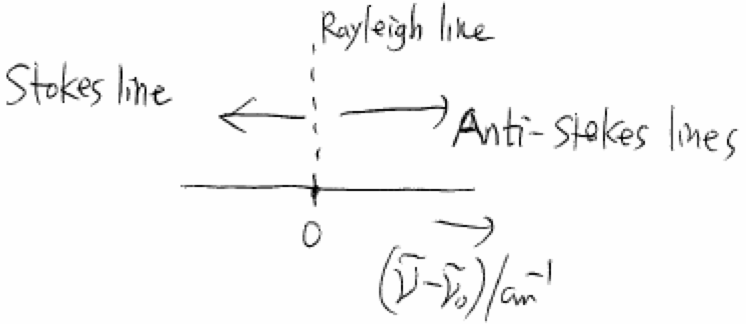




$$h(\nu-\nu_0) = -(E_f - E_i) < 0$$



$$h(\nu-\nu_0) = -(E_f - E_i) > 0$$



⇒ entire spectrum range is very small

→ incident light must be highly monochromatic (e.g. laser) anisotropically (비정방성) polarizable?

H_2

Induced dipole moment, $\mu = \alpha E$

α: polarizability

Atom: isotropically polarizable

Spherical rotor: isotropically polarizable (정방성)

→ CH_4, 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 α

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) $\mu_{ind} = \alpha E(t) = \alpha E\cos\omega_i t$, ω_i: angular frequency of incident photon

If molecule is rotating at a circular frequency ω_R

$\rightarrow \alpha = \alpha_0 + \Delta\alpha\cos 2\omega_R t$,   where $\Delta\alpha = \alpha_{II} - \alpha_{\perp}$, α from $\alpha_0 + \Delta\alpha$ to $\alpha_0 - \Delta\alpha$ as the molecule rotates → “2”; 1 revolution, polarizability twice

→ $\mu_{ind} = (\alpha_0 + \Delta\alpha\cos 2\omega_R t) \text{ x } (E\cos\omega_i t) = \alpha_0 E\cos\omega_i t + E\Delta\alpha\cos 2\omega_R t\cos\omega_i t =$

$\alpha_0 E\cos\omega_i t + (1/2)E\Delta\alpha[\cos(\omega_i + 2\omega_R)t + \cos(\omega_i - 2\omega_R)t]$

↓ ↓

ω_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

<u>Raman spectrum of a linear rotor</u>: $\Delta J = \pm 2$

$\Delta J = +2$, J → J + 2, Stokes lines

$\bar{\nu}(J \rightarrow J + 2) = \bar{\nu}_i - [B(J + 2)(J + 3) - BJ(J + 1)] = \bar{\nu}_i - 2B(2J + 3)$, J = 0, 1,2,..

Stokes lines: -6B, -10B, -14B,…

$\Delta J = -2$, J → J -2, Anti-Stokes lines

$\bar{\nu}(J \rightarrow J - 2) = \bar{\nu}_i + 2B(2J - 1)$, J = 2, 3, 4…

e.g., 16.4

The vibrations of diatomic molecules

Molecular vibrations

Diatomic molecule

H_2

Harmonic oscillator, $V = 1/2kx^2$, $x = R - R_e$

$-(\hbar^2/2\mu)(d^2\Psi/dx^2) + (1/2kx^2)\Psi = E\Psi$

$\mu = m_{eff} = m_1m_2/(m_1 + m_2)$: reduced or effective mass

$E_v = (v + ½)\hbar\omega$, $v = 0, 1, 2\ldots$

$\omega = \sqrt{(k/\mu)}$, $\omega = 2\pi\nu \rightarrow \nu = (1/2\pi)\sqrt{(k/\mu)}$

Vibrational term, $G(v) = (v + ½)\bar{\nu}$, $E_v = hcG(v)$

$\bar{\nu} = (1/2\pi c)\sqrt{(k/\mu)}$

Homonuclear diatomic molecule, $m_1 = m_2$, $\mu = 1/2m$

Selection rule

Gross selection rule: dipole moment $\mu \neq 0$

(dipole moment must change) → infrared active

Specific vibrational selection rule

$\Delta v = +1$: absorption, $\Delta v = -1$: emission

$\Delta G_{v+1/2} = G(v + 1) - G(v) = \overline{\nu}$

At room T, $kT/hc = 200\ \mathrm{cm}^{-1}$ → IR > $200\ \mathrm{cm}^{-1}$

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

$$V = hcD_e[1 - e^{-a(R - Re)}]^2$$

$a = [m_{eff}\omega^2/2hcD_e]^{1/2}$, D_e: depth of the potential minimum

$H = T + V$, $H\Psi = E\Psi$

$\rightarrow E_v = (v + ½)h\nu – (v + ½)^2 x_e h\nu + (v + ½)^3 y_e h\nu + \ldots$

$x_e = \hbar a^2/2\mu\omega = \bar{\nu}/4D_e$: anharmonicity constant

$G(v) = (v + ½)\bar{\nu} – (v + ½)^2 x_e \bar{\nu}..$, $v = 0, 1, 2, \ldots. v_{max}$

