

Chapter 8. The vibrational and rotational spectroscopy of diatomic molecules

General features

Interaction of electromagnetic field with atoms/molecules

Spectral range:

Wave number $\tilde{\nu}$ (frequency ν)

Wavelength λ

Radio	MW	IR	VIS	UV	X-ray
rot.		vib.	elec. (valence)		elec. (core)

Absorption and emission spectroscopy

Photon is absorbed or emitted when molecule makes transition

$$h\nu = |E_1 - E_2|$$

emission

absorption

Raman

Raman spectroscopy: Light scattered by molecule ($2 h\nu$ event)

$$h|\nu_s - \nu_i| = |E_1 - E_1'|$$

A spectrometer typically contains

- i. radiation source and dispersion element
- ii. sample chamber
- iii. detector

Beer-Lambert law:

$$\log \frac{I}{I_0} = -\varepsilon[C]L, \quad I = I_0 \times 10^{-\varepsilon[C]L}$$

I, I_0 : intensity

$[C]$: concentration of species

L : length

ε : absorption coefficient ($\text{L mol}^{-1} \text{cm}^{-1}$)

$A = \varepsilon[C]L$: absorbance

$T = I/I_0$: transmittance

$$A = -\log T$$

Very useful in analytical chemistry to measure concentration.

Transition probabilities

There are three types of transitions: stimulated absorption, stimulated emission, spontaneous emission.

Absorption rate (single molecule)

$$w = B\rho$$

Emission rate

$$w' = A + B'\rho$$

Rate coefficients:

A : Einstein coefficient of spontaneous emission.

B' : stimulated emission.

B : absorption.

ρ is energy density of radiation, for black-body

$$\rho = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} \quad (\text{Planck's dist.})$$

Total rates of emission and absorption:

$$W' = N'w', \quad W = Nw$$

N, N' : numbers of molecules in E_1 and E_2 .

Populations of states

At a given temperature T , the population of states is given by the Boltzmann factor:

$$f = \frac{N'}{N} = e^{-\Delta E/kT} = e^{-hc\tilde{\nu}/kT}$$

where k is the Boltzmann constant and T is the temperature.

At 25 °C, electronic transitions ($\tilde{\nu} \approx 10,000 \text{ cm}^{-1}$)

$$f = e^{-48} = 1.4 \times 10^{-19}\%$$

Vibrational transitions ($\tilde{\nu} \approx 1,000 \text{ cm}^{-1}$)

$$f = e^{-4.8} = 0.82\%$$

Rotational transitions ($\tilde{\nu} \approx 1 \text{ cm}^{-1}$)

$$f = e^{-0.0048} = 99\% \quad (\text{not including degeneracy})$$

At thermal equilibrium,

$$W = W'$$

or

$$NB\rho = N'(A + B'\rho)$$

Rearrange

$$\rho = \frac{N'A}{NB - N'B'} = \frac{A}{B} \frac{1}{\frac{N}{N'} - \frac{B'}{B}}$$

N'/N replaced by Boltzmann distribution $e^{-h\nu/kT}$:

$$\rho = \frac{A}{B} \frac{1}{e^{h\nu/kT} - \frac{B'}{B}}$$

Compare with Planck's distribution

$$B = B', \quad A = \frac{8\pi h \nu^3}{c^3} B$$

Stimulated absorption = emission

Spontaneous emission $\propto \nu^3$, (important only at high ν)

The Einstein coefficient B is an inherent property of the molecule:

$$B = \frac{|\mu_{fi}|^2}{6\epsilon_0 \hbar^2}$$

where $\mu_{fi} = \int \Psi_f \hat{\mu} \Psi_i d\tau$ is the transition dipole.

For vib. and rot. spectra, spontaneous emission can be ignored. Net rate of absorption:

$$W = NB\rho - N'B'\rho = (N - N')B\rho$$

At equilibrium,

$$W = N\left(1 - \frac{N'}{N}\right)B\rho = N(1 - e^{-h\nu/kT})B\rho$$

More population on lower state, smaller energy gap \rightarrow higher rate of absorption.

