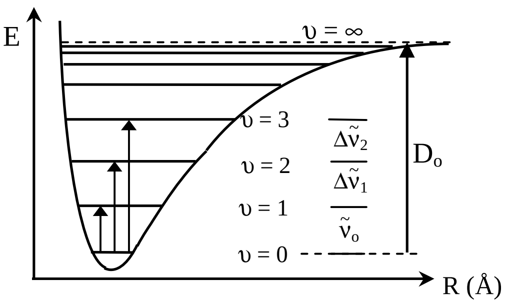
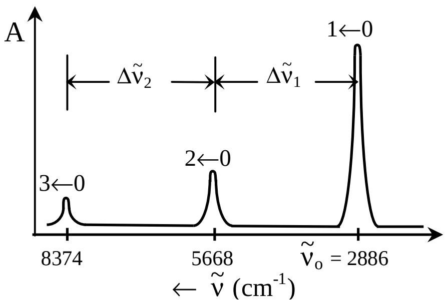
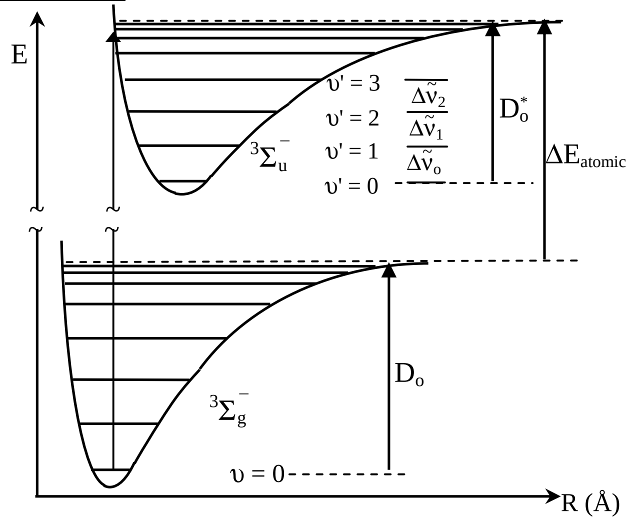
D_o : Birge-Sponer Extrapolation

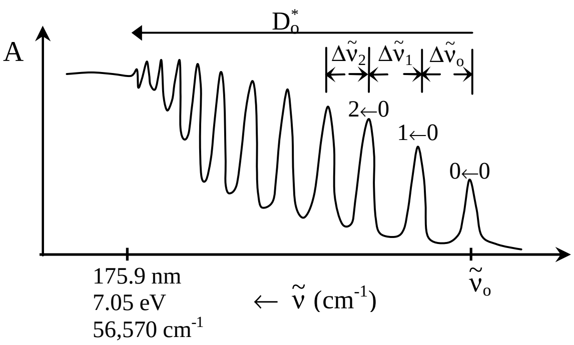
Vibrational





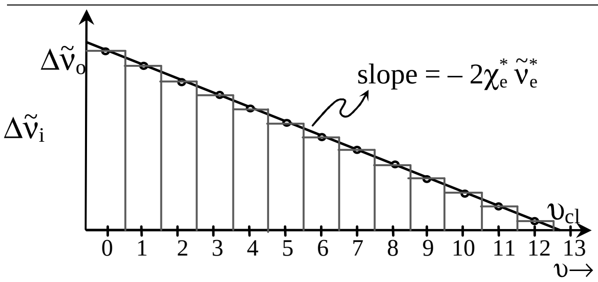
Electronic





$$D_o = \tilde{\nu}_o + \sum_{i=1}^{\infty} \Delta\tilde{\nu}_i$$

$$D_o + \Delta E_{atomic} = \tilde{\nu}_o + \sum_{i=0}^{\infty} \Delta\tilde{\nu}_i$$



width of each rectangle = 1

height of each rectangle = $\Delta\tilde{\nu}_i$

area of each rectangle = $\Delta\tilde{\nu}_i$

area = ½ base height

$D_o = \tilde{\nu}_o$ + area area = ½ $\Delta\tilde{\nu}_1\ \upsilon_{cl}$ $D_o + \Delta E_{atomic} = \tilde{\nu}_o$ + area area = ½ $\Delta\tilde{\nu}_o\ \upsilon_{cl}$

$E^*_\upsilon - E_o = E^* + h\nu^*_e (\upsilon + ½) - \chi^*_e h\nu^*_e (\upsilon + ½)^2 - E_o$ E^* = electronic energy of excited state

$$\Delta E = E^*_{\upsilon+1} - E^*_\upsilon = h\nu^*_e(\upsilon + 1 + ½) - \chi^*_e h\nu^*_e (\upsilon + 1 + ½)^2 - h\nu^*_e(\upsilon + ½) + \chi^*_e h\nu^*_e (\upsilon + ½)^2$$

$$\Delta E = h\nu^*_e - \chi^*_e h\nu^*_e [(\upsilon + ½) +1)]^2 + \chi^*_e h\nu^*_e (\upsilon + ½)^2$$

$$\Delta E = h\nu^*_e - \chi^*_e h\nu^*_e [(\upsilon + ½)^2 + 2(\upsilon + ½) +1)] + \chi^*_e h\nu^*_e (\upsilon + ½)^2 = h\nu^*_e - \chi^*_e h\nu^*_e (2\upsilon + 2)$$

$$\Delta\tilde{\nu}_i = \frac{\Delta E}{hc} = \tilde{\nu}^*_e - \chi^*_e \tilde{\nu}^*_e (2\upsilon + 2)$$

$$\Delta\tilde{\nu}_i = (\tilde{\nu}^*_e - 2\chi^*_e \tilde{\nu}^*_e) - 2\chi^*_e \tilde{\nu}^*_e\, \upsilon$$