

Molecular Spectroscopy

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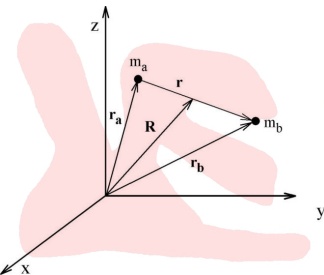
PHYSICAL CHEMISTRY I

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Hamiltonian

- Rotational-vibrational Hamiltonian (I.N. Levine, *Molecular Spectroscopy*, John Wiley & sons, 1975), A. Requena y J. Zúñiga, *Espectroscopía*, Pearson Education SA, 2004



$$\mathbf{r}_a = x_a \mathbf{i} + y_a \mathbf{j} + z_a \mathbf{k}$$

$$\mathbf{r}_b = x_b \mathbf{i} + y_b \mathbf{j} + z_b \mathbf{k}$$

$$\left[-\frac{\hbar^2}{2m_a} \nabla_a^2 - \frac{\hbar^2}{2m_b} \nabla_b^2 + V(r) \right] \psi_{\text{nuc}}(\mathbf{r}_a, \mathbf{r}_b) = E \psi_{\text{nuc}}(\mathbf{r}_a, \mathbf{r}_b)$$

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

$$\left. \begin{aligned} \mathbf{R} &= \frac{m_a \mathbf{r}_a + m_b \mathbf{r}_b}{m_a + m_b} \\ \mathbf{r} &= \mathbf{r}_b - \mathbf{r}_a \end{aligned} \right\} \Rightarrow \underbrace{\left[-\frac{\hbar^2}{2M} \nabla_{\mathbf{R}}^2 \right]}_{\text{translation}} \underbrace{\left[-\frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}}^2 + V(r) \right]}_{\text{rovib}} \psi(\mathbf{R}, \mathbf{r}) = E \psi(\mathbf{R}, \mathbf{r})$$



Hamiltonian

$$\psi(R, r) = \psi_{\text{tras}}(R) \psi_{\text{rovib}}(r) \quad \begin{cases} \left[-\frac{\hbar^2}{2M} \nabla_R^2 \right] \psi_{\text{trans}}(R) = E_{\text{trans}} \psi_{\text{trans}}(R) \\ E = E_{\text{trans}} + E_{\text{rovib}} \quad \left[-\frac{\hbar^2}{2\mu} \nabla_r^2 + V(r) \right] \psi_{\text{rovib}}(r) = E_{\text{rovib}} \psi_{\text{rovib}}(r) \end{cases}$$

⇒ Spherical polar coordinates $(x, y, z) \rightarrow (r, \theta, \phi)$

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{2\mu r^2} + V(r) \right] \psi_{\text{rovib}}(r, \theta, \phi) = E_{\text{rovib}} \psi_{\text{rovib}}(r, \theta, \phi)$$

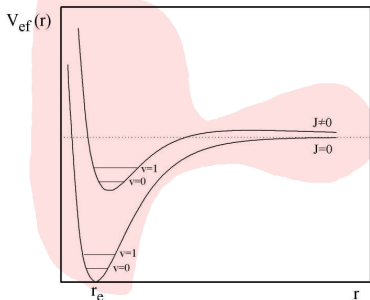
$$\left. \begin{aligned} \psi_{\text{rovib}}(r, \theta, \phi) &= R_{v,J}(r) Y_J^M(\theta, \phi) \\ \hat{L}^2 \psi_{\text{rovib}} &= J(J+1) \hbar^2 \psi_{\text{rovib}} \\ R_{v,J}(r) &= \phi_{v,J}(r)/r \end{aligned} \right\} \left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{J(J+1)\hbar^2}{2\mu r^2} + V(r) \right] \phi_{v,J}(r) = E_{\text{rovib}} \phi_{v,J}(r)$$



Hamiltonian

$$\hat{H}(r)\phi_{v,J}(r) = E_{v,J}\phi_{v,J}(r)$$

$$\hat{H}(r) = -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \underbrace{\frac{J(J+1)\hbar^2}{2\mu r^2}}_{V_{\text{ef},J}(r)} + V(r)$$



