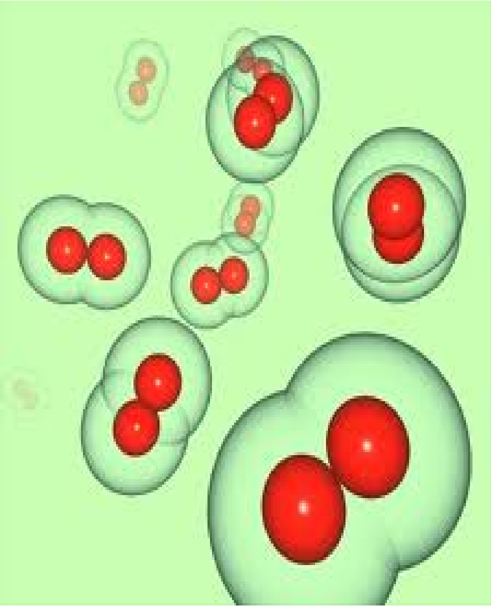
Molecular Spectroscopy



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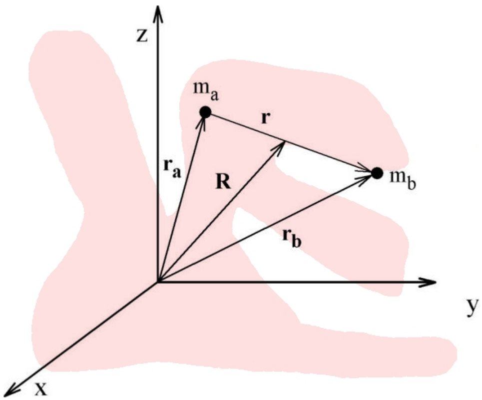
Universidad de Murcia. España.

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



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

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

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

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

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

I.A. Hamiltonian

$$\psi(\mathbf{R},\mathbf{r})=\psi_{\text{tras}}(\mathbf{R})\psi_{\text{rovib}}(\mathbf{r})$$

$$E=E_{\text{trans}}+E_{\text{rovib}}$$

$$\begin{cases} \left[-\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}}\right]\psi_{\text{trans}}(\mathbf{R})=E_{\text{trans}}\psi_{\text{trans}}(\mathbf{R}) \\ \left[-\frac{\hbar^2}{2\mu}\nabla^2_{\mathbf{r}}+V(r)\right]\psi_{\text{rovib}}(\mathbf{r})=E_{\text{rovib}}\psi_{\text{rovib}}(\mathbf{r}) \end{cases}$$

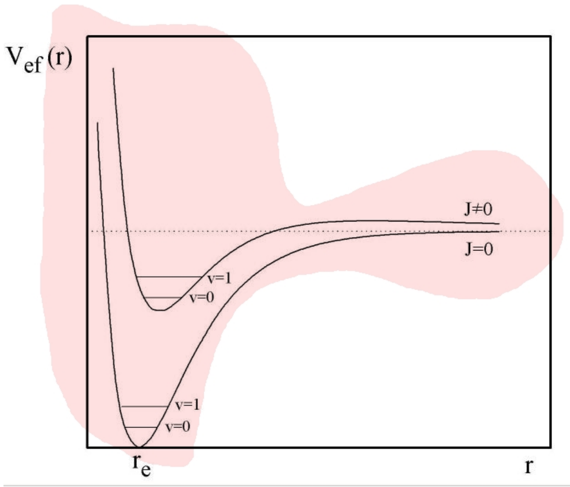
$\Rightarrow$ Spherical polar coordinates $(x,y,z)\rightarrow(r,\theta,\phi)$

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

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

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

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



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

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

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

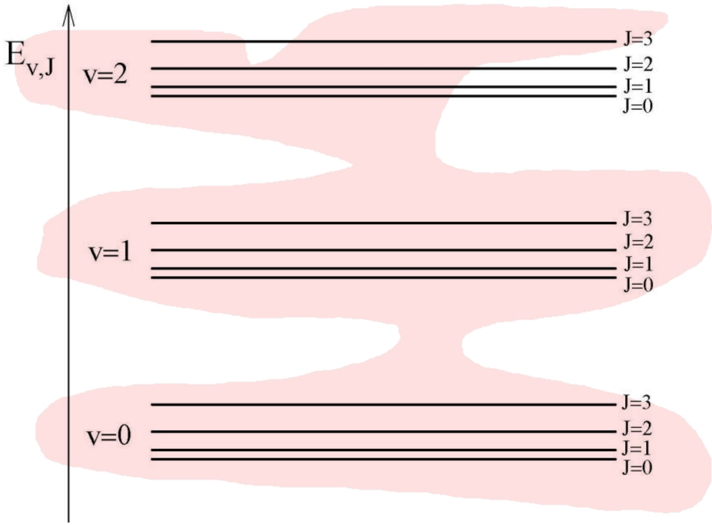
rigid rotor $\Rightarrow \dfrac{J(J+1)\hbar^2}{2\mu r^2} \approx \dfrac{J(J+1)\hbar^2}{2\mu r_e^2}$

