CHEM304 - HW#2

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1 Graphing Problems: 2-31, 2-32, 2-33, 2-34

I explain my work in detail in various comments, strings, and markdown write-ups throughout my code. I feel as though that would be easily to read and understand for a grader to read than to read summarizes here. The code with documentation for that can be found at the end of this document in the form of a PDF.

2 Schrier problems: C-1, C-2, C-3

C-1: For this question, we must calculate the first five rotational and vibrations states of the molecules H_2. With this, we will use the following two equations:

$$\varepsilon_{rot} = \frac{\hbar^2}{2I}(J+1)(J)$$

$$\varepsilon_{vib} = \frac{h}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}\left(v+\frac{1}{2}\right)$$

Where I is the moment of inertia. We are also given the following constants vibrational and rotational constants respectively: $\hbar\omega = 4401$ cm^{-1} and $\tilde{B} = 59.32$ cm^{-1}. Within our code, we define a function for both rotational and vibrational energies. Our rotational function takes in these three inputs: reduced mass (μ), bondlength (R_e), and J, and our vibrational function takes in these three inputs: reduced mass (μ), k, and v. To calculate reduced mass, we use the following equation:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

where recall that reduced mass is treating two rotating masses to be centralized. First, we will tackle the rotational question. We are able to calculate the reduced mass of hydrogen within our code (reference code for this); however, we must do some multiple manipulations to find bondlength

given our constant. (Note: we are also able to look up the bondlength for H_2). Recall that $I = \mu R_e{}^2$ (pg 19) and this relationship regarding $\tilde{B}$:

$$\tilde{B} = \frac{B}{c}$$
$$= \frac{h}{8\pi^2 cI}$$

where we are dealing with $\tilde{B}$ because the constant we were given is in wavenumbers. And, we can manipulate our above moment of inertia equation to get this relationship for bondlength:

$$R_e = \sqrt{\frac{I}{\mu}}$$

and, using our equation $\tilde{B}$:

$$I = \frac{h}{8\pi^2 c\tilde{B}}$$

therefore,

$$R_e = \left(\frac{h}{8\pi^2 c\tilde{B}}\right)^{\frac{1}{2}}$$

This is the equation I use in my program to find our last parameter. From there, using my calculated μ and R_e values, I calculate the first five rotational states, getting the following values:

J_0) 0.0 J

J_1) 2.32×10^{-21} J

J_2) 6.95×10^{-21} J

J_3) 1.39×10^{-20} J

J_4) 2.31×10^{-20} J

Now, we will consider the first five Vibrational Energies, where we are given the falling constant: $\hbar\omega = \tilde{v} = 4401$ cm^{-1} (constant given on table on pg. 15). Where, on pg. 15, we are given the following equation for k:

$$k = (2\pi\tilde{v}_{obs}c)^2\mu$$

From there, we calculate our constant k for our vibrational energy, and have our three required constants of k, v, and mu for our function. After calculating those values in my code, we get the following values:

v_0) 4.37×10^{-20} J

v_1) 1.31×10^{-19} J

v_2) 2.18×10^{-19} J

v_3) 3.05×10^{-19} J

v_4) 3.93×10^{-19} J

Therefore, we have calculated the energies for the first five vibrational and rotational states. $\square$

C-2: This question asks us to perform the following task: given the molecule H^{3}5CL with vibrational and rotational constants $\hbar\omega = 2886$ cm^{-1} and $\tilde{B} = 10.34$ cm^{-1}, what is the numerical difference in energy between the $v = 0, J = 1$ state and the $v = 1, J - 0$ state of this molecule? In question C-1, we have developed functions and techniques to calculate the parameters given vibrational and rotational constants. With this mind, our code is trying to complete the following task:

$$\varepsilon_{0,1} - \varepsilon_{1,0}$$

to generate a numerical difference where $\varepsilon_{0,1}$ is when $v = 0, J = 1$ and $\varepsilon_{1,0}$ is when $v = 1, J = 0$. To calculate this values, we sum up their vibrational and rotational energies. Where,

$$\varepsilon_{0,1} = \varepsilon_{\mathrm{vib},v_0} + \varepsilon_{\mathrm{rot},J_1}$$

and,

$$\varepsilon_{1,0} = \varepsilon_{\mathrm{vib},v_1} + \varepsilon_{\mathrm{rot},J_0}$$

Calculating each value through python gives us the following:

1) $\varepsilon_{\mathrm{vib},v_0} = 2.87 \times 10^{-20}$ J

2) $\varepsilon_{\mathrm{vib},v_0} = 8.60 \times 10^{-20}$ J

3) $\varepsilon_{\mathrm{rot},J_0} = 0.0$ J

4) $\varepsilon_{\mathrm{rot},J_1} = 4.14 \times 10^{-22}$ J

Now, we can calculate $\varepsilon_{0,1} - \varepsilon_{1,0}$ through python:

$$\varepsilon_{0,1} - \varepsilon_{1,0} = (\varepsilon_{\mathrm{vib},v_0} + \varepsilon_{\mathrm{rot},J_1}) - (\varepsilon_{\mathrm{vib},v_1} + \varepsilon_{\mathrm{rot},J_0})$$
$$= -5.29 \times 10^{-20} \text{ J}$$