- Rovibrational energy levels
- $\uparrow J \Rightarrow$ Rotational barrier



Basic approximations

• Approximations

- Vibration $\Rightarrow$ harmonic oscillator $\Rightarrow V(r) \simeq \frac{1}{2}k(r - r_e)^2$
- Rotation

$$\frac{1}{r^2} \simeq \frac{1}{r_e^2} - \frac{2(r - r_e)}{r_e^3} + \frac{3(r - r_e)^2}{r_e^4} + \dots$$

$$\text{rigid rotor} \Rightarrow \frac{J(J+1)\hbar^2}{2\mu r^2} \approx \frac{J(J+1)\hbar^2}{2\mu r_e^2}$$

$$\downarrow B_e = \frac{h}{8\pi^2\mu r_e^2} \rightarrow \text{rotational constant}$$

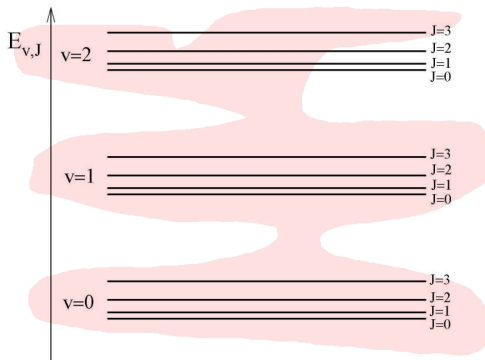
$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{J(J+1)\hbar^2}{2\mu r_e^2} + \frac{1}{2}k(r - r_e)^2 \right] \phi_{v,J}(r) = E_{v,J} \phi_{v,J}(r)$$



Basic approximations

Energy

$$E_{v,J} = (v + 1/2)\hbar\omega + J(J + 1)\hbar B_e \quad v, J = 0, 1, 2, \dots$$





Perturbations

- Perturbations ($q = r - r_e$)

$$V(r) = \frac{1}{2}kq^2 + \underbrace{k_3q^3 + k_4q^4}_{\text{anharmonicity}} + \dots$$

$$\frac{J(J+1)\hbar^2}{2\mu r_e^2} = J(J+1)hB_e + \underbrace{k_1q + k_2q^2}_{\substack{\text{centrifugal} \\ \text{distortion}}} + \dots$$

$$k_1 = -\frac{2J(J+1)hB_e}{r_e}, \quad k_2 = \frac{3J(J+1)hB_e}{r_e^2}, \quad k_3 = \frac{1}{3!} \left(\frac{d^3 V(r)}{dr^3} \right)_{r_e}, \quad k_4 = \frac{1}{4!} \left(\frac{d^4 V(r)}{dr^4} \right)_{r_e}$$

$$\hat{H}(q) \begin{cases} \hat{H}^{(0)} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{J(J+1)\hbar^2}{2\mu r_e^2} + \frac{1}{2}k(r - r_e)^2 \\ \hat{H}' = k_1q + k_2q^2 + k_3q^3 + k_4q^4 \end{cases}$$



Perturbations

- First order correction

$$E_{v,J}^{(1)} = \int \phi_v^{(0)} \hat{H}' \phi_v^{(0)} dq = \langle v | \hat{H}' | v \rangle = \sum_{i=1}^4 k_i \langle v | q^i | v \rangle$$

$\downarrow \quad \langle v | q | v \rangle = \langle v | q^3 | v \rangle = 0, \quad \langle v | q^2 | v \rangle = \frac{v+1/2}{\alpha}, \quad \langle v | q^4 | v \rangle = \frac{3(2v^2+2v+1)}{4\alpha^2}$

$$E_{v,J}^{(1)} = \frac{3hB_e J(J+1)(v+1/2)}{\alpha r_e^2} + \frac{k_4 3(2v^2+2v+1)}{4\alpha^2}$$

- Second order correction

$$E_{v,J}^{(2)} = \sum_{v' \neq v} \frac{|k_1 \langle v' | q | v \rangle + k_3 \langle v' | q^3 | v \rangle|^2}{E_v^0 - E_{v'}^0} = -\frac{k_3^2 (30v^2 + 30v + 11)}{8\alpha^2 h\nu_e} - \frac{2hB_e^2 [J(J+1)]^2}{\alpha r_e^2 \nu_e}$$

$$+ \frac{6B_e k_3 (v+1/2) J(J+1)}{\alpha^2 r_e \nu_e}$$



Perturbations

- Total energy (in wave numbers $\tilde{\nu} = \lambda^{-1} = \nu/c = (E_{v',J'} - E_{v,J})/hc$)