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

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

- Energy

$$E_{\mathrm{v},J} = (\mathrm{v}+1/2)\hbar\omega + J(J+1)hB_e \qquad \mathrm{v}, J = 0, 1, 2, \ldots$$



I.C. Perturbations

- Perturbations $(q = r - r_e)$

$$V(r) = \frac{1}{2}kq^2 + \underbrace{k_3 q^3 + k_4 q^4}_{\text{anharmonicity}} + \dots$$

$$\frac{J(J+1)\hbar^2}{2\mu r^2} = J(J+1)hB_e + \underbrace{k_1 q + k_2 q^2}_{\text{centrigugal distortion}} + \dots$$

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

$$\hat{H}(q) \begin{cases} \hat{H}^{(0)} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{J(J+1)\hbar^2}{2\mu r_e^2} + \frac{1}{2}k(r - r_e)^2 \\ \hat{H}' = k_1 q + k_2 q^2 + k_3 q^3 + k_4 q^4 \end{cases}$$

- 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

$$E_{v,J}^{(2)} = \sum_{v'\neq v} \frac{|k_1\langle v'|q|v\rangle + k_3\langle v'|q^3|v\rangle|^2}{E_v^0 - E_{v'}^0} = -\frac{k_3^2(30v^2+30v+11)}{8\alpha^2 h\nu_e} - \frac{2hB_e^2[J(J+1)]^2}{\alpha r_e^2 \nu_e} + \frac{6B_e k_3 (v+1/2)J(J+1)}{\alpha^2 r_e \nu_e}$$

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

$$\frac{E_{v,J}}{hc} = \underbrace{\omega_e(v+1/2)}_{\text{harmonic}} + \underbrace{B_e J(J+1)}_{\text{rigid rotor}} - \underbrace{\omega_e x_e (v+1/2)^2}_{\text{anharmonicity}}$$

$$- \underbrace{D_e[J(J+1)]^2}_{\text{centrigugal distortion}} - \underbrace{\alpha_e(v+1/2)J(J+1)}_{\text{rovibrational coupling}}$$

$$\omega_e=\frac{\nu_e}{c}=\frac{1}{2\pi c}\left(\frac{k_e}{\mu}\right)^{1/2} \qquad B_e = \frac{h}{8\pi^2 \mu r_e^2 c}$$

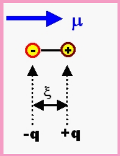
$$\omega_e x_e=\frac{6B_e^2 r_e^4}{\omega_e^2 hc}\left[\frac{5B_e k_3^2 r_e^2}{\omega_e^2 hc}-k_4\right] \qquad D_{e,r}=\frac{4B_e^3}{\omega_e^2}$$

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

Molecule[a]	ω_e[b]	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

[a]Data 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}.



- Momento dipolar eléctrico

$$\left.\begin{array}{r}\psi=\psi_{\text{elec}}\psi_{\text{nuc}}\\ \hat{\mu}=-\sum_i e\mathbf{r}_i+Z_a e\mathbf{r}_a+Z_b e\mathbf{r}_b\end{array}\right\}\langle\psi|\hat{\mu}|\psi'\rangle=\int\psi^*_{\text{nuc}}\psi'_{\text{nuc}}\Big[\underbrace{\int\psi^*_{\text{el}}\hat{\mu}\psi_{\text{el}}d\tau_{\text{el}}}\Big]d\tau_{\text{nuc}}$$

$\mu_e \rightarrow$ permanent electronic dipole moment

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

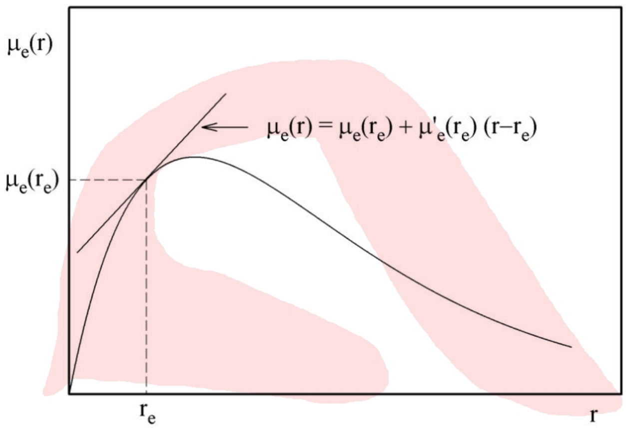
$$\mu_e=\mu_e(r)[\operatorname{sen}\theta\cos\phi\,\mathbf{i}+\operatorname{sen}\theta\operatorname{sen}\phi\,\mathbf{j}+\cos\theta\,\mathbf{k}]\ \downarrow$$

