Wavefunctions of the Harmonic Oscillator

The Schrödinger equation for the harmonic oscillator can be solved analytically. Derivations are found in many quantum mechanical textbooks.

$$V(r) = \frac{1}{2} \cdot k \cdot (r - r_e)^2 \qquad \text{Harmonic Oscillator Potential}$$

$V(r)$ qualitatively reproduces the potential energy surface (PES) for diatomics near r_e but fails to account for strong internuclear repulsion at $r < r_e$, and dissociation at $r > r_e$.

Solution of the Schrödinger equation leads to an expression for the wavefunction, Ψ,

$$\Psi(\alpha, v, x) := \sqrt{\frac{1}{2^v \cdot v!} \cdot \sqrt{\frac{\alpha}{\pi}}} \cdot \text{Her}(v, \sqrt{\alpha} \cdot x) \cdot e^{-\frac{\alpha \cdot x^2}{2}}$$

and vibrational energy levels

$$E_v = \omega_e \cdot \left(v + \frac{1}{2}\right)$$

ω_e is the harmonic constant and related to k, α is molecular constant, v is the vibrational quantum number, and x is the displacement from equilibrium ($x = r - r_e$).

$$\omega_e = \sqrt{\frac{k}{\mu}} \qquad\qquad \alpha = \frac{\mu \cdot \omega_e}{h\_} \qquad\qquad \omega_e = 2 \cdot \pi \cdot \nu$$

As simple as these equations are, units are annoying. As an ardent supporter of the inclusion of units, I must comment that, without proper units, the results will be seriously in err with little evidence thereof. The desired units in these calculations are: cm^{-1} for energy and Å for distance. 'c' and 'h' convert from SI units.

Molecular and Spectroscopic Parameters

$$mass_1 := 102.9 \cdot \frac{gm}{mol} \qquad mass_2 := 16 \cdot \frac{gm}{mol}$$

weights of the atoms or *effective* masses in DIM approximation

$$\mu := \frac{mass_1 \cdot mass_2}{mass_1 + mass_2} \qquad \mu = 13.847 \frac{gm}{mol}$$

reduced mass

Lower State   Upper State

$$r_{e.GS} := 1.717 \cdot \text{Å} \qquad r_{e.XS} := 1.795 \cdot \text{Å}$$

equilibrium bond length

$$\omega_{e.GS} := 805.4 \cdot cm^{-1} \qquad \omega_{e.XS} := 793 \cdot cm^{-1}$$

harmonic constant

$$vibs_{max.GS} := 4 \qquad vibs_{max.XS} := 4$$

maximum vibrational quanta to consider

Range & Graphing Parameters

$$r_{min} := 1.0 \cdot \text{Å} \qquad\qquad r_{max} := 2.5 \cdot \text{Å}$$

$$points := 500$$

$$chart_{max} := \left| \begin{array}{l} a_0 \leftarrow \dfrac{1.4}{cm^{-1}} \cdot \left[\omega_{e.GS} \cdot \left(vibs_{max.GS} + 0.5 \right) \right] \\[2em] a_1 \leftarrow \dfrac{1.4}{cm^{-1}} \cdot \left[\omega_{e.XS} \cdot \left(vibs_{max.XS} + 0.5 \right) \right] \\[1.5em] max(a) \end{array} \right.$$

$$t := 0 \, .. \, chart_{max}$$

Electronic Potential, Wavefunctions, and Energies

Ψ has the following column structure:

x axis | electronic PES | v=0 wavefunction | v=1 | v=2 ...

/Å /cm^{-1} /Å$^{0.5}$ ... ...

$$\Psi_{gen}(\omega_e, r_e, vibs) := \left| \begin{array}{l} \alpha \leftarrow \dfrac{\mu \cdot \omega_e}{h\_} \cdot c \\[3mm] k \leftarrow \mu \cdot \omega_e^{\,2} \cdot \dfrac{c}{h} \\[3mm] \text{for } i \in 0\,..\,\text{points} - 1 \\[2mm] \quad \left| \begin{array}{l} r_i \leftarrow r_{min} + \dfrac{(r_{max} - r_{min})}{\text{points} - 1} \cdot i \\[3mm] V_i \leftarrow 2 \cdot \pi \cdot \dfrac{k}{2} \cdot (r_i - r_e)^2 \end{array} \right. \\[5mm] \text{temp} \leftarrow \dfrac{r}{\text{Å}} \\[3mm] \text{temp} \leftarrow \text{augment}\left(\text{temp}, \dfrac{V}{cm^{-1}}\right) \\[4mm] \text{for } i \in 0\,..\,vibs \\[2mm] \quad \left| \begin{array}{l} \text{for } j \in 0\,..\,\text{points} - 1 \\[2mm] \quad \Psi_{temp_j} \leftarrow \Psi(\alpha, i, r_j - r_e) \cdot \sqrt{\text{Å}} \\[2mm] \text{temp} \leftarrow \text{augment}(\text{temp}, \Psi_{temp}) \end{array} \right. \\[4mm] \text{temp} \end{array} \right.$$

