Quiz 7
CHEM 325
Spring 2009

Name: ____

1. (6 Points) The molecule CH_2Cl_2 belongs to the point group C_{2v}. The displacement vectors of the atoms span 5 A_1 + 2 A_2 + 4 B_1 + 4 B_2. What are the symmetries of the normal modes?

There are 9 normal modes (3N-6 with N = 5) for CH_2Cl_2.

Removing the translations (A_1 + B_1 + B_2) leaves 4 A_1 + 2 A_2 + 3 B_1 + 3 B_2.

Removing the rotations (A_2 + B_1 + B_2) leaves 4 A_1 + A_2 + 2 B_1 + 2 B_2, which are a total of 9 normal modes.

C_{2v}	E	C_2	σ_v (xz)	σ_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

2. (4 Points) Will Cl_2 ($\tilde{\nu}$ = 559.7 cm^{-1}) or Br_2 ($\tilde{\nu}$ = 321.0 cm^{-1}) have a higher proportion of molecules in the first vibrational excited state at 300.0 K? Explain.

The vibrational terms are $G(v) = \left(v + \frac{1}{2}\right)\tilde{\nu}$**, assuming that we may treat these molecules as simple harmonic oscillators, and the difference between the** $v = 0$ **and** $v = 1$ **states would be** $G(1) - G(0) = \left(1 + \frac{1}{2}\right)\tilde{\nu} - \left(0 + \frac{1}{2}\right)\tilde{\nu} = \tilde{\nu}$**. The Boltzmann distribution predicts that states with higher energy will be less populated than states at lower energy at a given temperature. Since the splitting between the vibrational states is smaller for Br_2 (since it has the smaller** $\tilde{\nu}$**), there will be more Br_2 molecules than Cl_2 molecules in the first vibrational state at 300.0 K.**

3. (5 Points) The normal modes for CH_4 are A_1, E, T_2 and T_2. Which of these modes will be IR active (i. e., observable in an IR absorption spectrum) and which will be Raman active (i. e., observable in a Raman spectrum)?

The symmetry of a normal mode must be the same as x, y, or z (the mode must transform as x, y or z) to be IR allowed, while a normal mode must transform as a quadratic to be Raman allowed.

From the character table we see that A_1, E and <u>both</u> T_2 transform as quadractics, and are thus Raman allowed.

<u>Both</u> T_2 normal modes transform also transform as (x, y, z) and are thus allowed in IR.

T_d	E	8 C_3	3 C_2	6 S_4	6 σ_d		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

4. (7 Points) The allowed vibrational transitions of a diatomic molecule occur at wavenumbers of $\tilde{\nu} - 2(v+1)x_e\tilde{\nu}$. A graph of the wavenumber of the first three vibrational transitions of NaI as a function of v+1 yields a straight line with an intercept of 286.00 cm^{-1} and a slope of -1.5000 cm^{-1}. What is D_e (the depth of the Morse potential well)?

The given equation is in the form of a straight line with a slope of $-2x_e\tilde{\nu}$ and an intercept of $\tilde{\nu}$. Therefore, $x_e\tilde{\nu} = \frac{1.5000\ \text{cm}^{-1}}{2} = 0.75000\ \text{cm}^{-1}$.

Rearrange $x_e = \frac{\tilde{\nu}}{4D_e}$ to $D_e = \frac{\tilde{\nu}}{4x_e} = \frac{\tilde{\nu}^2}{4x_e\tilde{\nu}}$, and solve

$$D_e = \frac{\tilde{\nu}^2}{4x_e\tilde{\nu}} = \frac{\left(286.00\ \text{cm}^{-1}\right)^2}{4\left(0.75000\ \text{cm}^{-1}\right)} = 27265._3\ \text{cm}^{-1}$$

For NaI D_e is 27265. cm^{-1}.