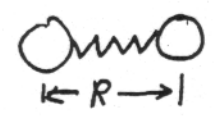
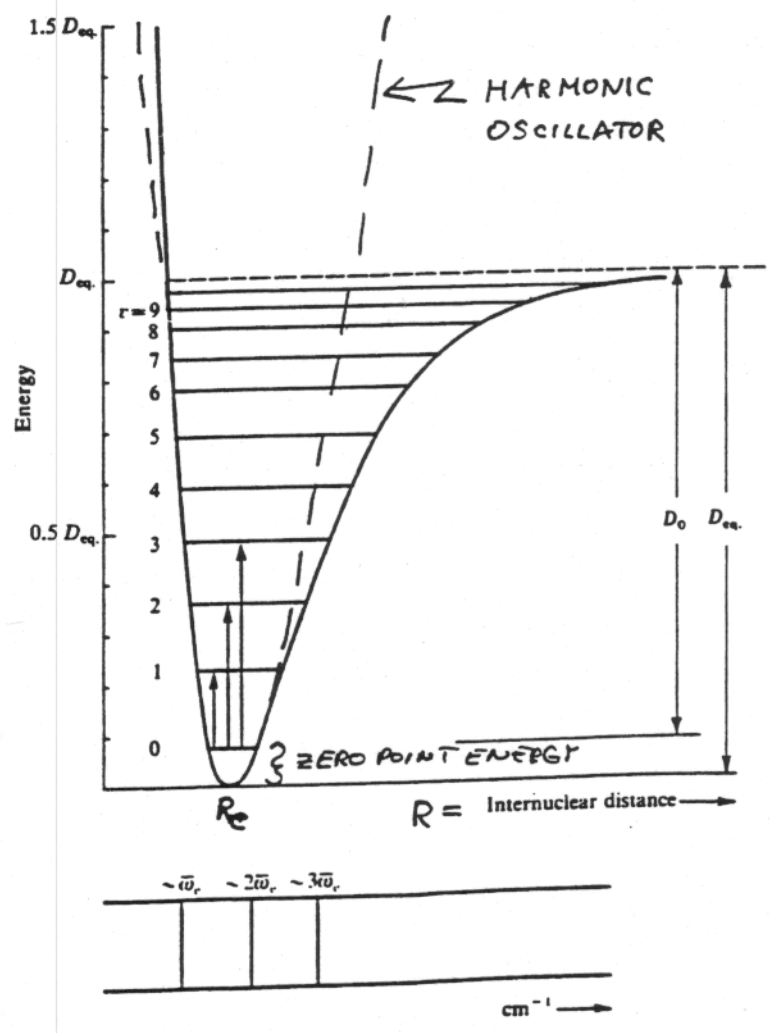


# VIBRATIONAL SPECTROSCOPY

## DIATOMIC MOLECULES



AT  $R=0$   $V \rightarrow \infty$

AT  $R \rightarrow \infty$ ,  $V \rightarrow D_{eq}$

$D_{eq}$  = DISSOCIATION ENERGY TO TAKE ATOMS INFINITELY FAR APART

$D_0$  = SAME BUT MEASURED FROM  $E_0$

$R_e$  = EQUILIBRIUM VALUE OF R

AT LOWER ENERGIES, THE HARMONIC OSCILLATOR MODEL DETERMINES THE QUANTUM LEVELS QUITE WELL

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

FOR A DIATOMIC MOLECULE (AS SEEN FOR ROTATIONS) THE WAVE EQUATION BECOMES

$$-\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2} kx^2 \psi = E\psi$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

REDUCED MASS

## Solution for Harmonic Oscillator Model (QM)

$$\bar{E}_v = \left(v + \frac{1}{2}\right) h\omega \quad (\bar{E} \text{ is in joules})$$

$$v = 0, 1, 2, \dots \quad \text{vibrational Q.N.}$$

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{classical vibration number given in Hz}$$

$$\bar{E}_v = \left(v + \frac{1}{2}\right) h \sqrt{\frac{k}{\mu}} \quad \begin{array}{l} k: \text{force constant} \\ \mu: \text{reduced mass} \end{array}$$

Since selection rule for vibrational transitions is

$$\Delta v = \pm 1$$

Then

$$\Delta \bar{E} = \bar{E}_{v+1} - \bar{E}_v = h \sqrt{\frac{k}{\mu}} \quad (\bar{E} \text{ is in joules})$$

More commonly, we use  $\nu$  (Hz) for QM. vibration numbers.