$$=\int_0^\infty\phi_{v,J}(r)\mu_e(r)\phi_{v',J}(r)dr\ \underbrace{\int_0^{2\pi}\int_0^{\pi}Y_{J'}^{M'^*}[\operatorname{sen}\theta\cos\phi\mathbf{i}+\operatorname{sen}\theta\operatorname{sen}\phi\mathbf{j}+\cos\theta\mathbf{k}]Y_{J'}^{M'}\operatorname{sen}\theta d\theta d\phi}$$

$$\Delta J=\pm1$$

$$\Delta M=0,\pm1$$

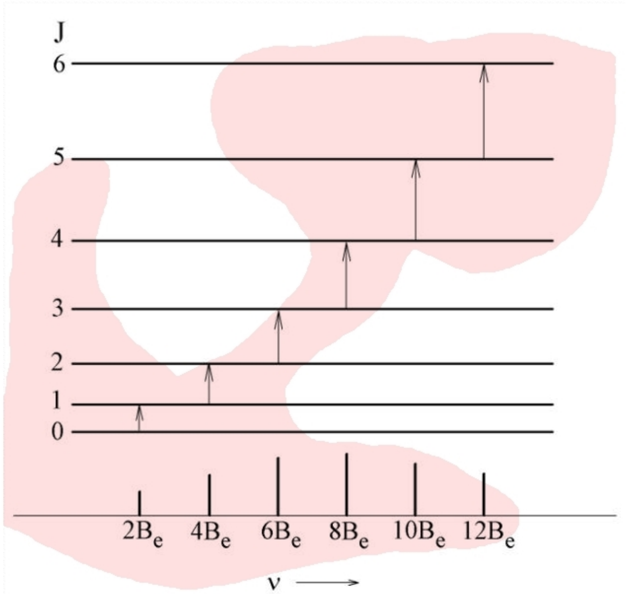
- Homonuclear molecules $\Rightarrow \mu_e(r) = 0$
- Heteronuclear molecules $\Rightarrow \int_0^\infty \phi_{v,J}(r)\,\mu_e(r)\,\phi_{v',J}(r)dr$



- $\lim_{r\to 0} \mu_e(r) = \lim_{r\to\infty} \mu_e(r) = 0$
- $\mu_e(r) = \mu_e(r_e) + \mu_e'(r_e)(r-r_e) + \frac{\mu_e''(r_e)}{2!}(r-r_e)^2 + \ldots$

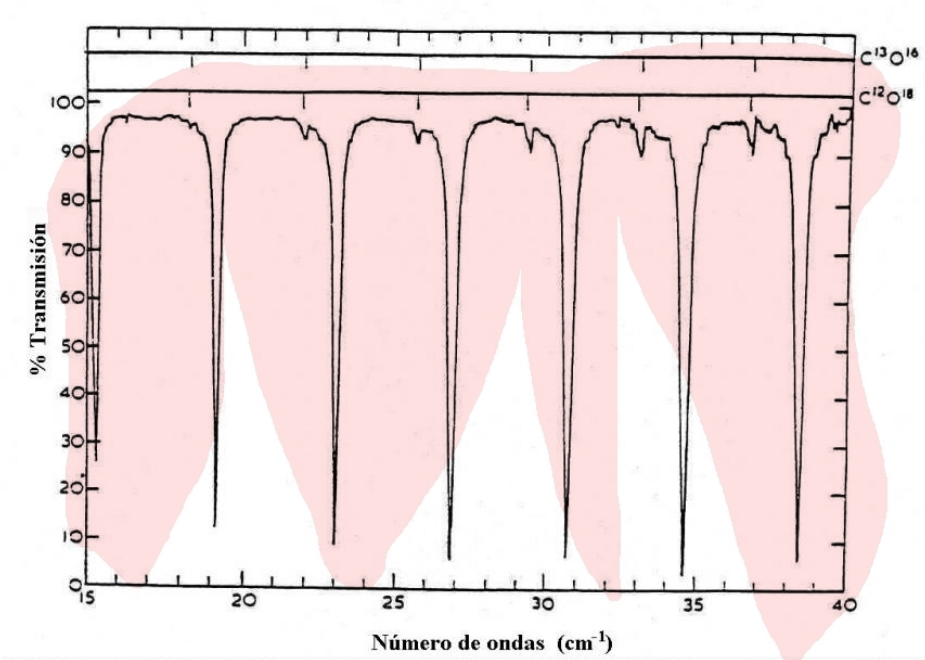
$$\int_0^\infty \phi_v(r)\mu_e(r)\phi_{v'}(r)dr = \mu_e(r_e)\underbrace{\int_{-\infty}^{\infty}\phi_{v'}(q)\phi_v(q)dq}_{\Delta v=0} + \mu_e'(r_e)\underbrace{\int_{-\infty}^{\infty}\phi_{v'}(q)q\phi_v(q)dq}_{\Delta v=\pm 1} + \ldots$$

