P8.13
A strong absorption band in the infrared region of the electromagnetic spectrum is observed at $\tilde{v} = 2170$ cm^{-1} for $^{12}C^{16}O$. Assuming that the harmonic potential applies, calculate the fundamental frequency v in units of inverse seconds, the vibrational period in seconds, and the zero point energy for the molecule in joules and electron-volts.

$$v = \tilde{v}c = 2170\,cm^{-1} \times 3.00 \times 10^{10}\,cm\,s^{-1} = 6.51 \times 10^{13}\,s^{-1}$$

$$T = \frac{1}{v} = \frac{1}{6.51 \times 10^{13}\,s^{-1}} = 1.54 \times 10^{-14}\,s$$

$$E = \frac{1}{2}hv = \frac{1}{2} \times 6.626 \times 10^{-34}\,Js \times 6.51 \times 10^{13}\,s^{-1} = 2.16 \times 10^{-20}\,J \times \frac{6.241 \times 10^{18}\,eV}{J} = 0.134\,eV$$

P8.7
A measurement of the vibrational energy levels of $^{12}C^{16}O$ gives the relationship

$$\tilde{v}(n) = 2170.21\left(n + \frac{1}{2}\right)\,cm^{-1} - 13.461\left(n + \frac{1}{2}\right)^2\,cm^{-1}$$ where n is the vibrational quantum number. The fundamental vibrational frequency is $\tilde{v}_0 = 2170.21$ cm^{-1}. From these data, calculate the depth D_e of the Morse potential for $^{12}C^{16}O$. Calculate the bond energy of the molecule.

We convert the expression to one in terms of energy

$$E(n) = 2170.21 \times hc\left(n + \frac{1}{2}\right) - 13.461 \times hc\left(n + \frac{1}{2}\right)^2$$

and compare it with Equation (19.5) for the Morse potential.

$$E_n = hv\left(n + \frac{1}{2}\right) - \frac{(hv)^2}{4D_e}\left(n + \frac{1}{2}\right)^2$$

from which we see that

$$13.461 \times hc = \frac{(hv)^2}{4D_e}$$

$$D_e = \frac{hv^2}{4 \times 13.461 \times c} = \frac{hc\tilde{v}^2}{4 \times 13.461}$$

$$= \frac{6.626 \times 10^{-34}\,J\,s \times 2.998 \times 10^{10}\,cm\,s^{-1} \times (2170\,cm^{-1})^2}{4 \times 13.461} = 1.738 \times 10^{-18}\,J$$

$$D_0 = D_e - \frac{1}{2}hc\tilde{v}_0 = 1.738 \times 10^{-18}\,J - \frac{1}{2} \times 6.626 \times 10^{-34}\,J\,s \times 2.998 \times 10^{10}\,cm\,s^{-1} \times 2170\,cm^{-1}$$

$$= 1.717 \times 10^{-18}\,J$$

The bond energy per mole is $D_0 N_A = 1.034 \times 10^3$ kJ mol^{-1}.

P8.16
Calculate the moment of inertia, the magnitude of the rotational angular momentum, and the energy in the $J = 1$ rotational state for $^1H_2$ in which the bond length of $^1H_2$ is 74.6 pm. The atomic mass of ^1H is 1.007825 amu.

9. $I = \mu r_0^2 = \dfrac{1.007825^2 \text{ amu}}{2 \times 1.007825} \times 1.6605402 \times 10^{-27} \text{ kg amu}^{-1} \times \left(74.6 \times 10^{-12} \text{ m}\right)^2$

$= 4.657 \times 10^{-48} \text{ kg m}^2$

$|J| = \sqrt{J(J+1)}\hbar = \sqrt{2} \times 1.0554 \times 10^{-34} \text{ J s} = 1.4914 \times 10^{-34} \text{ J s}$

$\qquad = 1.49 \times 10^{-34} \text{ kg m s}^{-2}$

$E_J = \dfrac{J(J+1)\hbar^2}{2I} = \dfrac{2 \times \left(1.0554 \times 10^{-34} \text{ J s}\right)^2}{2 \times 4.657 \times 10^{-48} \text{ kg m}^2} = 2.39 \times 10^{-21} \text{ J}$

(0) i) For ICN N=#atoms=3, and, since it is a linear molecule n_v =# vibrational degrees of freedom (normal modes of vibration)= 3N-5 = 4.

ii) For CH$_4$, N=5, and, since it is a nonlinear molecule, n_v = 3N-6 = 9.