$$\begin{aligned} \frac{E_{v,J}}{hc} = & \underbrace{\omega_e(v + 1/2)}_{\text{harmonic}} + \underbrace{B_e J(J + 1)}_{\text{rigid rotor}} - \underbrace{\omega_e x_e(v + 1/2)^2}_{\text{anharmonicity}} \\ & - \underbrace{D_e[J(J + 1)]^2}_{\text{centrifugal distortion}} - \underbrace{\alpha_e(v + 1/2)J(J + 1)}_{\text{rovibrational coupling}} \end{aligned}$$

$$\omega_e = \frac{\nu_e}{c} = \frac{1}{2\pi c} \left(\frac{k_e}{\mu} \right)^{1/2}$$

$$B_e = \frac{h}{8\pi^2 \mu r_e^2 c}$$

$$\omega_e x_e = \frac{6B_e^2 r_e^4}{\omega_e^2 hc} \left[\frac{5B_e k_3^2 r_e^2}{\omega_e^2 hc} - k_4 \right]$$

$$D_{e,r} = \frac{4B_e^3}{\omega_e^2}$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e} \left[1 + \frac{4k_3 B_e r_e^3}{hc \omega_e^2} \right]$$



Perturbations

Molecule	ω_e	B_e	$\omega_e x_e$	α_e	$D_{e,r}$	r_e (Å)	D_e (eV)
H ₂	4401.2	60.85	121.3	3.06	4.7×10^{-2}	0.74	4.7
HF	4138.3	20.96	89.88	0.80	2.2×10^{-3}	0.92	6.1
HCl	2990.9	10.59	52.82	0.31	5.3×10^{-4}	1.27	4.6
N ₂	2358.6	1.998	14.32	0.0173	5.8×10^{-6}	1.10	9.9
CO	2169.8	1.931	13.29	0.0175	6.1×10^{-6}	1.13	11.2
NO	1904.2	1.672	14.08	0.0171	5.4×10^{-6}	1.15	6.6
O ₂	1580.2	1.438	12.00	0.0159	4.8×10^{-6}	1.21	5.2
I ₂	214.50	0.0374	0.61	0.0001	4.3×10^{-9}	2.67	1.6

^aData from *Molecules and their spectroscopic properties*, S. V. Kristenko, A. I. Maslov y V. P. Shevelko, Springer-Verlag, Berlin (1998).

^b ω_e , B_e , $\omega_e x_e$, α_e y $D_{e,r}$ en cm^{-1} .



Electric dipole moment

- Electric dipole moment

$$\left. \begin{array}{l} \psi = \psi_{\text{elec}} \psi_{\text{nuc}} \\ \hat{\mu} = - \sum_i e r_i + Z_a e r_a + Z_b e r_b \end{array} \right\} \langle \psi | \hat{\mu} | \psi' \rangle = \int \psi_{\text{nuc}}^* \psi'_{\text{nuc}} \left[\underbrace{\int \psi_{\text{el}}^* \hat{\mu} \psi_{\text{el}} d\tau_{\text{el}}}_{\mu_e} \right] d\tau_{\text{nuc}}$$

$\mu_e \rightarrow$ permanent
electronic
dipole
moment

$$= \int \psi_{\text{rovib}}^* \mu_e \psi'_{\text{rovib}} d\tau_{\text{rovib}}$$

$$\mu_e = \mu_e(r) [\sin \theta \cos \phi \mathbf{i} + \sin \theta \sin \phi \mathbf{j} + \cos \theta \mathbf{k}] \downarrow$$

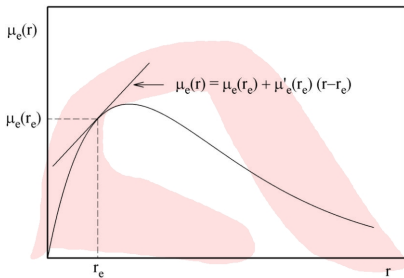
$$= \int_0^\infty \phi_{v,J}(r) \mu_e(r) \phi_{v',J'}(r) dr \underbrace{\int_0^{2\pi} \int_0^\pi Y_{J'}^{M'} [\sin \theta \cos \phi \mathbf{i} + \sin \theta \sin \phi \mathbf{j} + \cos \theta \mathbf{k}] Y_J^{M'} \sin \theta d\theta d\phi}_{\Delta J = \pm 1}$$

$$\Delta M = 0, \pm 1$$



Electric dipole moment

- Homonuclear molecules $\Rightarrow \mu_e(r) = 0$
- Heteronuclear molecules $\Rightarrow \int_0^\infty \phi_{v,J}(r) \mu_e(r) \phi_{v',J}(r) dr$



$$\circ \lim_{r \rightarrow 0} \mu_e(r) = \lim_{r \rightarrow \infty} \mu_e(r) = 0$$