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

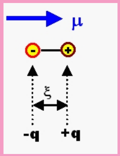


$\Rightarrow$ Microwaves (0.03-10 cm^{-1}) (1-300 GHz)

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



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



I.F. Rovibrational spectrum

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

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

$$\downarrow$$

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

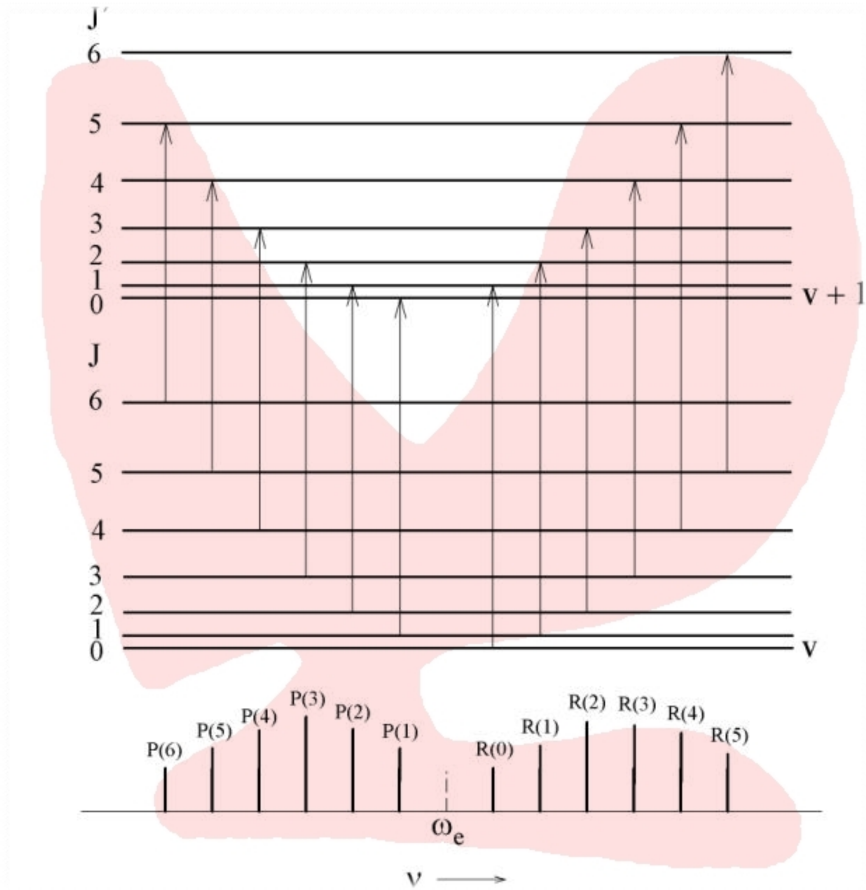
  - $\Delta J = -1 \Rightarrow$ P branch

