22.4.1: i. Exercises

Q1

Consider the molecules $CCl_4, CHCl_3,$ and CH_2Cl_2.
a. What kind of rotor are they (symmetric top, ect; do not bother with oblate, or near-prolate, etc.)
b. Will they show pure rotational spectra?
c. Assume that ammonia shows a pure rotational spectrum. If the rotational constrants are 9.44 and 6.20 cm^{-1}, use the energy expression:

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

to calculate the energies (in cm^{-1}) of the first three lines (i.e., those with lowest K, J quantum number for the adsorbing level) in the absorption spectrum (ignoring higher order terms in the energy expression).

Q2

The molecule $^{11}B^{16}O$ has a vibrational frequency $\omega_e = 1885 cm^{-1}$, a rotational constant $B - e = 1,78 cm^{-1}$, and a bond energy from the bottom of the potential well of $D_e^0 = 8.28 eV$.

Use integral atomic masses in the following:
a. In the approximation that the molecule can be represented as a Morse oscillaor, calculate the bond length, R_e in angstroms, the centrifugal distortion constant, D_e in cm^{-1} , the anharmonicity constant, $\omega_e X_e$ in cm^{-1}, the zero-point corrected bond energy, D_0^0 in eV, the vibrational rotation interaction constant, α_e in cm^{-1}, and the vibrational state specific rotation constants, B_0 and B_1 in cm^{-1}. Use the vibration-rotation energy expression for a Morse oscillator:

$$E = \hbar\omega_e\left(v + \frac{1}{2}\right) - \hbar\omega_e X_e\left(v = \frac{1}{2}\right)^2 + B_v J(J+1) - D_e J^2(J+1)^2, \text{ where} \tag{22.4.1.1}$$

$$B_v = B_e - \alpha_e\left(v + \frac{1}{2}\right), \alpha_e = \frac{-6B_e^2}{\hbar\omega_e} + \frac{6\sqrt{B_e^3\hbar\omega_e X_e}}{\hbar\omega_e}, \text{ and } D_e = \frac{4B_e^3}{\hbar\omega_e^2} \tag{22.4.1.2}$$

b. Will this molecule show a pure rotation spectrum? A vibration-rotation spectrum? Assume that it does, what are the energies $(in cm^{-1})$ of the first three lines in the P branch $(\Delta v = +1, \Delta J = -1)$ of the fundamental absorption?

Q3

Consider trans-$C_2H_2Cl_2$. The vibrational normal modes of this molecule are shown below. What is the symmetry of the molecule? Label each of the modes with the appropriate irreducible representation.