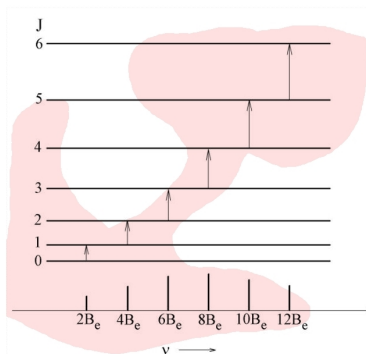
$$\circ \mu_e(r) = \mu_e(r_e) + \mu'_e(r_e)(r-r_e) + \frac{\mu''_e(r_e)}{2!}(r-r_e)^2 + \dots$$

$$\int_0^\infty \phi_v(r) \mu_e(r) \phi_{v'}(r) dr = \underbrace{\mu_e(r_e) \int_{-\infty}^\infty \phi_{v'}(q) \phi_v(q) dq}_{\Delta v=0} + \underbrace{\mu'_e(r_e) \int_{-\infty}^\infty \phi_{v'}(q) q \phi_v(q) dq}_{\Delta v=\pm 1} + \dots$$



Pure rotational spectrum

- $\Delta v = 0$
- Rigid rotor $\Rightarrow \tilde{\nu}(J \rightarrow J+1) = 2(J+1)B_e \Rightarrow \Delta\tilde{\nu} = 2B_e$

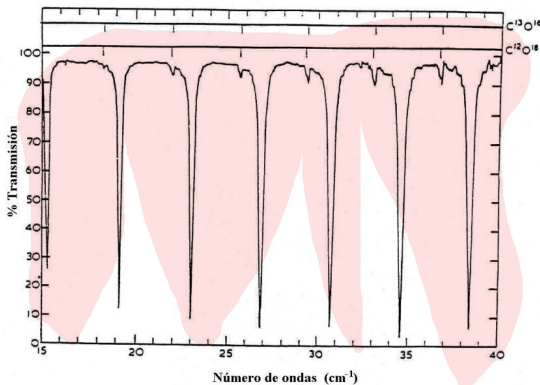


$\Rightarrow$ Microwaves ($0.03\text{-}10\text{ cm}^{-1}$) ($1\text{-}300\text{ GHz}$)



Pure rotational spectrum

- Non-rigid rotor $\Rightarrow \tilde{\nu}(J \rightarrow J+1) = 2(J+1)B_v - 4D_{e,r}(J+1)^3$



$$\Rightarrow B_v = B_e - \alpha_e(v + 1/2)$$



Rovibrational spectrum

- Harmonic oscillator/Rigid rotor $\Rightarrow \frac{E_{v,J}}{hc} = \omega_e(v+1/2) + B_e J(J+1)$
- Absorption spectrum $\Rightarrow \Delta v = +1$
 - $\Delta J = +1 \Rightarrow R$ branch

$$\tilde{\nu}_R[v \rightarrow v+1, J \rightarrow J+1] = \omega_e + 2(J+1)B_e \quad J = 0, 1, 2, \dots$$

$$\Delta \tilde{\nu}_R = 2 B_e$$

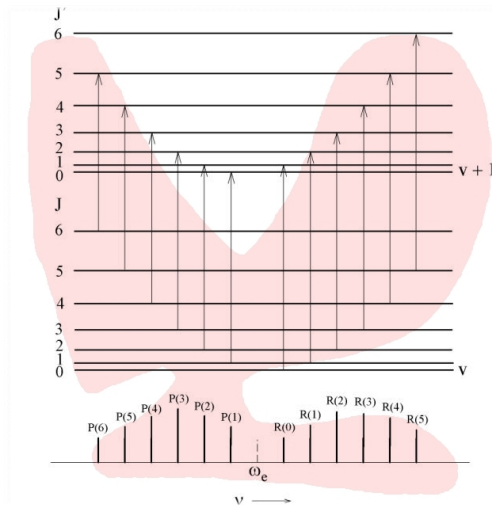
- $\Delta J = -1 \Rightarrow$ P branch

$$\tilde{\nu}_p[v \rightarrow v + 1, J \rightarrow J - 1] = \omega_e - 2JB_e \quad J = 1, 2, 3, \dots$$