Thus:

$$\nu \text{ (Hz)} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\therefore \Delta \bar{E} = h \nu$$

$\begin{array}{cc} \uparrow & \uparrow \\ \text{J.s} & \text{s}^{-1} \end{array}$

$$\nu \text{ (Hz)} = \frac{\Delta \bar{E}}{h} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\bar{\nu} \text{ (cm}^{-1}\text{)} = \frac{\nu}{c} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

# SOLUTIONS FOR HARMONIC OSCILLATOR:

$$\psi_v = N_v e^{-\alpha q^2} H_v(\sqrt{\alpha} q) \quad \text{where } v = 0, 1, 2, \dots$$

$$q = x$$

$$N_v = \left( \frac{\sqrt{\alpha}}{2^v v! \sqrt{\pi}} \right)^{\frac{1}{2}}$$

$$\alpha = \frac{2\pi \sqrt{\mu k}}{h}$$

THE FIRST 5 WAVE FUNCTIONS ARE

$$\psi_0 = \left( \frac{\alpha}{\pi} \right)^{\frac{1}{4}} e^{-\alpha q^2}$$

$$\psi_1 = \sqrt{2\alpha} \left( \frac{\alpha}{\pi} \right)^{\frac{1}{4}} q e^{-\alpha q^2}$$

$$\psi_2 = \frac{1}{\sqrt{2}} \left( \frac{\alpha}{\pi} \right)^{\frac{1}{4}} (2\alpha q^2 - 1) e^{-\alpha q^2}$$

$$\psi_3 = \sqrt{\frac{\alpha}{3}} \left( \frac{\alpha}{\pi} \right)^{\frac{1}{4}} (2\alpha^{\frac{3}{2}} q^3 - 3\alpha^{\frac{1}{2}} q) e^{-\alpha q^2}$$

$$\psi_4 = \frac{1}{\sqrt{6}} \left( \frac{\alpha}{\pi} \right)^{\frac{1}{4}} (4\alpha^2 q^4 - 12\alpha q^2 + 3) e^{-\alpha q^2}$$

$$\left( \frac{\alpha}{\pi} \right)^{\frac{1}{4}}$$

$$E_v = \left( v + \frac{1}{2} \right) h \left( \frac{k}{\mu} \right)^{\frac{1}{2}}$$

$$\left( \frac{\partial M}{\partial q} \right)_{q=0} \neq 0$$

DIPOLE MOMENT CHANGE

SELECTION RULE:  $\Delta v = \pm 1$

$$\Delta E = h\nu = h \left( \frac{k}{\mu} \right)^{\frac{1}{2}}$$

$$\nu = \frac{\Delta E}{h} = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{\frac{1}{2}}$$

$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c} \left( \frac{k}{\mu} \right)^{\frac{1}{2}}$$

$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$  is written for classical picture of vibration

VIBRATIONAL FREQUENCY IN  $\text{cm}^{-1}$

FORCE CONSTANT

$$k = 4\pi^2 c^2 \bar{\nu}^2 \mu$$

More realistic to express

$1 \text{ dyne} = 10^{-5} \text{ N}$   
 $1 \text{ N} = 10^5 \text{ dyne}$

UNITS:  $10^5 \text{ dyne/cm} = \frac{\text{mdyne}}{\text{\AA}} = 100 \text{ N/m}$

**TABLE 2-1** Frequencies of Fundamental Vibrational Transitions  $v = 0$  to  $v = 1$  and the Bond Force Constants Calculated from These Data  
(Values for homonuclear molecules are from Raman spectral studies)

Molecule	$\bar{\nu}$ (cm <sup>-1</sup> )	k (dynes/cm)
H <sub>2</sub>	4,159.2	5.2 × 10 <sup>6</sup>
D <sub>2</sub>	2,990.3	5.3
HF	3,958.4	8.8
HCl	2,885.6	4.8
HBr	2,559.3	3.8
HI	2,230.0	2.9
CO	2,143.3	18.7
NO	1,876.0	15.5
F <sub>2</sub>	892	4.5
Cl <sub>2</sub>	556.9	3.2
Br <sub>2</sub>	321	2.4
I <sub>2</sub>	213.4	1.7
O <sub>2</sub>	1,556.3	11.4
N <sub>2</sub>	2,330.7	22.6
Li <sub>2</sub>	246.3	1.3
Na <sub>2</sub>	157.8	1.7
NaCl	378	1.2
KCl	278	0.8

