Chapter 4 Homework

1. Calculate the scalar product and cross product of the of the two vectors:

$$\vec{A} = 3\vec{i} - \vec{j} + 2\vec{k} \qquad \vec{B} = 2\vec{i} + 4\vec{j} - 3\vec{k}$$

2. Consider a rigid rotor in the state characterized by: $\psi = Ae^{-2i\varphi}\sin^2\theta$

   (a) Verify that ψ is a solution to the Rigid Rotor Schrödinger Equation (below). What is the eigenvalue (i.e. energy)?

   Note: You will probably find it useful to use the trigonometric identity, $\sin^2\theta + \cos^2\theta = 1 \quad \rightarrow \quad \cos^2\theta = 1 - \sin^2\theta$

   (b) Calculate the squared angular momentum, L^2, of the rotor.

   (c) Calculate the z-component of angular momentum, L_z, of the rotor:

3. As discussed in class, the rotational motion of a diatomic molecule chemisorbed on a crystalline surface can be modelled as the rotation of a 2D Rigid Rotor. Consider F_2 adsorbed on a platinum surface. The F_2 bond length is 0.142 nm.

   Calculate the frequency (in cm^{-1}) of the rotational transition of an F_2 molecule from the $m = \pm 2$ level to the $m = \pm 8$ level.

4. The first two lines the rotational Raman spectrum of $H^{79}Br$ are found at 50.2 cm^{-1} and 83.7 cm^{-1}. Calculate the H-Br bond length, in Å.

5. Which of the following molecules will have a rotational microwave absorption spectrum?: H_2O, H-C≡C-H, H-C≡C-Cl, cis-1,2-dichloroethylene, benzene, NH_3.

6. The first microwave absorption line in $^{12}C^{16}O$ occurs at 3.84 cm^{-1}

   (a) Calculate the CO bond length.

   (b) Predict the frequency (in cm^{-1}) of the 7th. line in the microwave spectrum of CO..

   (c) Calculate the ratio of the intensities of the 5th. line to the 2nd line in the spectrum at 25 °C

   (d) Calculate the the initial state (J'') corresponding to the most intense transition in the microwave absorption spectrum of $^{12}C^{16}O$ at 25 °C.

7. The C≡C and C-H bond lengths in the linear molecule, acetylene (H-C≡C-H) are 1.21 Å and 1.05 Å, respectively

(a) What are the frequencies of the first two lines in the rotational Raman spectrum?

(b) What are the frequencies of the first two lines in the rotational Mookster absorption spectrum, for which the selection rule is $\Delta J = +3$?

(c) Calculate the ratio of intensities in the 20th. lowest frequency line to that of the 5th. lowest frequency line in the rotational Raman spectrum at 100 °C.

8. For **two (2)** moles of the non-linear molecule $NO_2(g)$ at 150 °C, calculate the rotational contributions to the internal energy, enthalpy, constant pressure heat capacity, entropy, Helmholtz energy and Gibbs energy. The Moments of Inertia are:
$I_a = 3.07\text{x}10^{-47}$ kg-m^2 , $I_b = 6.20\text{x}10^{-46}$ kg-m^2 , $I_c = 6.50\text{x}10^{-46}$ kg-m^2.
The symmetry number is 2.

9. The molecular rotational partition function of H_2 at 25 °C is $q^{rot} = 1.70$.

(a) What is q^{rot} for D_2 at 25 °C?

(b) What is q^{rot} for H_2 at 3000 °C?

DATA

$h = 6.63\text{x}10^{-34}$ J·s
$\hbar = h/2\pi = 1.05\text{x}10^{-34}$ J·s
$c = 3.00\text{x}10^{8}$ m/s $= 3.00\text{x}10^{10}$ cm/s
$N_A = 6.02\text{x}10^{23}$ mol^{-1}
$k = 1.38\text{x}10^{-23}$ J/K
$R = 8.31$ J/mol-K
$R = 8.31$ Pa-m^3/mol-K
$m_e = 9.11\text{x}10^{-31}$ kg (electron mass)

1 J = 1 kg·m^2/s^2
1 Å = 10^{-10} m
$k \cdot N_A = R$
1 amu = $1.66\text{x}10^{-27}$ kg
1 atm. = $1.013\text{x}10^{5}$ Pa
1 eV = $1.60\text{x}10^{-19}$ J

Rigid Rotor Schrödinger Equation:

$$\frac{\hat{L}^2\psi}{2I} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2(\theta)}\frac{\partial^2\psi}{\partial\varphi^2}\right] = E\psi$$

The L_z Equation:

$$\hat{L}_z\psi = \frac{\hbar}{i}\frac{\partial\psi}{\partial\phi} = m\hbar\psi$$