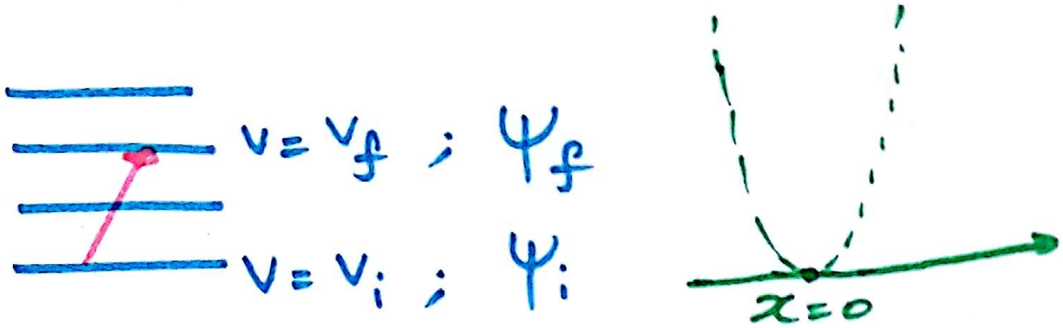
SELECTION RULES FOR VIBRATIONAL TRANSITIONS



TRANSITION DIPOLE MOMENT INTEGRAL

$$I_{i\to f} = \int_{\vec{r}} \psi_f^*(\vec{r})\, \hat{\mu}\, \psi_i(\vec{r})\, d\vec{r}$$

DIPOLE MOMENT OF AN N-PARTICLE SYSTEM

$$\mu = \sum_{i=1}^{N} \underbrace{Q_i}_{\text{CHARGE}} \underbrace{\vec{r}_i}_{\text{POSITION}}$$

$$\mu(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \simeq \mu(\vec{r}_{1,0}, \vec{r}_{2,0}, \ldots, \vec{r}_{N,0}) + (\vec{\nabla}_{3N}\mu)\cdot \vec{\Delta r}_{3N} + \cdots$$

(IGNORE HIGHER-ORDER TERMS)

HERE

$(\vec{r}_{1,0}, \vec{r}_{2,0}, \ldots, \vec{r}_{N,0}) \Rightarrow$ EQUILIBRIUM CONFIGURATION (ENERGY-MINIMUM CONFIGURATION)

$\mu(\vec{r}_{1,0}, \vec{r}_{2,0}, \ldots, \vec{r}_{N,0}) \Rightarrow$ PERMANENT DIPOLE MOMENT (MAY OR MAY NOT BE EQUAL TO ZERO)

$$\vec{\nabla}_{3N} \equiv \left(\frac{\partial}{\partial \vec{r}_1}, \frac{\partial}{\partial \vec{r}_2}, \ldots, \frac{\partial}{\partial \vec{r}_N}\right)$$

$$\vec{\Delta r}_{3N} = (\vec{r}_1 - \vec{r}_{1,0}, \vec{r}_2 - \vec{r}_{2,0}, \ldots, \vec{r}_N - \vec{r}_{N,0})$$

FOR A DIATOMIC MOLECULE

$$x = R_{AB} - R_0$$

$$\mu(x) = \mu(x=0) + \left.\frac{d\mu}{dx}\right|_{x=0} x + \cdots$$

$$I_{i\to f} = \int_x \psi_f^*(x) \left[\mu(x=0) + \left.\frac{d\mu}{dx}\right|_{x=0} x \right] \psi_i(x)\, dx$$

$$= \mu(x=0) \underbrace{\int_x \psi_f^*(x)\, \psi_i(x)\, dx}_{0} + \left.\frac{d\mu}{dx}\right|_{x=0} \int_x \psi_f^*(x)\, x\, \psi_i(x)\, dx$$

0 (ψ_f AND ψ_i ARE ORTHOGONAL)

$$I_{i\to f} \approx \boxed{\left.\frac{d\mu}{dx}\right|_{x=0}} \boxed{\int_x \psi_f^*(x)\, x\, \psi_i(x)\, dx}$$

FOR $I_{i\to f} \neq 0$;

$$\boxed{\left.\frac{d\mu}{dx}\right|_{x=0} \neq 0}$$ SELECTION RULE 1

$$\boxed{\int_x \psi_f^*(x)\, x\, \psi_i(x)\, dx \neq 0}$$ SELECTION RULE 2

CONSIDER $\int_x \psi_f^*(x)\, x\, \psi_i(x)\, dx$

RECALL: FOR AN ONE-DIMENSIONAL QUANTUM HARMONIC OSCILLATOR

$$\psi_v(x) = N_v H_v(q)\, e^{-\frac{q^2}{2}}$$

HERE $N_v = \left(\dfrac{1}{\alpha \pi^{1/2} 2^v v!}\right)^{1/2}$

$$\alpha = \left(\frac{\hbar}{m\omega}\right)^{1/2} \qquad q = \frac{x}{\alpha} \quad ; \quad \alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4}$$

