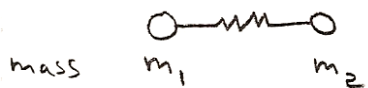


Vibration of Diatomics

need to know

- vibrational energy levels
- selection rules
- molecular parameters from spectral information

Vibrational Motion R_e equilibrium separation

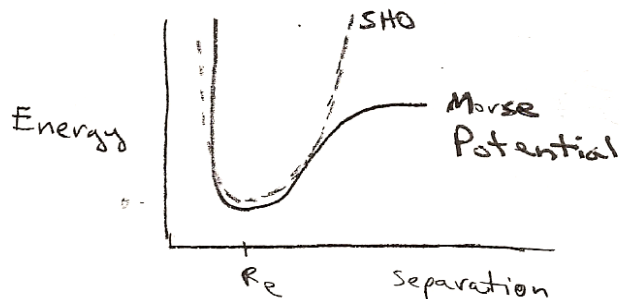


reduced mass

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

$$m_2 \ll m_1 \rightarrow \mu \approx m_2$$

$$m = m_2 = m_1 \rightarrow \mu = \frac{m}{2}$$



$$V(R) = \frac{1}{2} k (R - R_e)^2 \quad \text{SHO simple harmonic oscillator potential}$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$V(R) = D_e \left\{ 1 - \exp(-a(R - R_e)) \right\}^2 \quad \text{Morse potential}$$

D_e depth of potential energy

$$a = (\mu / 2D_e)^{1/2} 2\pi \nu$$

Vibrational levels SHO (approximation)

$$E_v = (v + 1/2) h \nu$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Morse potential energy (more exact)

$$E_v = (v + 1/2) h \nu - (v + 1/2)^2 x_e h \nu$$

x_e anharmonicity constant

$$x_e = \frac{\hbar a^2}{4\pi \mu \nu}$$

difference of two levels

Solution to Schrodinger Eq. →

for diff. potential

Vibrational Spectra

Yes heteronuclear

No homonuclear

most have motions which result in change in dipole moment

Specific selection rule $\Delta v = \pm 1$ (for harmonic)

harmonic oscillator $\Delta E_v = h\nu$

anharmonic oscillator $\Delta E_v = h\nu - 2(v+1)x_e h\nu$

$\nu = \frac{1}{\lambda} = \frac{\Delta E_v}{hc}$

$^1\text{H}^{35}\text{Cl}$ $k = 516 \text{ Nm}^{-1}$ $\mu = 1.63 \times 10^{-27} \text{ kg}$ $\nu = 2990 \text{ cm}^{-1}$
Infrared region

room temp $kT \sim 200 \text{ cm}^{-1}$ so most HCl molecules in vibrational ground state $v=0 \rightarrow v=1$

higher transitions or in excited species with emission lines anharmonicity must be considered more than one line observed

Selection rule

$\Delta v = \pm 1$ first harmonic fundamental

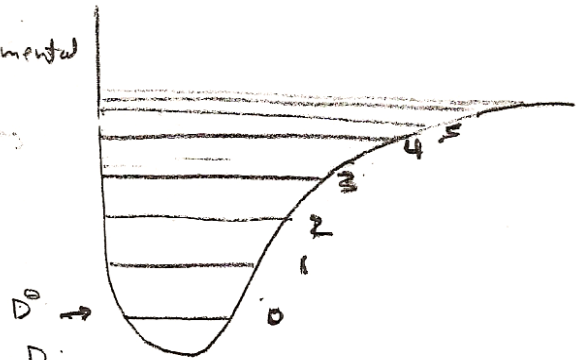
$\Delta v = \pm 2$ second harmonic

find ν and x_e

bond dissociation energy

$D^0 = D_e - \frac{1}{2} h\nu (1 - \frac{x_e}{2})$

$D^0 \approx D_e - \frac{1}{2} h\nu$



can't go to very bottom of well only to level 0

$D_e = D^0 + \frac{1}{2} h\nu$

depth of well

energy step to first level
bond dissociation energy