

PChem Handin Homework 12

1. For a diatomic molecule, the rotational energy is $E_J = \tilde{B} hc J(J+1)$.

(a.) Evaluate q_r for a diatomic molecule by numerically calculating $e^{-E_J/kT}$ and summing over many energy levels. You will need to use EXCEL or BASIC. Take $\frac{\tilde{B}hc}{kT} = 0.001$. Remember the degeneracy of each level is $g = 2J+1$.

(b.) Compare your numerical answer to the formula we will derive in class using the high temperature approximation:

$$q_r = \frac{kT}{\tilde{B}hc}$$

Chapter 5 from our “Molecular Mechanics Exercises, MOE Tutorial” concerns conformational equilibria. Do problems 5.1-5.3. What percentage of molecules are in the gauche form? (By the way the MOPAC, PM3 energy difference is less, -0.612 kcal/mol.)

Problem 5.1: Butane

Contribution	anti (kcal/mol)	gauche (kcal/mol)	difference (kcal/mol)	avored conformer
bond <u>str</u> energy				
<u>angle</u> energy				
<u>torsional</u> energy				
<u>Van der Waals</u>				
<u>electrostatic</u>				
total				

Which force field contribution dominates the conformational preference? _____

Report the gauche dihedral angle _____

Problem 5.2, Dichloroethane:

Equilibrium constant for the anti to gauche conformers _____

Dihedral angle in the gauche conformer. _____

Why is this angle different from butane?

Contribution	anti (kcal/mol)	gauche (kcal/mol)	difference (kcal/mol)	avored conformer
bond <u>str</u> energy				
<u>angle</u> energy				
<u>torsional</u> energy				
<u>Van der Waals</u>				
<u>electrostatic</u>				
total				

Problem 5.3

Conformation	Energy, E_i (kJ)	E_i / RT	$e^{-E_i/RT}$	$g e^{-E_i/RT}$	$g e^{-E_i/RT} / q$
gauche					
anti	0	0	1	1	
sum=q=				q=	

$K =$ _____