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

$$\downarrow$$

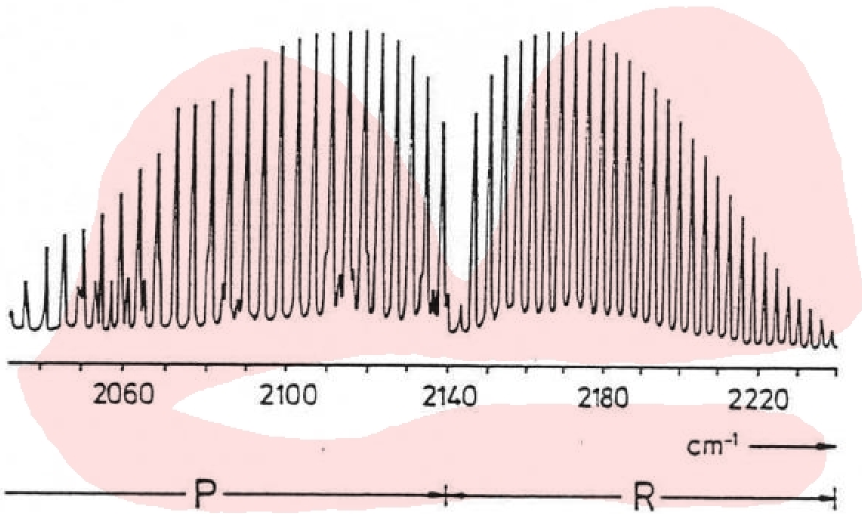
$$\Delta\tilde{\nu}_P = 2B_e$$

I.F. Rovibrational spectrum



I.F. Rovibrational spectrum

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



I.F. Rovibrational spectrum

- Anharmonicity and centrigugal distortion

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

$$\Delta\mathrm{v}=\pm1,\pm2,\ldots$$

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

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

    - $0\rightarrow1\Rightarrow$ Fundamental band
    - $0\rightarrow2,3,\ldots\Rightarrow$ First, second,... overtones
    - $\mathrm{v}\neq0\Rightarrow$ Hot bands

I.F. Rovibrational spectrum

- Rotational structure
  - R branch ⇒ Band head

$$\tilde{\nu}_R(\mathrm{v}\to\mathrm{v}', J\to J+1) = \tilde{\nu}_0(\mathrm{v}\to\mathrm{v}') + [2B_e - \alpha_e(\mathrm{v}'+\mathrm{v}+1)](J+1) - \alpha_e(\mathrm{v}'-\mathrm{v})(J+1)^2$$
$$-4D_{e,r}(J+1)^3 \qquad J=0,1,2,\ldots$$

  - P branch

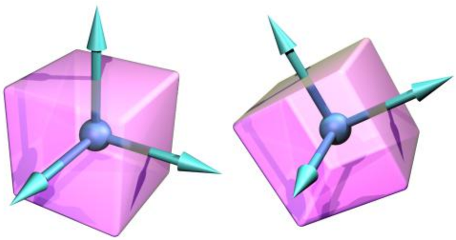
$$\tilde{\nu}_P(\mathrm{v}\to\mathrm{v}', J\to J-1) = \tilde{\nu}_0(\mathrm{v}\to\mathrm{v}') - [2B_e - \alpha_e(\mathrm{v}'+\mathrm{v}+1)]J - \alpha_e(\mathrm{v}'-\mathrm{v})J^2$$
$$+4D_{e,r}J^3 \qquad J=1,2,\ldots$$

  - Intensities ⇒ Rotational populations

$$\frac{N_{\mathrm{v},J}}{N_{\mathrm{v}.0}} = (2J+1)e^{-B_eJ(J+1)h/K_BT}$$

II.A. Motion equations

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



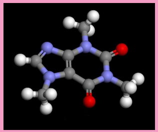
- Mass-weighted cartesian coordinates $\Rightarrow (q_1, \ldots, q_{3N_\mathrm{S}})$

$$q_1 = \sqrt{m_1}(x_1^{\mathrm{bf}} - x_{1,e}^{\mathrm{bf}}), \quad q_2 = \sqrt{m_1}(y_1^{\mathrm{bf}} - y_{1,e}^{\mathrm{bf}}), \quad q_3 = \sqrt{m_1}(z_1^{\mathrm{bf}} - z_{1,e}^{\mathrm{bf}})$$

$$q_4 = \sqrt{m_2}(x_2^{\mathrm{bf}} - x_{2,e}^{\mathrm{bf}}), \quad q_5 = \sqrt{m_2}(y_2^{\mathrm{bf}} - y_{2,e}^{\mathrm{bf}}), \quad q_6 = \sqrt{m_2}(z_2^{\mathrm{bf}} - z_{2,e}^{\mathrm{bf}})$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$q_{3N_\mathrm{S}-2} = \sqrt{m_{N_\mathrm{S}}}(x_{N_\mathrm{S}}^{\mathrm{bf}} - x_{N_\mathrm{S},e}^{\mathrm{bf}}), \quad q_{3N_\mathrm{S}-1} = \sqrt{m_{N_\mathrm{S}}}(y_{N_\mathrm{S}}^{\mathrm{bf}} - y_{N_\mathrm{S},e}^{\mathrm{bf}}), \quad q_{3N_\mathrm{S}} = \sqrt{m_{N_\mathrm{S}}}(z_{N_\mathrm{S}}^{\mathrm{bf}} - z_{N_\mathrm{S},e}^{\mathrm{bf}})$$