$$\Delta \tilde{\nu}_p = 2 B_e$$



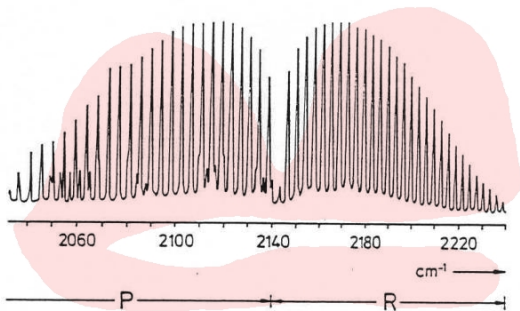
Rovibrational spectrum





Rovibrational spectrum

- Band origin $\Rightarrow \tilde{\nu}_0 = \omega_e \in (10 - 4000 \text{ cm}^{-1})$
- $\tilde{\nu}_0 \in \text{IR } (10 - 13000 \text{ cm}^{-1})$
- Example $\Rightarrow \text{CO molecule}$





Rovibrational spectrum

- Anharmonicity and centrifugal distortion

$$\frac{E_{v,J}}{hc} = \omega_e(v+1/2) + B_e J(J+1) - \omega_e x_e (v+1/2)^2 - \alpha_e (v+1/2) J(J+1) - D_{e,r} [J(J+1)]^2$$

$$\Delta v = \pm 1, \pm 2, \dots$$

- Band origin $\Rightarrow \tilde{\nu}_0(v \rightarrow v') = \omega_e(v' - v) - \omega_e x_e [v'(v' + 1) - v(v + 1)]$
- Room temperature $\Rightarrow v = 0$

$$\tilde{\nu}_0(0 \rightarrow v') = \omega_e v' - \omega_e x_e v'(v' + 1)$$

- ▷ $0 \rightarrow 1 \Rightarrow$ Fundamental band
- ▷ $0 \rightarrow 2, 3, \dots \Rightarrow$ First, second, ... overtones
- ▷ $v \neq 0 \Rightarrow$ Hot bands



Rovibrational spectrum

○ Rotational structure

▷ R branch $\Rightarrow$ Band head

$$\begin{aligned}\tilde{\nu}_R(v \rightarrow v', J \rightarrow J+1) = & \tilde{\nu}_0(v \rightarrow v') + [2B_e - \alpha_e(v' + v + 1)](J+1) - \alpha_e(v' - v)(J+1)^2 \\ & - 4D_{e,r}(J+1)^3 \quad J=0,1,2,\dots\end{aligned}$$

▷ P branch

$$\begin{aligned}\tilde{\nu}_P(v \rightarrow v', J \rightarrow J-1) = & \tilde{\nu}_0(v \rightarrow v') - [2B_e - \alpha_e(v' + v + 1)]J - \alpha_e(v' - v)J^2 \\ & + 4D_{e,r}J^3 \quad J=1,2,\dots\end{aligned}$$

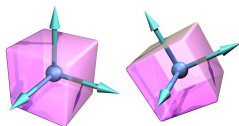
▷ Intensities $\Rightarrow$ Rotational populations

$$\frac{N_{v,J}}{N_{v,0}} = (2J+1)e^{-B_e J(J+1)h/K_B T}$$



Motion equations

- Body fixed cartesian coordinates $\Rightarrow (x_{\alpha}^{\text{bf}}, y_{\alpha}^{\text{bf}}, z_{\alpha}^{\text{bf}})$