$\bar{\nu} \propto \sqrt{\frac{k}{\mu}}$

Taylor's Series

$$V(x) = \sum_{i=0}^{\infty} \frac{1}{i!} \left( \frac{\partial^i V}{\partial x^i} \right)_{x_e} x^i = V_0 + \frac{1}{1} \left( \frac{\partial V}{\partial x} \right)_{x_e} x + \frac{1}{2} \left( \frac{\partial^2 V}{\partial x^2} \right)_{x_e} x^2 + \frac{1}{6} \left( \frac{\partial^3 V}{\partial x^3} \right)_{x_e} x^3 + \dots$$

ANHARMONICITY

$$V = \underbrace{\frac{1}{2} \left( \frac{d^2V}{dx^2} \right)_{x=0}}_k x^2 + \underbrace{\frac{1}{6} \left( \frac{d^3V}{dx^3} \right)_{x=0}}_{\text{ANHARMONICITY}} x^3 + \dots$$

PERTURBATION THEORY GIVES

$$\bar{G}(v) = \bar{E}_v = \underbrace{\bar{w}_e}_{\text{HARMONIC FREQUENCY}} \left( v + \frac{1}{2} \right) - \underbrace{\bar{w}_e x_e}_{\text{ANHARMONICITY}} \left( v + \frac{1}{2} \right)^2 + \underbrace{\bar{w}_e y_e}_{\text{ONE VALUE EACH}} \left( v + \frac{1}{2} \right)^3 + \dots$$

FOR  $v=0 \rightarrow 1$

$$\Delta E_{0 \rightarrow 1} = E_1 - E_0 = \bar{w}_e - 2\bar{w}_e x_e$$

$\bar{w}_e x_e$  is a -ve value that is why by convention the 2nd term is -ve.

V=4

FOR HCl,

$\bar{\nu}_{vib} = 2886 \text{ cm}^{-1}$        $\bar{\omega}_e = 2989 \text{ cm}^{-1}$        $\frac{\bar{\omega}_e X_e}{\bar{\omega}_e} = 51.6 \text{ cm}^{-1}$   
 $\frac{\bar{\omega}_e X_e}{\bar{\omega}_e} = 0.2244 \text{ cm}^{-1}$

$\bar{\omega}_e X_e$  is estimated as half of the value of the difference between  $\bar{\nu}_{vib}$  and  $\bar{\omega}_e$ .

TABLE 2-2 Frequencies of the Vibrational Transitions of HCl. Comparison of the Observed Frequencies with Those Calculated from the Harmonic Oscillator Approximation and with Those from the Anharmonic Expression  $\bar{\nu}_e - \epsilon_0 = 2,988.90(v) - 51.60v(v+1)$

$\Delta v$	Description	$\bar{\nu}_{obs} \text{ cm}^{-1}$	$\bar{\nu}_{calc} \text{ cm}^{-1}$	
			Harmonic oscillator	Anharmonic oscillator
0 → 1	Fundamental	2,885.9	(2,885.9)	2,885.70
0 → 2	First overtone	5,668.0	5,771.8	5,668.20
0 → 3	Second overtone	8,347.0	8,657.7	8,347.50
0 → 4	Third overtone	10,923.1	11,543.6	10,923.6
0 → 5	Fourth overtone	13,396.5	14,429.5	13,396.5

FOR HCl ALMOST ALL MOLECULES ARE IN  $v=0$  AT  $25^\circ \text{C}$

$\frac{N_1}{N_0} = e^{-\Delta E/KT} = e^{-2886/207} = e^{-14} = 8 \times 10^{-7}$

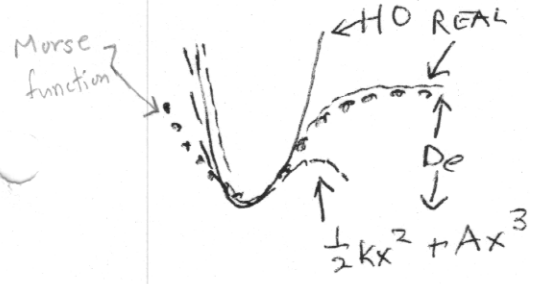
ANHARMONICITY GIVES SOME INTENSITY TO THE OVERTONES:  $0 \rightarrow 2, 0 \rightarrow 3, \text{ETC.}$

THE MORSE FUNCTION IS A BETTER WAY TO REPRESENT ANHARMONICITY

$V(x) = D_e [1 - e^{-ax}]^2$

$D_e = \text{DISSOCIATION ENERGY}$

$a = (\pi^2 c \mu / D_e h)^{1/2} \bar{\omega}_e$



GOOD AT  $x \rightarrow \infty$

NOT SO GOOD AT  $x \rightarrow -R_e$  (where  $R=0$ )