II.A. Motion equations

- Internal energy

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

$$V = \cancel{V^e + \sum_{i=1}^{3N_s}\left(\frac{\partial V}{\partial q_i}\right)_e q_i} + \frac{1}{2!}\sum_{i=1}^{3N_s}\sum_{j=1}^{3N_s}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_e q_i q_j$$

$$+\frac{1}{3!}\sum_{i=1}^{3N_s}\sum_{j=1}^{3N_s}\sum_{k=1}^{3N_s}\left(\frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k}\right)_e q_i q_j q_k + \cdots$$

$$\approx \frac{1}{2}\sum_{i=1}^{3N_s}\sum_{j=1}^{3N_s} u_{ij} q_i q_j \rightarrow u_{ij}$$ Hessian matrix

- Newton's law

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

$$\downarrow$$

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

- Equilibrium normal modes

$$\mathbf{L}^{\dagger}\mathbf{U}\mathbf{L} = \Lambda \;\rightarrow\; Q_i = \sum_{k=1}^{3N_\mathrm{s}} l_{ki} q_k \qquad\qquad i = 1, \ldots, 3N_\mathrm{s}$$

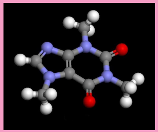
$$\underbrace{\lambda_{3N_\mathrm{s}-z} = \ldots = \lambda_{3N_\mathrm{s}} = 0}_{\text{translation+rotation}} \;\rightarrow\; \begin{cases} z = 5 \rightarrow \text{linear molecules} \\ z = 6 \rightarrow \text{non-linear molecules} \end{cases}$$

$$Q_1, Q_2, \ldots, Q_{3N_\mathrm{s}-z} \rightarrow \text{vibrations}$$

- Kinetic energy

$$T = \frac{1}{2}\sum_{k=1}^{3N_s}\left(\frac{dq_k}{dt}\right)^2 = \frac{1}{2}\sum_{i=1}^{3N_s}\left(\sum_{k=1}^{3N_s} l_{ik}\frac{dQ_k}{dt}\sum_{l=1}^{3N_s} l_{il}\frac{dQ_l}{dt}\right)$$

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



- Potential energy

$$V = \frac{1}{2}\sum_{i=1}^{3N_s}\sum_{j=1}^{3N_s} u_{ij}q_iq_j = \frac{1}{2}\sum_{i=1}^{3N_s}\sum_{j=1}^{3N_s} u_{ij}\left(\sum_{k=1}^{3N_s} l_{ik}Q_k \sum_{l=1}^{3N_s} l_{jl}Q_l\right)$$

$$= \frac{1}{2}\sum_{k=1}^{3N_s}\sum_{l=1}^{3N_s} Q_kQ_l\left(\sum_{i=1}^{3N_s}\sum_{j=1}^{3N_s} l_{ik}u_{ij}l_{jl}\right)$$

$$= \frac{1}{2}\sum_{k=1}^{3N_s}\sum_{l=1}^{3N_s} Q_kQ_l\delta_{kl}\lambda_k = \frac{1}{2}\sum_{k=1}^{3N_s-z} \lambda_k Q_k^2$$