- Mass-weighted cartesian coordinates $\Rightarrow (q_1, \dots, q_{3N_s})$

$$q_1 = \sqrt{m_1}(x_1^{\text{bf}} - x_{1,e}^{\text{bf}}),$$

$$q_2 = \sqrt{m_1}(y_1^{\text{bf}} - y_{1,e}^{\text{bf}}),$$

$$q_3 = \sqrt{m_1}(z_1^{\text{bf}} - z_{1,e}^{\text{bf}})$$

$$q_4 = \sqrt{m_2}(x_2^{\text{bf}} - x_{2,e}^{\text{bf}}),$$

$$q_5 = \sqrt{m_2}(y_2^{\text{bf}} - y_{2,e}^{\text{bf}}),$$

$$q_6 = \sqrt{m_2}(z_2^{\text{bf}} - z_{2,e}^{\text{bf}})$$

$$\vdots$$

$$\vdots$$

$$\vdots$$

$$q_{3N_s-2} = \sqrt{m_{N_s}}(x_{N_s}^{\text{bf}} - x_{N_s,e}^{\text{bf}}),$$

$$q_{3N_s-1} = \sqrt{m_{N_s}}(y_{N_s}^{\text{bf}} - y_{N_s,e}^{\text{bf}}),$$

$$q_{3N_s} = \sqrt{m_{N_s}}(z_{N_s}^{\text{bf}} - z_{N_s,e}^{\text{bf}})$$



Motion equations

- Internal energy

$$H = T + V = \frac{1}{2} \sum_{i=1}^{3N_s} \left(\frac{dq_i}{dt} \right)^2 + V(q_1, \dots, q_{3N_s})$$

$$\begin{aligned} V &= \cancel{V^e} + \cancel{\sum_{i=1}^{3N_s} \left(\frac{\partial V}{\partial q_i} \right)_e q_i} + \frac{1}{2!} \sum_{i=1}^{3N_s} \sum_{j=1}^{3N_s} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_e q_i q_j \\ &+ \frac{1}{3!} \sum_{i=1}^{3N_s} \sum_{j=1}^{3N_s} \sum_{k=1}^{3N_s} \left(\frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k} \right)_e q_i q_j q_k + \dots \\ &\approx \frac{1}{2} \sum_{i=1}^{3N_s} \sum_{j=1}^{3N_s} u_{ij} q_i q_j \rightarrow u_{ij} \text{ Hessian matrix} \end{aligned}$$



Motion equations

- Newton's law

$$\frac{d^2 q_k}{dt^2} = - \frac{\partial V}{\partial q_k} \quad k = 1, \dots, 3N$$

↓

$$\sum_{j=1}^{3N_s} u_{kj} q_j \rightarrow \text{coupled differential equations}$$





Equilibrium normal modes

- Equilibrium normal modes

$$L^\dagger U L = \Lambda \rightarrow Q_i = \sum_{k=1}^{3N_s} l_{ki} q_k \quad i = 1, \dots, 3N_s$$

$$\underbrace{\lambda_{3N_s-z} = \dots = \lambda_{3N_s} = 0}_{\text{translation+rotation}} \rightarrow \begin{cases} z = 5 \rightarrow \text{linear molecules} \\ z = 6 \rightarrow \text{non-linear molecules} \end{cases}$$

$$Q_1, Q_2, \dots, Q_{3N_s-z} \rightarrow \text{vibrations}$$



Equilibrium normal modes

○ Kinetic energy

$$\begin{aligned}
 T &= \frac{1}{2} \sum_{k=1}^{3N_s} \left(\frac{dq_k}{dt} \right)^2 = \frac{1}{2} \sum_{i=1}^{3N_s} \left(\sum_{k=1}^{3N_s} l_{ik} \frac{dQ_k}{dt} \sum_{l=1}^{3N_s} l_{il} \frac{dQ_l}{dt} \right) \\
 &= \frac{1}{2} \sum_{k=1}^{3N_s} \frac{dQ_k}{dt} \sum_{l=1}^{3N_s} \frac{dQ_l}{dt} \underbrace{\sum_{i=1}^{3N_s} l_{ik} l_{il}}_{\delta_{kl}} = \frac{1}{2} \sum_{k=1}^{3N_s} \left(\frac{dQ_k}{dt} \right)^2
 \end{aligned}$$



Equilibrium normal modes

○ Potential energy

$$\begin{aligned}
 V &= \frac{1}{2} \sum_{i=1}^{3N_s} \sum_{j=1}^{3N_s} u_{ij} q_i q_j = \frac{1}{2} \sum_{i=1}^{3N_s} \sum_{j=1}^{3N_s} u_{ij} \left(\sum_{k=1}^{3N_s} l_{ik} Q_k \sum_{l=1}^{3N_s} l_{jl} Q_l \right) \\
 &= \frac{1}{2} \sum_{k=1}^{3N_s} \sum_{l=1}^{3N_s} Q_k Q_l \left(\sum_{i=1}^{3N_s} \sum_{j=1}^{3N_s} l_{ik} u_{ij} l_{jl} \right) \\
 &= \frac{1}{2} \sum_{k=1}^{3N_s} \sum_{l=1}^{3N_s} Q_k Q_l \delta_{kl} \lambda_k = \frac{1}{2} \sum_{k=1}^{3N_s-z} \lambda_k Q_k^2
 \end{aligned}$$