constants

generates the x-range at regular intervals

generates the PES

generates the vibrational wavefunctions for each vibrational level

$$\Psi_{GS} := \Psi_{gen}(\omega_{e.GS}, r_{e.GS}, vibs_{max.GS})$$

$$\Psi_{XS} := \Psi_{gen}(\omega_{e.XS}, r_{e.XS}, vibs_{max.XS})$$

generates the PESs for the lower and upper states

$$E_{gen}(\omega_e, \Psi, vibs) := \begin{vmatrix} temp \leftarrow submatrix(\Psi, 0, points - 1, 2, vibs + 2) \cdot 200 \\ for \quad i \in 0 .. vibs \\ \quad \begin{vmatrix} E_i \leftarrow \omega_e \cdot (i + 0.5) \\ temp^{\langle i \rangle} \leftarrow temp^{\langle i \rangle} + \dfrac{E_i}{cm^{-1}} \end{vmatrix} \\ temp \end{vmatrix}$$

adds energy to the vibrational wavefunctions to separate when displaying

$$E_{GS} := E_{gen}(\omega_{e.GS}, \Psi_{GS}, vibs_{max.GS})$$

$$E_{XS} := E_{gen}(\omega_{e.XS}, \Psi_{XS}, vibs_{max.XS})$$

Harmonic Oscillator Wavefunctions

Vibrational Wavefunctions of the Harmonic Oscillator.mcd

© Roy Jensen
09 12 02
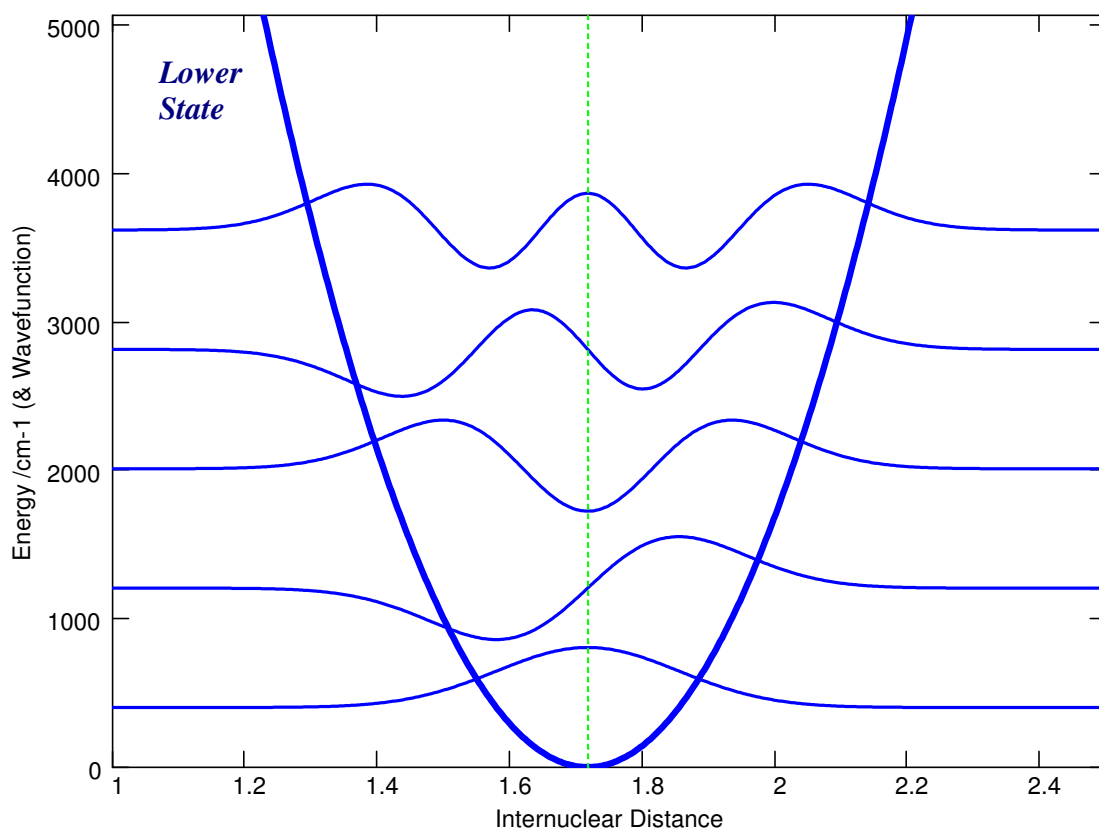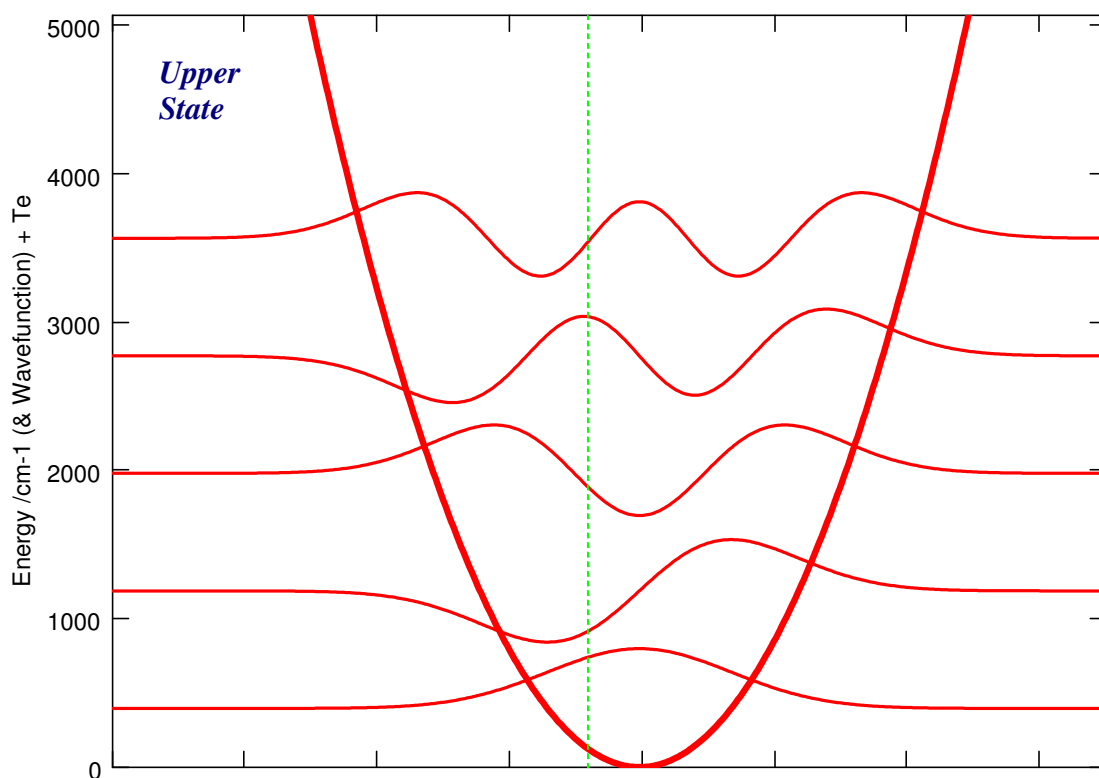
Franck-Condon Factor (overlap of wavefunctions)

$$\Delta x := \Psi GS_{1,0} - \Psi GS_{0,0}$$

$$
S := \left|
\begin{array}{l}
\text{for } i \in 0 \,..\, \text{vibs}_{max.GS} \\
\quad \text{for } j \in 0 \,..\, \text{vibs}_{max.XS} \\
\qquad S_{i,j} \leftarrow \left| \displaystyle\sum_{k=0}^{points-1} \Psi GS_{k,\,i+2} \cdot \Psi XS_{k,\,j+2} \cdot \Delta x \right| \\
S
\end{array}
\right.
$$

$$
\begin{array}{c}
v' \lozenge \\
v'' \\
\circledR
\end{array}
\quad S =
\begin{pmatrix}
0.924 & 0.370 & 0.100 & 0.021 & 0.003 \\
0.367 & 0.777 & 0.483 & 0.164 & 0.040 \\
0.108 & 0.475 & 0.642 & 0.546 & 0.221 \\
0.027 & 0.176 & 0.532 & 0.518 & 0.580 \\
0.006 & 0.052 & 0.235 & 0.560 & 0.404
\end{pmatrix}
$$