- Vibrational energy

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

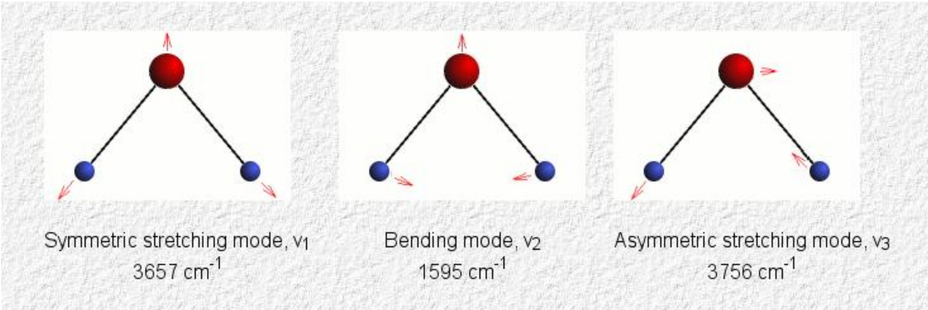
$$\downarrow$$

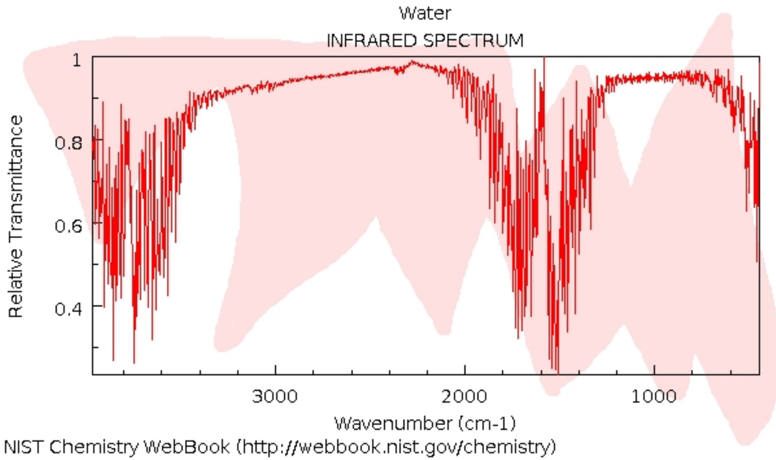
$$\frac{d^2 Q_i}{dt^2} + \lambda_i Q_i = 0 \qquad i = 1, \ldots, 3N_s - z$$

$$\downarrow$$

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

- Water molecule





- Hamiltonian operator

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

$$\downarrow$$

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

$$\downarrow$$

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

II.D. Eigenfunctions and eigenvalues

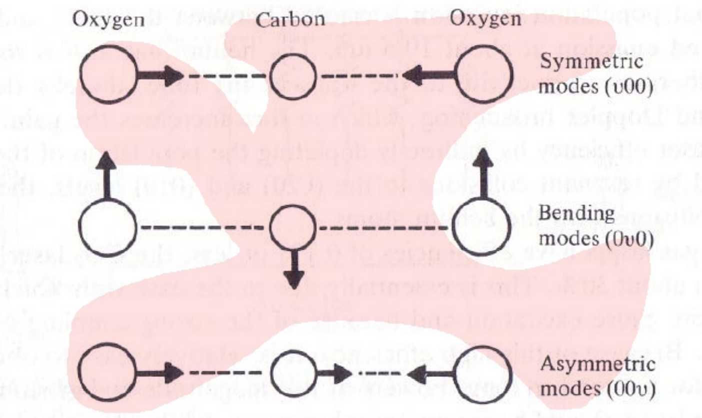
- $3N_\mathrm{s} - z$ dimensional function

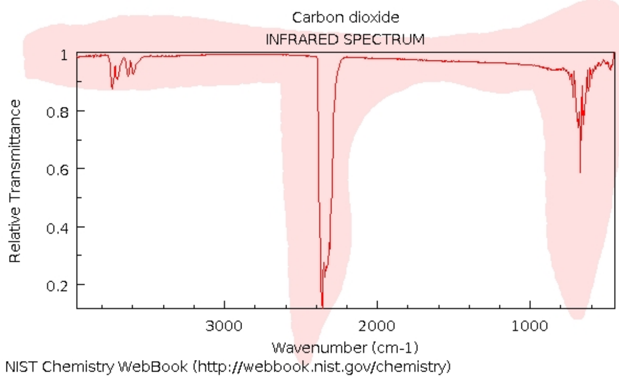
$$\hat{H}_\mathrm{vib}\Psi_\mathrm{vib} = E_\mathrm{vib}\Psi_\mathrm{vib} \rightarrow \Psi_\mathrm{vib} = \prod_{k=1}^{3N_\mathrm{s}-z} \varphi_k(Q_k)$$

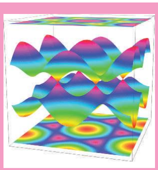
$$\downarrow$$

$$E_\mathrm{vib} = \sum_{k=1}^{3N_\mathrm{s}-z} \varepsilon_k = \sum_{k=1}^{3N_\mathrm{s}-z} (\mathrm{v}_k + \frac{1}{2})h\nu_k$$

- CO_2 molecule







- Electronic dipole moment $\boldsymbol{\mu}$

$$\int \psi'^{*}_{\mathrm{vib}}\,\boldsymbol{\mu}\,\psi_{\mathrm{vib}}\,dQ_1\cdots dQ_{3N_{\mathrm{S}}-z} \rightarrow \boldsymbol{\mu} = \mu_x\,\mathbf{i}_{\mathrm{bf}} + \mu_{\mathbf{y}}\,\mathbf{j}_{\mathrm{bf}} + \mu_{\mathbf{z}}\,\mathbf{k}_{\mathrm{bf}}$$