Wavenumbers of transitions with $\Delta v = +1$

$\Delta G_{v+1/2} = G(v + 1) – G(v) = \bar{\nu} – 2(v + 1)x_e\bar{\nu} +..$

(or ΔE $(v \rightarrow v + 1) = h\nu – 2(v + 1)x_e h\nu..$)

→ when $x_e \neq 0$, the transitions move to lower wavenumbers as v increases

Mainly $\Delta v = \pm 1$ (fundamental frequency), however, anharmonicity allows additional weak lines corresponding $\Delta v = \pm 2, \pm 3,..$ ("**overtones**")

1st overtone, $G(v + 2) – G(v) = 2\bar{\nu} – 2(2v + 3)xe\bar{\nu} + \ldots$

Selection rule is derived from harmonic oscillator, for an anharmonic oscillator, all values of Δv are allowed, but transitions with $\Delta v > 1$ 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

$E = E_{vib} + E_{rot} + E_{ele}, \quad E_{ele} > E_{vib} > E_{rot}$

IR radiation → no electronic transition,

vib. transition + rotational transition

Diatomic molecule

$E_{v,J} = (v + ½)h\nu + hcBJ(J + 1)$ H.O.

$E_{v,J} = (v + ½)h\nu – (v + ½)2x_e h\nu + hcBJ(J + 1)$ 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) $\Delta J = -1$, $\Delta E = h\nu - 2BJ$, $\bar{\nu}_p(J) = S(v+1, J-1) - S(v, J) = \bar{\nu} - 2BJ$

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

ii) $\Delta J = 0$, $\Delta E = h\nu$, $\bar{\nu}_Q(J) = S(v+1, J) = \bar{v}$ Q-branch

allowed: NO, forbidden: HCl

iii) $\Delta J = +1$, $\Delta E = h\nu + 2B(J + 1)$, $\bar{\nu}_R(J) = S(v+1, J+1) - S(v, J) = \bar{\nu} + 2B(J + 1)$

R-branch

Vibrational Raman spectra of diatomic molecule

Gross selection rule: polarizability shoud 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 16.2 Properties of diatomic molecules

	$\tilde{\nu}_0$/cm^{-1}	θ_V/K	B/cm^{-1}	θ_R/K	r/pm	k/(N m^{-1})	D/(kJ mol^{-1})	σ
$^1H_2^+$	2321.8	3341	29.8	42.9	106	160	255.8	2
$^1H_2$	4400.39	6332	60.864	87.6	74.138	574.9	432.1	2
$^2H_2$	3118.46	4487	30.442	43.8	74.154	577.0	439.6	2
$^1H^{19}F$	4138.32	5955	20.956	30.2	91.680	965.7	564.4	1
$^1H^{35}Cl$	2990.95	4304	10.593	15.2	127.45	516.3	427.7	1
$^1H^{81}Br$	2648.98	3812	8.465	12.2	141.44	411.5	362.7	1
$^1H^{127}I$	2308.09	3321	6.511	9.37	160.92	313.8	294.9	1
$^{14}N_2$	2358.07	3393	1.9987	2.88	109.76	2293.8	941.7	2
$^{16}O_2$	1580.36	2274	1.4457	2.08	120.75	1176.8	493.5	2
$^{19}F_2$	891.8	1283	0.8828	1.27	141.78	445.1	154.4	2
$^{35}Cl_2$	559.71	805	0.2441	0.351	198.75	322.7	239.3	2
$^{12}C^{16}O$	2170.21	3122	1.9313	2.78	112.81	1903.17	1071.8	1
$^{79}Br^{81}Br$	323.2	465	0.0809	10.116	283.3	245.9	190.2	1

Data: AIP

The vibrations of polyatomic molecules

Diatomic molecule: one mode of vibration → bond stretch

Polyatomic molecules: several modes

N atoms → degree of freedom for vibration (p. 522, Justification 16.9)

f_v 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)

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

$$G_p(v) = (v + \tfrac{1}{2})\bar{\nu}_q, \qquad \bar{\nu}_q = (1/2\pi c)\sqrt{(k_q/m_q)}$$

H_2O, $f_v = 3 \times 3 - 6 = 3$ modes

Gross selelction rule for IR: change of dipole moment
e.g., symmetric stretch of CO_2: no dipole moment change → IR inactive
antisymmetric stretch, bending modes → 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, $\tilde{\nu}/\mathrm{cm}^{-1}$

C—H stretch	2850–2960	C—F stretch	1000–1400
C—H bend	1340–1465	C—Cl stretch	600–800
C—C stretch, bend	700–1250	C—Br stretch	500–600
C=C stretch	1620–1680	C—I stretch	500
C≡C stretch	2100–2260	CO_3^{2-}	1410–1450
O—H stretch	3590–3650	NO_3^-	1350–1420
H-bonds	3200–3570	NO_2^-	1230–1250
C=O stretch	1640–1780	SO_4^{2-}	1080–1130
C≡N stretch	2215–2275	Silicates	900–1100
N—H stretch	3200–3500		

Data: L.J. Bellamy, *The infrared spectra of complex molecules* and *Advances in infrared group frequencies*. Chapman and Hall.

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

$$\rho = I_{\perp}/I_{II}$$

Measuring ρ: polarizing filter
If emergent light is not polarized: $\rho \sim 1$
$\rho \geq 0.75$: depolarized, $\rho < 0$: polarized