Equilibrium normal modes

○ Vibrational energy

$$E_{\text{vib}} = \sum_{k=1}^{3N_s - z} \frac{1}{2} \left(\dot{Q}_k^2 + \lambda_k Q_k^2 \right) \rightarrow \text{uncoupled harmonic oscillators}$$

↓

$$\frac{d^2 Q_i}{dt^2} + \lambda_i Q_i = 0 \quad i = 1, \dots, 3N_s - z$$

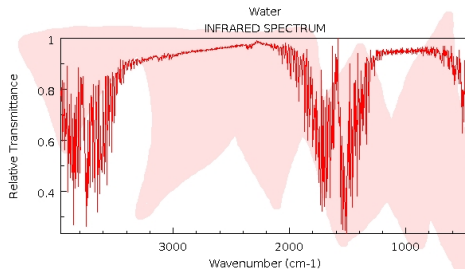
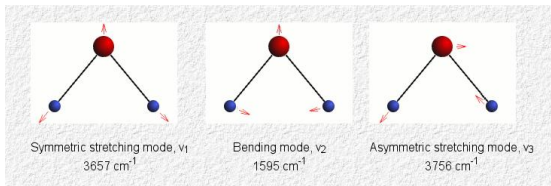
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$$Q_i(t) = A_i \sin(\lambda_i^{1/2} t + a_i) \begin{cases} A_i \rightarrow \text{amplitude} \\ a_i \rightarrow \text{phase} \end{cases}$$



Equilibrium normal modes

Water molecule



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)



Quantum Hamiltonian

- Hamiltonian operator

$$\hat{H}_{\text{vib}} = \sum_{k=1}^{3N_s - z} \hat{h}_k$$

↓

$$\hat{h}_k(Q_k) = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_k^2} + \frac{1}{2} \lambda_k Q_k^2$$

↓

$$\hat{h}_k \varphi_k(Q_k) = \epsilon_k \varphi_k(Q_k)$$



Eigenfunctions and eigenvalues

- $3N_s - z$ dimensional function

$$\hat{H}_{\text{vib}}\psi_{\text{vib}} = E_{\text{vib}}\psi_{\text{vib}} \rightarrow \psi_{\text{vib}} = \prod_{k=1}^{3N_s-z} \varphi_k(Q_k)$$

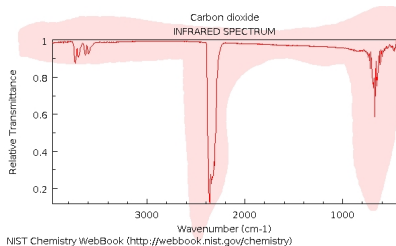
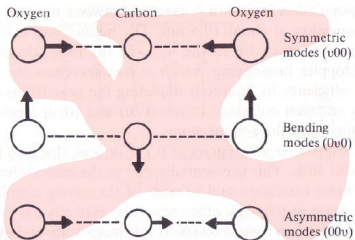
↓

$$E_{\text{vib}} = \sum_{k=1}^{3N_s-z} \epsilon_k = \sum_{k=1}^{3N_s-z} \left(v_k + \frac{1}{2}\right) h\nu_k$$



Eigenfunctions and eigenvalues

CO₂ molecule





Selection rules

- Electronic dipole moment μ

$$\int \psi_{\text{vib}}^* \mu \psi_{\text{vib}} dQ_1 \cdots dQ_{3N_s-z} \rightarrow \mu = \mu_x \mathbf{i}_{\text{bf}} + \mu_y \mathbf{j}_{\text{bf}} + \mu_z \mathbf{k}_{\text{bf}}$$

↓

$$\alpha=x,y,z \quad \mu_\alpha = \mu_{\alpha,e} + \sum_{k=1}^{3N_s-z} \left(\frac{\partial \mu_\alpha}{\partial Q_k} \right)_e Q_k + \sum_{k=1}^{3N_s-z} \sum_{j=1}^{3N_s-z} \left(\frac{\partial^2 \mu_\alpha}{\partial Q_j \partial Q_k} \right)_e Q_j Q_k + \dots$$

