Spectroscopy

Exercises Chapter 2B

1. As we have seen in class a molecule is not strictly a rigid rotor. As the molecule rotates the atoms experience a centrifugal force in the rotating molecular reference frame that changes the internuclear distance. For a diatomic molecule one can obtain an expression for the stretching of the internuclear separation *r* by allowing the bond to stretch from the equilibrium distance r_e to r_c under action of the centrifugal force:

$$F_c = \frac{\mu v^2}{r} = \frac{J^2}{\mu r^3}$$

The centrifugal force is balanced by the restoring force, which we assume to obey Hook's law (harmonic oscillator approximation):

$$F_r = k\left(r_c - r_e\right)$$

Show that total energy of the molecules is given by:

$$E = \frac{J^2}{2\mu r_c^2} - \frac{1}{2}k\left(r_c - r_e\right)^2$$

and gives rise to a centrifugal distortion term of approximately:

$$E_{cd} = -\frac{1}{2\mu^2 r_e^6 k}J^4$$

Show that by replacing J^2 by its quantum mechanical eigenvalue the energy can be written as:

$$E = BJ\left(J+1\right) - DJ^2\left(J+1\right)^2$$

with

$$D = \frac{4B_e^3}{\omega_e^2}$$

Calculate the distortion constant for HCl, given the equilibrium bond length r_e=1.27 Å and the force constant *k*= 478 N/m.

2. Using perturbation theory one can relate the terms $\omega_e x_e$ and α in the expression of the energy of a diatomic molecule to the potential energy.

One finds:

$$\omega_e x_e = \frac{B_e^2 r_e^4}{4h\omega_e^2}\left\{\frac{10B_e r_e^2\left[V_e^{(3)}\right]^2}{3h\omega_e^2} - V_e^{(4)}\right\}$$

and

$$\alpha = -\frac{2B_e^2}{\omega_e}\left\{\frac{2B_e r_e^3 V_e^{(3)}}{h\omega_e^2} + 3\right\}$$

with

$$V_e^{(3)} = \left(\frac{d^3U(r)}{dr^3}\right)_{r_e} \quad \text{and} \quad V_e^{(4)} = \left(\frac{d^4U(r)}{dr^4}\right)_{r_e}$$

For HCl one finds the following molecular constants:

$$\omega_e = 2989.74 \text{ cm}^{-1}$$
$$\omega_e x_e = 52.05 \text{ cm}^{-1}$$
$$B_e = 10.59 \text{ cm}^{-1}$$
$$\alpha = 0.3019 \text{ cm}^{-1}$$

Using this information determine the bond length, the force constant *k*, and the cubic and quadratic force constants $V_e^{(3)}$ and $V_e^{(4)}$.