

Rovibrational Spectroscopy

Tuesday, March 15, 2016 11:03 AM

Vibrational Spectroscopy

Vibrations of Diatomics

$$H = T_N + T_e + V_{nn} + V_{ne} + V_{ee}$$

In the Born oppenheimer approximation

$$T_n \cong 0$$

$$V_{nn} \cong \text{constant}$$

$$\hat{H} = T_E + V_{ee} + V_{en}$$



$$H_{el}\psi_i(r, R) = E_i(R)\psi(r, R)$$

$\psi_i = i^{th}$ electronic eigen state w nuclei R

$$H_n = T_n + V_i(R)$$

$V_i(R)$ is the effective potential between the two nuclei

$$V_i(R) = E_i(R) + V_{nn} = E_i(|R|) + \frac{ke^2Z_1Z_2}{R}, \quad k = \frac{1}{4\pi\epsilon_0}$$

The T_n term contains the rotational KE included

Schrodinger Equation for nuclei

$$H_n\psi_{(rot)}^{(vib)} = E_{vr}\psi_{vr}$$

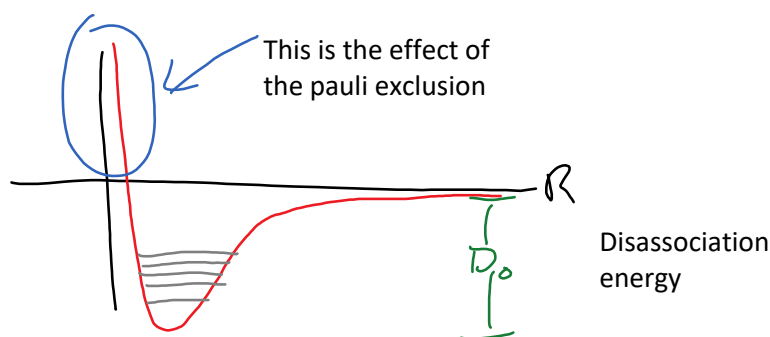
$$\psi_{(rot)}^{(vib)} = \psi_{vib} \times \psi_{rot}$$

$$\psi_{rot} = Y_{JM}(\theta, \phi)$$

$$\psi_{vib} = \chi_v^i(R)$$

Total vibronic wave function

$$\Phi(r, R) = \psi(r, R)\chi_v^i(R)$$



To find $V_i(R)$ —need detailed quantum chemical calculation

e.g. C_2 molecule

A reasonable mathematical form to represent the potential is the **Morse Potential**

A Morse potential

$$V_{morse}(R) = D_e[e^{-2\beta q} - 2e^{-\beta q}]$$

Where $q = R - R_e$

—pure phenomenology depth of well

$$q = 0, \rightarrow V_m = -D_e$$

$$q \rightarrow \infty \rightarrow V_m = 0$$

Harmonic Approximation

Take a Taylor series expansion of $V_i(R)$ close to its minimum at $R = R_e$

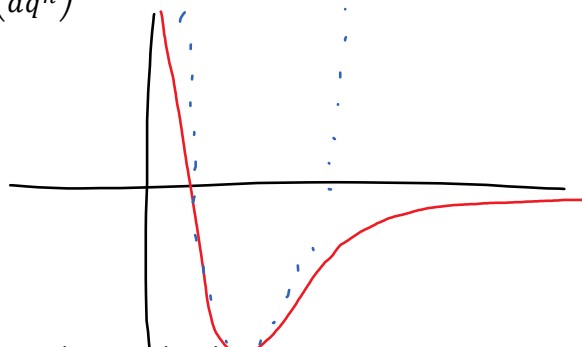
$$V(q) = V(0) + \left(\frac{dV}{dq}\right)_{q=0} q + \frac{1}{2} \left(\frac{d^2V}{dq^2}\right)_{q=0} q^2 + \dots + \frac{1}{n} \left(\frac{d^n V}{dq^n}\right) q^n$$

$$\frac{d^2V}{dq^2} = \text{curvature of potential at } q = 0$$

Harmonic approximation: truncate after q^2

$$V(q) \cong \text{constant} + \frac{1}{2} \left(\frac{d^2V}{dq^2}\right)_{q=0} q^2 = V_o + \frac{1}{2} k q^2$$

$V(q)$ = a parabola like a spring



The blue curve is the harmonic approximation

The harmonic approximation is accurate for low vibrational energy levels

$$\begin{aligned} \frac{dV}{dq} &= D_e [-2\beta e^{-2\beta q} + 2\beta e^{-\beta q}] \\ &= 2\beta D_e [e^{-\beta q} - e^{-2\beta q}] \end{aligned}$$

$$\left(\frac{dV}{dq}\right)_{q=0} = 0 = 2\beta D_e [e^{-\beta q} - e^{-2\beta q}] = 1 - 1 = 0$$

$$\begin{aligned} \frac{d^2V}{dq^2} &= 2\beta D_e [-\beta e^{-\beta q} + 2\beta e^{-2\beta q}] \\ &= 2\beta^2 D_e [2e^{-2\beta q} - e^{-\beta q}] \end{aligned}$$