How to obtain molecular constants from spectroscopic constants

(1) *If B_e is given in cm^{-1} and masses in amu, how to find the R_e in Å ?*

$$E_{rot} = B_e J(J+1) \quad \text{where } B_e = \frac{\hbar^2}{2\mu R_e^2}$$

$$hcB_e = \frac{\hbar^2}{2} \bullet \frac{1}{\mu R_e^2}$$

$$\underset{cm^{-1}}{B_e} = \frac{h}{8\pi^2 c} \bullet \underset{amu\ Å^2}{\frac{1}{\mu R_e^2}}$$

$$\frac{h}{8\pi^2 c} = \frac{6.62618\text{x}10^{-34}\ J\ s}{8\pi^2 \text{ x } 3 \text{ x}10^8\ ms^{-1}} \bullet \frac{m^2\ kg\ s^{-2}}{J} \bullet \left[\frac{10^{10}\ Å}{1\ m}\right]^2$$

$$\bullet \frac{6.0224\text{x}10^{23}\ amu}{1\ g} \bullet \frac{10^3\ g}{1\ kg} \bullet \frac{1\ m}{10^2\ cm}$$

$$\frac{h}{8\pi^2 c} = 16.846 \text{ amu Å}^2\ cm^{-1}$$

$$\underset{cm^{-1}}{B_e} = (16.846 \text{ amu Å}^2\ cm^{-1}) \bullet \underset{amu\ Å^2}{\frac{1}{\mu R_e^2}}$$

(2) *If vibrational frequency ν_e and the U(R) potential energy function are given in cm^{-1} and masses in amu, how to find the second derivative of U(R) at the equilibrium bond length in units of cm^{-1} $Å^{-2}$?*

$$hc\nu_e = (h/2\pi)\ [\ U''(R_e) / \mu\ ]^{1/2}$$

$$U''(R_e) = \left[\frac{\partial^2 U(R)}{\partial R^2}\right]_{R_e} = 4\pi^2\mu c^2 \nu_e^2 \qquad \text{U(R) in joule per molecule}$$

$$\underset{J\ Å^{-2}}{U''(R_e)} = \underset{amu\ (cm^{-1})^2}{4\pi^2\mu\nu_e^2} \bullet (3\text{x}10^8\ m\ s^{-1})^2 \bullet \frac{1\ kg}{6.022\text{x}10^{26}\ amu} \bullet \left[\frac{1\ cm}{10^8\ Å}\right]^2$$

If U(R) is in cm^{-1}, then we want U"(R_e) in units of cm^{-1} $Å^{-2}$. To get this,

$$\underset{cm^{-1}\,Å^{-2}}{U''(R_e)} = \frac{4\pi^2\mu\nu_e^2}{hc}$$

$$= \frac{4\pi^2\mu\nu_e^2}{amu\ cm^{-1}} \bullet (3\times10^8\ m\ s^{-1})^2 \bullet \frac{1\ kg}{6.022\times10^{26}\ amu} \bullet \left[\frac{1\ cm}{10^8\ Å}\right]^2 \bullet \frac{1}{6.62618\times10^{-34}\ J\ s\ \times 3\times10^{10}\ cm\ s^{-1}} \bullet \frac{1\ J}{m^2\ kg\ s^{-2}}$$

$$\underset{cm^{-1}\,Å^{-2}}{U''(R_e)} = (0.029681\ amu^{-1}\ cm\ Å^{-2}) \bullet \underset{amu}{\mu}\ \underset{(cm^{-1})^2}{(\nu_e)^2}$$

(3) *If the vibrational-rotational coupling constant frequency α_e is given in cm^{-1} and masses in amu, how to find the third derivative of U(R) at the equilibrium bond length in units of cm^{-1} $Å^{-3}$?*

$$\alpha_e = -\frac{2B_e^2}{h\nu_e} \bullet \left[3 + \frac{2B_e\ U'''(R_e)\ R_e^3}{(h\nu_e)^2}\right]$$

Rearrange to find

$$\underset{cm^{-1}\,Å^{-3}}{U'''(R_e)} = \left[\frac{\partial^3 U(R)}{\partial R^3}\right]_{R_e} = \underset{\text{dimensionless}}{\left[-\frac{\alpha_e\nu_e}{2B_e^2} - 3\right]} \bullet \underset{\text{dimensionless}}{\left[\frac{\nu_e}{2B_e}\right]} \bullet \underset{cm^{-1}\,Å^{-3}}{\left[\frac{\nu_e}{R_e^3}\right]}$$

Some conversion factors

$$\underset{\text{J per molecule}}{\Delta E} = h\nu = 6.62618\times10^{-34}\ J\ s \bullet \underset{s^{-1}\text{ or Hz}}{\nu}$$

$$\underset{\text{J per molecule}}{\Delta E} = 6.62618\times10^{-34}\ J\ s \bullet \frac{s^{-1}}{Hz} \bullet \frac{10^6\ Hz}{1\ MHz} \bullet \underset{MHz}{\nu}$$

$$\underset{\text{J per molecule}}{\Delta E} = hc(1/\lambda) = 6.62618\times10^{-34}\ J\ s \bullet 3\times10^8\ m\ s^{-1} \bullet \frac{10^2\ cm}{1\ m} \bullet \underset{cm^{-1}}{(1/\lambda)}$$

1 eV = 8065.46 cm^{-1} 1 eV per molecule = 96, 485 J mol^{-1}