Vibration spectroscopy

Harmonic oscillator (H.O.)

$$V = \frac{1}{2}k(R - R_e)^2$$

Vibrational energy:

$$E_\nu = \left(\nu + \frac{1}{2}\right)\hbar\omega, \quad \nu = 0, 1, 2, \dots$$

Vibrational frequency:

$$\omega = \sqrt{\frac{k}{\mu}},$$

where μ is the reduced mass.

Anharmonicity (deviations from H.O.)

Morse potential:

$$V = D_e \left[1 - e^{-\alpha(R - R_e)} \right]^2$$

where D_e is well depth and

$$\alpha = \sqrt{\frac{\mu\omega^2}{2D_e}}$$

Vibrational energy

$$E_v = \left(v + \frac{1}{2}\right) \hbar \omega - \left(v + \frac{1}{2}\right)^2 \hbar \omega x_e$$

where the anharmonicity constant :

$$x_e = \frac{\alpha^2 \hbar}{2\mu\omega}$$

Generally, vibrational term (cm^{-1}):

$$G(v) = \left(v + \frac{1}{2}\right) \tilde{\nu} - \left(v + \frac{1}{2}\right)^2 \tilde{\nu} x_e + \left(v + \frac{1}{2}\right)^3 \tilde{\nu} y_e + \dots$$

where x_e and y_e can be fitted to experimental data.

Selection rules:

- active if dipole changes during vibration.
- $\Delta v = \pm 1$, ($\Delta v = \pm 2, \pm 3, \dots$, are possible due to anharmonicity)

H_2 , N_2 are vibrationally inactive

NO , OCS , H_2O , CO_2 , C_6H_6 are vibrationally active.

Example. Calc. k of CO from vib. spectrum, if $\tilde{\nu} = 2162 \text{ cm}^{-1}$.

$$\mu = 1.15 \times 10^{-26} \text{ kg}$$

$$\omega = 2\pi c \tilde{\nu} = \sqrt{\frac{k}{\mu}}$$

$$\begin{aligned} k &= \mu(2\pi c \tilde{\nu})^2 \\ &= (1.15 \times 10^{-26} \text{ kg})(2 \times 3.14 \times 3.0 \times 10^{10} \text{ cm/s} \times 2162 \text{ cm}^{-1})^2 \\ &= 1907 \text{ N/m} \end{aligned}$$

Force constant reflects the bonding strength ($k(\text{H}_2)=510 \text{ N/m}$).

Vibrations of polyatomic molecules

Number of vibrational modes: $3N-6$ ($3N-5$ for linear molecules)

H_2 has 1 vib. mode.

H_2O has 3 vib. modes.

CO_2 has 4 vib. modes (linear).

Normal modes: combined, synchronous vib. motion.

Normal modes for CO_2 and H_2O :

symmetric stretch antisymmetric stretch bend

Total energy:

$$E(\nu_1, \nu_2, \dots, \nu_{3N-6}) = \sum_i \left(\nu_i + \frac{1}{2} \right) \hbar \omega_i$$

Pure rotational spectra

Moment of inertia:

$$I = \sum_i m_i x_i^2$$

x_i : distance to the axis

m_i : atomic mass

Example. H₂

For axis along H-H bond:

$$I_{//} = 0 \quad (\text{true for all linear molecules})$$

For axis perpendicular to H-H bond

$$\begin{aligned} I_{\perp} &= m_H \left(\frac{r}{2} \right)^2 + m_H \left(\frac{r}{2} \right)^2 = \mu r^2 \\ &= (1.672 \times 10^{-27} / 2) (7.41 \times 10^{-11} \text{ m})^2 \\ &= 1.87 \times 10^{-47} \text{ kg m}^2 \end{aligned}$$

Rotational energy levels

$$E_{\text{classical}} = \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_z^2}{2I_z}$$

$$E_{\text{classical}} \xrightarrow{J^2 \rightarrow J(J+1)\hbar^2} E_{\text{quantum}}$$

Spherical rotors: CH₄, SF₆

$$I_x = I_y = I_z = I$$

$$J^2 = J_x^2 + J_y^2 + J_z^2$$

Energy:

$$E_{\text{classical}} = \frac{1}{2I} (J_x^2 + J_y^2 + J_z^2) = \frac{J^2}{2I}$$

$$E_J = \frac{J(J+1)\hbar^2}{2I} = J(J+1)Bhc$$

Rotational constant B (cm⁻¹):

$$hcB = \frac{\hbar^2}{2I}$$

Rotational term (cm⁻¹):

$$F(J) = J(J+1)B$$

Transition frequency for $J \rightarrow J+1$:

$$\begin{aligned} \tilde{\nu} &= F(J+1) - F(J) \\ &= [(J+1)(J+2) - J(J+1)]B = (2J+2)B \end{aligned}$$

Pure rotational spectra consist of nearly equally spaced lines separated by $2B$.