$H_v(q) \rightarrow$ HERMITE POLYNOMIAL

RECURRENCE OR RECURSION RELATION:

$$H_{v+1}(q) = 2q H_v(q) - 2v H_{v-1}(q)$$

$$\Rightarrow \quad q H_v(q) = \frac{H_{v+1}(q) + 2v H_{v-1}(q)}{2}$$

$\times N_v e^{-q^2/2}$ ON BOTH SIDES

$$q \psi_v(x) = \frac{\left(\frac{N_v}{N_{v+1}}\right) \psi_{v+1}(x) + 2v \left(\frac{N_v}{N_{v-1}}\right) \psi_{v-1}(x)}{2}$$

$$x \psi_v(x) = \left(\frac{\alpha}{2}\right) \left[\frac{N_v}{N_{v+1}} \psi_{v+1}(x) + 2v \left(\frac{N_v}{N_{v-1}}\right) \psi_{v-1}(x)\right]$$

$$\int_x \psi_{v_f}^*(x)\, x\, \psi_{v_i}(x)\, dx$$

$$= \int_x \psi_{v_f}^*(x)\left(\frac{\alpha}{2}\right)\left[\frac{N_{v_i}}{N_{v_i+1}}\psi_{v_i+1}(x) + 2v_i\left(\frac{N_{v_i}}{N_{v_i-1}}\right)\psi_{v_i-1}(x)\right] dx$$

$$= \left(\frac{\alpha}{2}\right)\frac{N_{v_i}}{N_{v_i+1}}\int_x \psi_{v_f}^*(x)\,\psi_{v_i+1}(x)\, dx$$

$$+ \left(\frac{\alpha}{2}\right)\left(\frac{2v_i N_{v_i}}{N_{v_i-1}}\right)\int_x \psi_{v_f}^*(x)\,\psi_{v_i-1}(x)\, dx$$

FIRST INTEGRAL

$$\int_x \psi_{v_f}^*(x)\,\psi_{v_i+1}(x)\, dx \neq 0$$

ONLY WHEN $v_f = v_i + 1$

$$\Rightarrow \boxed{\Delta v = v_f - v_i = +1}$$

SECOND INTEGRAL

$$\int_x \psi_{v_f}^*(x)\,\psi_{v_i-1}(x)\, dx \neq 0$$

ONLY WHEN $v_f = v_i - 1$

$$\Rightarrow \boxed{\Delta v = v_f - v_i = -1}$$

SELECTION RULE 2 : $\boxed{\Delta v = \pm 1}$

HERMITE POLYNOMIALS

$$\frac{d^2 H_v(y)}{dy^2} - 2y\frac{dH_v(y)}{dy} + 2v H_v(y) = 0$$

THE SOLUTIONS OF THIS DIFFERENTIAL EQUATION ARE HERMITE POLYNOMIALS

v	$H_v(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$

USING LADDER OPERATORS:

$$q = \left(\frac{m\omega}{\hbar}\right)^{1/2} x$$

LADDER UP OPERATOR $b^+ \equiv \frac{1}{\sqrt{2}}\left(-\frac{d}{dq} + q\right)$

$$b^+ \psi_v(x) = C_+ \psi_{v+1}(x)$$

LADDER DOWN OPERATOR $b^- \equiv \frac{1}{\sqrt{2}}\left(\frac{d}{dq} + q\right)$

$$b^- \psi_v(x) = C_- \psi_{v-1}(x)$$

$$q = \frac{b^+ + b^-}{\sqrt{2}}$$

$$\Rightarrow \quad x = \sqrt{\frac{\hbar}{m\omega}}\left(\frac{b^+ + b^-}{\sqrt{2}}\right)$$

$$x\,\psi_{v_i}(x) = \sqrt{\frac{\hbar}{m\omega}}\left(\frac{b^+\psi_{v_i}(x) + b^-\psi_{v_i}(x)}{\sqrt{2}}\right)$$

$$= \sqrt{\frac{\hbar}{m\omega}}\left(\frac{C_{+v_i}\psi_{v_i+1}(x) + C_{-v_i}\psi_{v_i-1}(x)}{\sqrt{2}}\right)$$

$$\int \psi_{v_f}^*(x)\, x\, \psi_{v_i}(x)\, dx$$

$$= B \int_x \psi_{v_f}^*(x)\, \psi_{v_i+1}(x)\, dx + D \int_x \psi_{v_f}^*(x)\, \psi_{v_i-1}(x)\, dx$$

$$\Rightarrow \boxed{\Delta v = v_f - v_i = \pm 1}$$

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