$$\downarrow$$

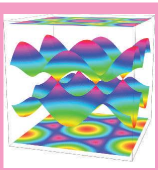
$$\alpha = x,y,z \qquad \mu_\alpha = \mu_{\alpha,\mathrm{e}} + \sum_{k=1}^{3N_{\mathrm{S}}-z}\left(\frac{\partial\mu_\alpha}{\partial Q_k}\right)_{\mathrm{e}} Q_k + \sum_{k=1}^{3N_{\mathrm{S}}-z}\sum_{j=1}^{3N_{\mathrm{S}}-z}\left(\frac{\partial^2\mu_\alpha}{\partial Q_j\partial Q_k}\right)_{\mathrm{e}} Q_j Q_k + \ldots$$

$$\downarrow$$

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

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

  pure rotational spectrum



II.E. Selection rules

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

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

Fundamental bands

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

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

Overtones

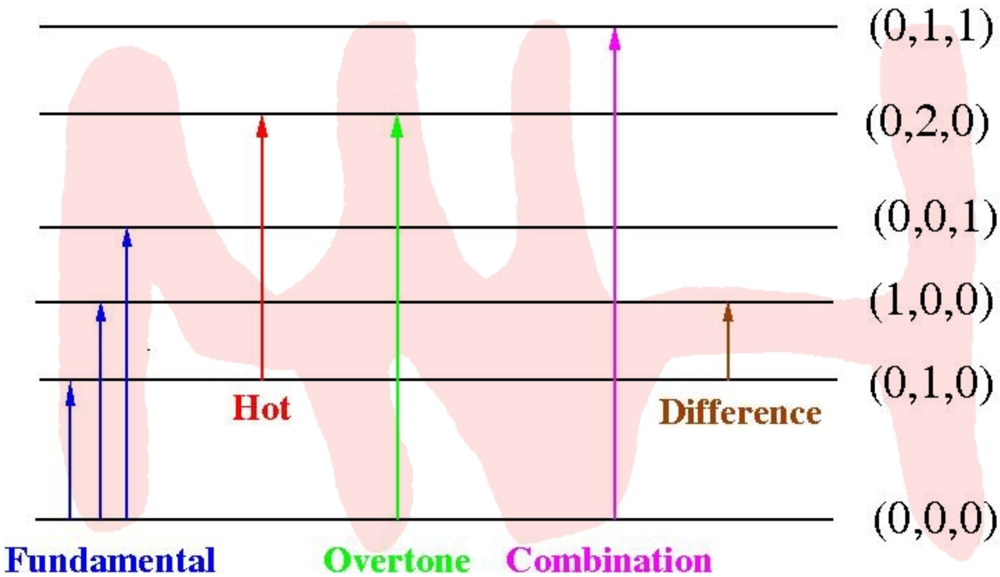
II.E. Selection rules

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

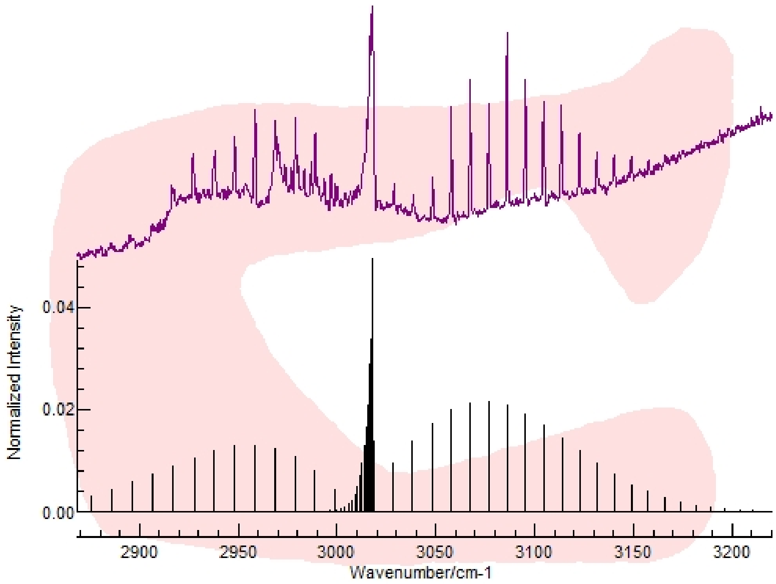
$$\Rightarrow \begin{cases} \mathrm{v}'_k = \mathrm{v}_k, \ \forall k \neq i, j \\ \mathrm{v}'_i = \mathrm{v}_i \pm 1 \\ \mathrm{v}'_j = \mathrm{v}_j \pm 1 \end{cases}$$

Combination bands

- Vibrational bands



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



$$\begin{cases} \Delta J = -1 & \rightarrow P \text{ branch} \\ \Delta J = 0 & \rightarrow Q \text{ branch} \\ \Delta J = +1 & \rightarrow R \text{ branch} \end{cases}$$