Intensity is determined by population:

$$f_J = g_J e^{-E_J/kT} = (2J+1)e^{-J(J+1)hcB/kT}$$

Linear rotors: CO₂

$$I_x = I_y = I, \quad I_z = 0$$

$$J^2 = J_x^2 + J_y^2$$

Energy:

$$E_{classical} = \frac{1}{2I} (J_x^2 + J_y^2) = \frac{J^2}{2I}$$

$$E_J = \frac{J(J+1)^2 \hbar^2}{2I} = J(J+1)Bhc$$

Rotational constant B (cm⁻¹):

$$hcB = \frac{\hbar^2}{2I}$$

Rotational terms and spectra are the same as spherical rotors.

Gross selection rule:

$$\text{Intensity } (B) \propto |\mu|^2$$

Active if permanent dipole (μ) is not zero.

H₂, O₂, CO₂, (D_{∞h}), CH₄ (spherical rotor) have no rot. spectra.

Specific selection rules:

$$\Delta J = \pm 1$$

Example. Rot. spec. of CO consists of lines separated by 3.86 cm⁻¹. Calc. its bond length.

$$B = 3.86/2 = 1.93 \text{ cm}^{-1}$$

$$\mu = \frac{12 \times 16}{12 + 16} \times 1.66 \times 10^{-27} \text{ kg} = 11.5 \times 10^{-27} \text{ kg}$$

$$hcB = \frac{\hbar^2}{2\mu r^2}$$

$$r = \sqrt{\frac{\hbar^2}{2\mu hcB}} = \sqrt{\frac{\hbar}{4\pi\mu cB}}$$

$$= \sqrt{\frac{1.05 \times 10^{-34} \text{ Js}}{4 \times 3.14 \times 11.5 \times 10^{-27} \text{ kg} \times 3.0 \times 10^{10} \text{ cm/s} \times 1.93 \text{ cm}^{-1}}}$$

$$= 1.12 \times 10^{-10} \text{ m} = 0.112 \text{ nm}$$

Vibration-rotation spectra:

Vibrational excitation inevitably involves rotational excitation.

Vibration-rotation term (linear rotor):

$$S(\nu, J) = G(\nu) + F(J) = \left(\nu + \frac{1}{2} \right) \tilde{\nu} + J(J + 1)B$$

Combined selection rules (linear rotor):

$$\Delta\nu = \pm 1, \quad \Delta J = 0, \pm 1$$

$\Delta J = -1, 0, +1$ correspond to the P, Q, R branches:

$$\begin{array}{ll} \tilde{\nu}_P(J) = \tilde{\nu} - 2BJ, & J \rightarrow J-1 \\ \tilde{\nu}_Q(J) = \tilde{\nu}, & J \rightarrow J \\ \tilde{\nu}_R(J) = \tilde{\nu} + 2B(J + 1), & J \rightarrow J+1 \end{array}$$

In highly excited ro-vibrational states, both the rigid rotor and harmonic oscillator approximations break down.

Raman spectra

Two-photon process, involving incident and scattered photons.

Selection rules

- polarizability should change with vibration.
- $\Delta\nu = \pm 1$, $\Delta J = 0, \pm 2$

H₂, N₂, O₂ are Raman active.

$$\begin{aligned}\tilde{\nu}_O(J) &= \tilde{\nu}_i - \tilde{\nu} - 2B + 4BJ, & J \rightarrow J-2 \\ \tilde{\nu}_Q(J) &= \tilde{\nu}_i - \tilde{\nu}, & J \rightarrow J \\ \tilde{\nu}_S(J) &= \tilde{\nu}_i - \tilde{\nu} - 6B - 4BJ, & J \rightarrow J+2\end{aligned}$$

Lines are separated by $4B$.