(1) From class notes, we know: $\vec{x}_1 = \vec{X} - \dfrac{m_2}{M}\vec{r}$, $\vec{x}_2 = \vec{X} + \dfrac{m_1}{M}\vec{r}$. Thus:

$$T = \frac{1}{2}m_1\dot{\vec{x}}_1^2 + \frac{1}{2}m_2\dot{\vec{x}}_2^2$$

$$= \frac{1}{2}m_1\left(\dot{\vec{X}} - \frac{m_2}{M}\dot{\vec{r}}\right)^2 + \frac{1}{2}m_2\left(\dot{\vec{X}} + \frac{m_1}{M}\dot{\vec{r}}\right)^2$$

$$= \frac{1}{2}m_1\left(\dot{\vec{X}}^2 - \frac{2m_2}{M}\dot{\vec{r}}\cdot\dot{\vec{X}} + \frac{m_2^2}{M^2}\dot{\vec{r}}^2\right) + \frac{1}{2}m_2\left(\dot{\vec{X}}^2 + \frac{2m_1}{M}\dot{\vec{r}}\cdot\dot{\vec{X}} + \frac{m_1^2}{M^2}\dot{\vec{r}}^2\right)$$

$$= \frac{1}{2}M\dot{\vec{X}}^2 + \frac{1}{2}\mu\dot{\vec{r}}^2 \quad, \text{QED.}$$

Note: Here $\vec{a}\cdot\vec{b}$ is the dot product between two 3D vectors $\vec{a},\vec{b}$, and $\vec{a}^2 = \vec{a}\cdot\vec{a}$.

(2) a). Assume the desired energy eigenfunction can be written in the product form $\psi(r,\theta,\phi) = R_l(r)Y_{lm}(\theta,\phi)$ where Y_{lm} is the standard spherical harmonic function, and $R_l(r)$ is a radial function to be determined. [Note: We anticipate that it will depend on the value of l in the companion spherical harmonic.]

Note the following useful version of the 3D Laplacian operator:

$$\nabla^2 = \frac{1}{r}\frac{\partial^2(r\quad)}{\partial r^2} + \frac{\hat{\Lambda}^2}{r^2} \quad,$$

where the "Legendrian"

$$\hat{\Lambda}^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

operates (obviously) on the angles (θ,ϕ). Substituting all this into the Schrödinger Eq.:

$$\left[\frac{-\hbar^2}{2\mu}\left\{\frac{1}{r}\frac{\partial^2(r\quad)}{\partial r^2}+\frac{\hat{\Lambda}^2}{r^2}\right\}+v(r)\right]R_l(r)Y_{lm}(\theta,\phi)=ER_l(r)Y_{lm}(\theta,\phi)\quad\text{[A1]}$$

Now, using the fact that the spherical harmonics are eigenfunction of the Legendrian, namely $\hat{\Lambda}^2 Y_{lm}(\theta,\phi)=-l(l+1)Y_{lm}(\theta,\phi)$, Eq. A1 implies the radial wave equation:

$$\frac{-\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2(rR_l(r))}{\partial r^2}+\left(v(r)+\frac{\hbar^2 l(l+1)}{2\mu r^2}\right)R_l(r)=ER_l(r)$$

Finally, defining the reduced radial wavefunction $\chi_l(r)$ according to $rR_l(r)=\chi_l(r)$, we obtain a "standard" 1D Schrödinger Eq. for the reduced radial wave function:

$$\frac{-\hbar^2}{2\mu}\frac{\partial^2\chi_l(r)}{\partial r^2}+v_l^{eff}(r)\chi_l(r)=E\chi_l(r),$$

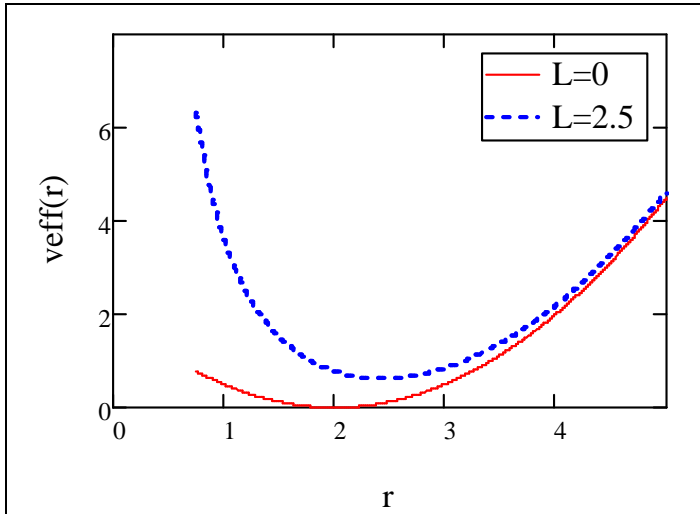with the effective radial potential $v_l^{eff}(r)\equiv v(r)+\dfrac{\hbar^2 l(l+1)}{2\mu r^2}$, QED.

Fig A1. $v_l^{eff}(r)\equiv v(r)+\dfrac{L^2}{2\mu r^2}$ vs r, (with the harmonic oscillator form of $v(r)$ stated above). Parameters are: $\kappa=\mu=1, r_e=2$.

b) Adding the repulsive "centrifugal" potential term $\dfrac{\hbar^2 l(l+1)}{2\mu r^2}$ to $v(r) = \dfrac{1}{2}\kappa(r - r_{eq})^2$ pushes the equilibrium position of the potential well $v_l^{eff}(r)$ out to a larger value; cf. Fig. A1. Thus, increasing l *increases* the equilibrium separation of the two particles in the diatomic.