↓

$$\langle \psi'_{\text{vib}} | \mu_\alpha | \psi_{\text{vib}} \rangle = \mu_{\alpha,e} \langle \psi'_{\text{vib}} | \psi_{\text{vib}} \rangle + \sum_{k=1}^{3N_s-z} \left(\frac{\partial \mu_\alpha}{\partial Q_k} \right)_e \langle \psi'_{\text{vib}} | Q_k | \psi_{\text{vib}} \rangle + \dots$$

$$\circ \langle \psi'_{\text{vib}} | \psi_{\text{vib}} \rangle = \prod_{k=1}^{3N_s-z} \langle \varphi_{v'_k} | \varphi_{v_k} \rangle \neq 0 \Rightarrow v'_k = v_k, \forall k$$

pure rotational spectrum



Selection rules

$$\circ \langle \psi'_{\text{vib}} | Q_j | \psi_{\text{vib}} \rangle = \prod_{k=1}^{3N_s-z} \langle \varphi_{v'_k} | Q_j | \varphi_{v_k} \rangle = \underbrace{\langle \varphi_{v'_j} | Q_j | \varphi_{v_j} \rangle \prod_{\substack{k=1 \\ k \neq j}}^{3N_s-z} \langle \varphi_{v'_k} | \varphi_{v_k} \rangle}_{\neq 0}$$

$$\Rightarrow \begin{cases} v'_k = v_k, & \forall k \neq j \\ v'_j = v_j \pm 1 \end{cases}$$

Fundamental bands

$$\circ \langle \psi'_{\text{vib}} | Q_j^2 | \psi_{\text{vib}} \rangle = \prod_{k=1}^{3N_s-z} \langle \varphi_{v'_k} | Q_j^2 | \varphi_{v_k} \rangle = \underbrace{\langle \varphi_{v'_j} | Q_j^2 | \varphi_{v_j} \rangle \prod_{\substack{k=1 \\ k \neq j}}^{3N_s-z} \langle \varphi_{v'_k} | \varphi_{v_k} \rangle}_{\neq 0}$$

$$\Rightarrow \begin{cases} v'_k = v_k, & \forall k \neq j \\ v'_j = v_j \pm 2 \end{cases}$$

Overtones



Selection rules

$$\circ \langle \psi'_{\text{vib}} | Q_i Q_j | \psi_{\text{vib}} \rangle = \prod_{k=1}^{3N_s-z} \langle \varphi_{v'_k} | Q_i Q_j | \varphi_{v_k} \rangle = \langle \varphi_{v'_i} | Q_i | \varphi_{v_i} \rangle \langle \varphi_{v'_j} | Q_j | \varphi_{v_j} \rangle \underbrace{\prod_{\substack{k=1 \\ k \neq i,j}}^{3N_s-z} \langle \varphi_{v'_k} | \varphi_{v_k} \rangle}_{\neq 0}$$

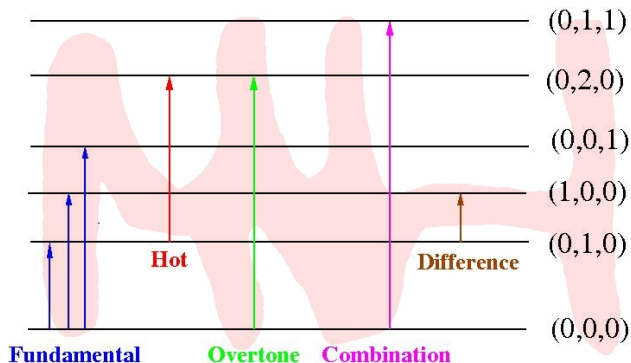
$$\Rightarrow \begin{cases} v'_k = v_k, \quad \forall k \neq i, j \\ v'_i = v_i \pm 1 \\ v'_j = v_j \pm 1 \end{cases}$$

Combination bands



Selection rules

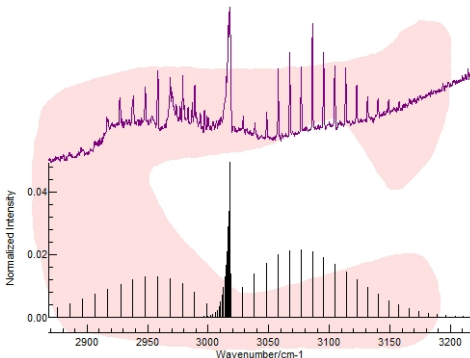
- Vibrational bands





Selection rules

- Rotational structure of the vibrational bands (Example: CH_4)



$$\left\{ \begin{array}{ll} \Delta J = -1 & \rightarrow P \text{ branch} \\ \Delta J = 0 & \rightarrow Q \text{ branch} \\ \Delta J = +1 & \rightarrow R \text{ branch} \end{array} \right.$$