Where, we know can see that $\varepsilon_{0,1} < \varepsilon_{1,0}$ showing how the first vibrational energy state is larger than the first rotational energy state. $\square$

C-3: This question asks us to find the force constant k for both H$_2$ and H^{3}5Cl; however, I have already found those values to solve C-1 through the following equation:

$$k = (2\pi\tilde{v}_{obs}c)^2\mu$$

With that, I can find the force constants to be the following:

$$k_{H_2} = (2\pi(4401 \text{ cm}^{-1})(100 \text{ cm}^{-1} \cdot \text{ m}^{-1})2.998 \times 10^9 \text{m})^2 \cdot 8.36 \times 10^{-28} kg$$
$$= 575 \text{ kg} \cdot \text{s}^{-2} = 575 \text{ N} \cdot \text{m}^{-1}$$
$$k_{H^{35}Cl} = (2\pi(10.44 \text{ cm}^{-1})(100 \text{ cm}^{-1} \cdot \text{ m}^{-1})2.998 \times 10^9 \text{m})^2 \cdot 1.62 \times 10^{-27} kg$$
$$= 481 \text{ kg} \cdot \text{s}^{-2} = 481 \text{ N} \cdot \text{m}^{-1}$$

3 In-Class Activity using WebMO

1) After doing the necessary calculations at the level MP2/"accurate" basis set, these are our results about whether the ground electronic state of O_2 is a singlet or a triplet: We determined that the ground electronic state to be when O_2 is a triplet. We did the following calculations to determine this:

   1. Created a O_2 system in WebMO
   2. Performed a geometry optimization on this system
   3. Did a vibrational frequency calculation to acquire the MP2 Energy of our optimized system

   After performing vibrational frequency calculations, we acquired the following results for the singlet system and triplet system:

   Singlet System Energy: -150.01495995948 Hartree
   Triplet System Energy: -150.06201190368 Hartree

   Where, we know that the system with the lower energy will the ground state. Therefore, the triplet system will be the electronic ground state. □

2) The rotational constant of oxygen in its electronic group state at the same level of theory is 1.33300788708 cm^{-1}. The vibrational frequency of oxygen is 1.333 cm^{-1}.

3) The ground state of ozone is a bent molecule. While performing a geometry optimization on a O_3 system, it will determine the optimized geometry to be a bent molecule.

4) We expect ozone to have $3n - 6$ normal modes, where n is the number of atoms present in the molecule, for vibrational normal modes, and 3 normal modes for rotational and translational. Therefore, we expect to have 9 normal modes. Our simulation confirms this through calculating the following values: three rotational constants and three vibrational modes.

   Rotational Constants:

   1. 0.97810666071 cm^{-1}
   2. 0.97706794212 cm^{-1}
   3. 0.48879348392 cm^{-1}

   Vibrational Modes:

   1. 794.6289 cm^{-1}
   2. 795.8217 cm^{-1}
   3. 1029.2994 cm^{-1}

   And, there will be three translational states because there are three coordinates (x,y,z) that our molecule is allowed to travel in. Therefore, we have shown how there are 9 normal modes. □

4 McQ: 1-2, 1-3

1-2: Given $\tilde{v} = 10^{-3}$ cm$^{-1} = 10^5 = \frac{1}{\lambda}$, Calculate v, λ, and ε for radiation. So,

$$\lambda = \frac{1}{\tilde{v}} = \frac{1}{10^5 \text{ m}^{-1}} = 10^{-5} \text{ m}$$

where,

$$\Delta\varepsilon = hc\tilde{v}$$
$$= (6.62 \times 10^{-34}\text{J/Hz})(2.99 \times 10^9 \text{ m})(10^5 \text{ m}^{-1})$$
$$= 1.98 \times 10^{-20} \text{ J}$$

and,

$$\Delta\varepsilon = hv \implies v = \frac{\Delta\varepsilon}{h}$$
$$= \frac{1.98 \times 10^{-20} \text{ J}}{6.62 \times 10^{-34}\text{J/Hz}}$$
$$= 2.99 \times 10^{13} \text{ J}$$

Comparing our wavelength value of 10^{-5} shows that we are in the infrared region!

1.3: Given $v = 2.0 \times 10^4$ Hz, Calculate $\tilde{v}$, λ, and ε. So,

$$\Delta\varepsilon = hv$$
$$= (6.62 \times 10^{-34}\text{J/Hz}) \left(2.0 \times 10^4 \text{ Hz} \times \frac{1000000 Hz}{1 \text{ MHz}} \right)$$
$$= 1.324 \times 10^{-23} \text{ J}$$

where,

$$\Delta\varepsilon = hc\tilde{v} \implies \tilde{v} = \frac{\Delta\varepsilon}{hc}$$
$$= \frac{1.324 \times 10^{-23} \text{ J}}{(6.62 \times 10^{-34}\text{J/Hz})(2.99 \times 10^9 \text{ m})}$$
$$= 66.67 \text{ m}^{-1}$$

and,

$$\tilde{v} = \frac{1}{\lambda} \implies \lambda = \frac{1}{\tilde{v}}$$
$$= \frac{1}{66.67 \text{ m}^{-1}}$$
$$= 1.5 \times 10^{-2} \text{ m}$$

Our 1.5×10^{-2} m aligns with edge of the microwave region!