22.4.3: iii. Exercise Solutions

Q1

a. CCl_4 is tetrahedral and therefore is a spherical top. $CHCl_3$ has C_{3v} symmetry and therefore is a symmetric top. CH_2Cl_2 has C_{2v} symmetry and therefore is an asymmetric top.
b. CCl_4 has such high symmetry that it will not exhibit pure rotational spectra. $CHCl_3$ and CH_2Cl_2 will both exhibit pure rotation spectra.
c. NH_3 is a symmetric top (oblate). Use the given energy expression,|

$$E = (A-B)K^2 + BJ(J+1),$$

A = 6.20 cm^{-1}, B = 9.44cm^{-1}, selection rules $\Delta J = \pm 1$, and the fact that $\vec{\mu_0}$ lies along the figure axis such that $\Delta K = 0$, to give:

$$\Delta E = 2B(J+1) = 2B, 4B, \text{and } 6B(J = 0, 1, \text{and } 2).$$

So, lines are at 18.88cm^{-1}, 37.76cm^{-1}. and 56.64cm^{-1}.

Q2

To convert between cm^{-1} and energy, multiply by hc = $6.62618x10^{-34}$ J sec $)(2.997925x10^{10}$ cm sec$^{-1}) = 1.9865x10^{23}$ J cm
Let all quantities in cm^{-1} be designated with a bar,
e.g. $\bar{B}_e$ = 1.78cm^{-1}.
a.

$$\begin{aligned}
hc\bar{B}_e &= \frac{\hbar^2}{2\mu R_e^2} && (22.4.3.1)\\
R_e &= \frac{\hbar}{\sqrt{2\mu hc\bar{B}_e}}, && (22.4.3.2)\\
\mu &= \frac{m_B m_O}{m_B+m_O} = \frac{(11)(16)}{(11+16)} x 1.66056x10^{-27}\text{kg} && (22.4.3.3)\\
&= 1.0824x10^{26}\text{kg} && (22.4.3.4)\\
hc\bar{B}_e &= hc(1.78\text{cm}^{-1} = 3.5359x10^{-23}\text{J} && (22.4.3.5)\\
R_e &= \frac{1.05459x10^{-34}\text{J sec}}{\sqrt{(2)1.0824x10^{-26}\text{kg}.3.35359x10^{-23}\text{ J}}} && (22.4.3.6)\\
R_e &= 1.205x10^{-10}\text{m} = 1.205\text{Å} && (22.4.3.7)\\
D_e &= \frac{4B_e^3}{\hbar\omega_e^2}, \bar{D}_e = \frac{4\bar{B_e}^3}{\bar{\omega_e}^2} = \frac{(4)(1.78\text{cm}^{-1})^3}{(4)(66782.2\text{cm}^{-1})} = 6.35x10^{-6}\text{cm}^{-1} && (22.4.3.8)\\
\omega_e x_e &= \frac{\hbar\omega_e^2}{4D_e^0}, \omega_e\bar{x}_e = \frac{\bar{\omega_e^2}}{4\bar{D_e^0}} = \frac{(1885\text{cm}^{-1})^2}{(4)(66782.2\text{cm}^{-1})} = 13.30\text{cm}^{-1}. && (22.4.3.9)\\
D_0^0 &= D_e^0 - \frac{\hbar\omega_e}{2} + \frac{\hbar\omega_e x_e}{4}, \bar{D_0^0} = \bar{D_e^0} - \frac{\bar{\omega_e}}{2} + \frac{\omega_e\bar{x}_e}{4} && (22.4.3.10)\\
&= 66782.2 - \frac{1885}{2} + \frac{13.3}{4} && (22.4.3.11)\\
&= 65843.0\text{cm}^{-1} = 8.16eV. && (22.4.3.12)\\
\alpha_e &= \frac{-6B_e^2}{\hbar\omega_e} + \frac{6\sqrt{B_e^3\hbar\omega_e x_e}}{\hbar\omega_e} && (22.4.3.13)\\
\bar{\alpha_e} &= \frac{-6\bar{B_e^2}}{\bar{\omega_e}} + \frac{6\sqrt{\bar{B_e^3}\omega_e\bar{x}_e}}{\bar{\omega_e}} && (22.4.3.14)\\
\bar{\alpha_e} &= \frac{(-6)(1.78)^2}{(1885)} + \frac{6\sqrt{(1.78)^3(13.3)}}{(1885)} = 0.0175\text{cm}^{-1}. && (22.4.3.15)\\
B_0 &= B_e - \alpha_e\left(\frac{1}{2}\right), \bar{B}_0 = \bar{B}_e - \bar{\alpha_e}\left(\frac{1}{2}\right) = 1.78 - \frac{0.0175}{2} && (22.4.3.16)\\
&= 1.77\text{cm}^{-1} && (22.4.3.17)\\
B_1 &= B_e - \alpha_e\left(\frac{3}{2}\right), \bar{B}_1 = \bar{B}_e - \bar{\alpha_e}\left(\frac{3}{2}\right) = 1.78 - 0.0175(1.5) && (22.4.3.18)\\
&= 1.75\text{cm}^{-1} && (22.4.3.19)
\end{aligned}$$

b. The molecule has a dipole moment and so it should have a pure rotational spectrum. In addition, the dipole moment should change with R and so it should have a vibration rotation spectrum.
The first three lines correspond to J $= 1 \rightarrow 0, J = 2 \rightarrow 1, J = 3 \rightarrow 2$

$$\begin{aligned}
E &= \hbar\omega_e\left(v+\frac{1}{2}\right) - \hbar\omega_e x_e\left(v+\frac{1}{2}\right)^2 + B_v J(J+1) - D_e J^2(J+1)^2 && (22.4.3.20)\\
\Delta E &= \hbar\omega_e - 2\hbar\omega_e x_e - B_0 J)J+1) + B_1 J(J-1) - 4D_e J^3 && (22.4.3.21)\\
\Delta\bar{E} &= \bar{\omega_e} - 2\omega_e\bar{x}_e - \bar{B}_0 J(J=1) + \bar{B}_1 J(J-1) - 4\bar{D}_e J^3 && (22.4.3.22)\\
\Delta\bar{E} &= 1885 - 2(13.3) - 1.77J(J+1) + 1.75J(J-1) - 4(6.35x10^{-6})J^3 && (22.4.3.23)\\
&= 1858.4 - 1.77J(J+1) + 1.75J(J-1) - 2.54x10^{-5}J^3 && (22.4.3.24)\\
\Delta\bar{E}(J=1) &= 1854.9\text{cm}^{-1} && (22.4.3.25)\\
\Delta\bar{E}(J=2) &= 1851.3\text{cm}^{-1} && (22.4.3.26)\\
\Delta\bar{E}(J=3) &= 1847.7\text{cm}^{-1} && (22.4.3.27)
\end{aligned}$$

Q3

The $C_2H_2Cl_2$ molecule has a σ_h plane of symmetry (plane of molecule) a C_2 axis ($\perp$ to plane), and inversion symmetry, this result in C_{2h} symmetry. Using C_{2h} symmetry labels the modes can be labeled as follows: $\nu_1, \nu_2, \nu_3, \nu_4$, and ν_5 are a_g, ν_6 and ν_7 are a_u, ν_8 is b_g, and $\nu_9, \nu_{10}, \nu_{11}$, and ν_{12} are b_u.