

HOMEWORK 7

1. The average kinetic energy of a sample of gas molecules is a function of temperature and given by

$$KE = \frac{3k_b T}{2}.$$

Thus, we find that

$$T = \frac{2 \cdot KE}{3k_b}.$$

Plugging in values and setting $KE = 4.7 \text{ eV} = 7.52 \times 10^{-19} \text{ J}$, we have

$$T = 3.63 \times 10^4 \text{ K}.$$

At this temperature, the average kinetic energy of the molecules would exceed the binding energy, and the molecules would dissociate into free H atoms.

2. The zero point energy is given by

$$E_{zp} = \frac{1}{2} h v_0,$$

where

$$v_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}.$$

Since H_2 and HD contain the same atoms, their k should be identical, meaning that only their reduced mass, μ , will be different.

For H_2 , we have

$$\mu_{\text{H}_2} = \frac{m_H \cdot m_H}{m_H + m_H} = \frac{m_H}{2}.$$

For HD, we have

$$\mu_{\text{HD}} = \frac{2m_H \cdot m_H}{2m_H + m_H} = \frac{2m_H}{3}.$$

Thus, we have $\mu_{\text{HD}} > \mu_{\text{H}_2}$, and therefore the zero point energy for H_2 is larger than that for HD.

The dissociation energy is equal to

$$E_d = V_0 - E_{zp},$$

thus, the binding energy for HD is larger than the binding energy for H_2 .

Table 12-1 in E&R confirms these results.

3. (a) We have the equation for inverse wavelength:

$$\frac{1}{\lambda} = \frac{\hbar}{2\pi I c} l.$$

Taking the reciprocal, we have

$$\lambda = \frac{2\pi I c}{\hbar l}.$$

Thus, for $l = 1 \rightarrow l = 2$, we have

$$\lambda = 1.47 \text{ mm}.$$

And for $l = 2 \rightarrow l = 3$, we have

$$\lambda = 0.983 \text{ nm}$$

(b) We have

$$r^2 = \frac{hl}{(2\pi)^2 \mu f} = 1.21 \times 10^{-47} \text{ m}^2,$$

and using the same internuclear distance, r , we have the reduced mass for the different carbon isotope,

$$\mu = \frac{hl}{(2\pi)^2 r^2 f} = 12.56 \text{ amu}.$$

Hence, the mass number for this isotope of carbon is 13.

(c) We have the reduced mass,

$$\mu = \frac{m_C \cdot m_O}{m_C + m_O} = 6.857 \text{ amu} = 1.14 \times 10^{-26} \text{ kg}.$$

For the energy of ground state vibrations, we have

$$E = hf = \frac{1}{2} h v_0$$

where

$$v_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}.$$

Hence, we have

$$k = (4\pi f)^2 \mu = 7.41 \times 10^3 \text{ kg s}^{-2}$$

To find the amplitude, we have

$$\frac{1}{2} k A^2 = \frac{1}{2} h v_0,$$

thus,

$$A = \sqrt{\frac{h}{2\pi k} \sqrt{\frac{k}{\mu}}} = 3.39 \times 10^{-12} \text{ m}.$$

The carbon monoxide bond length is 0.112 nm, thus the amplitude of the ground-state vibrations is around 3.03 % of the bond length.

4. We start with the equation

$$\begin{aligned} \frac{1}{\lambda} &= \frac{\hbar}{2\pi I c} l \\ &= \frac{\hbar}{2\pi c \mu r^2} l \end{aligned}$$

Since we don't know the specific quantum numbers, l , we must instead look at the transitions between these states. Hence, we use the equation

$$\frac{1}{\lambda_1} - \frac{1}{\lambda_2} = \frac{\hbar}{2\pi c \mu r^2} \cdot 1.$$

Plugging in values for the wavelengths, we get the differences

$$1.28 \times 10^{-10} \text{ m}, 1.31 \times 10^{-10} \text{ m}, 1.29 \times 10^{-10} \text{ m and } 1.30 \times 10^{-10} \text{ m}.$$

Taking the average, we have

$$r \approx 1.30 \times 10^{-10} \text{ m}$$

which is close to the actual value of $1.27 \times 10^{-10} \text{ m}$.