Chemistry 410A **Exam 5** **Fall 2008**

NAME:

Instructions:

1. Keep this exam closed until instructed to begin.
2. **Please write your name on this page but not on any other page.**
3. Please silence any noisy electronic devices you have.
4. Attached sheet(s) provide potentially useful constants and equations. You may detach these from the exam.
5. To receive full credit for your work, please
   (a) show all your work, using only the exam papers, including the back of this sheet if necessary;
   (b) specify the correct units, if any, for your final answers;
   (c) use an appropriate number of significant digits for final numerical answers;
   (d) **stop writing and close your exam immediately when time is called.**

Other notes:

- **The first page portion of the exam is worth 40 points.** Partial credit for these problems is not necessarily available.
- **Your 2 best scores of the 3 remaining problems will count towards the other 60 points.** Partial credit is available for these problems, so try each problem and do not erase any of your work.

1. **40 points.**

   (a) Write the complete MO configuration that you would expect for B_2, if you follow the line for N_2 in the schematic homonuclear diatomics correlation diagram (Fig. 6.2).

   (b) Write the term symbol for the BH_3^+ ion, with MO configuration $1a_1'^2 2a_1'^2 1e'^3$.

   (c) Circle the molecule that you would expect to have the **lowest** vibrational constant ω_e:
   MgO CaO CaS

   (d) Circle the molecule that you would expect to have the **lowest** vibrational constant for the CC stretch:
   H_3CCH_3 (ethane) H_2CCH_2 (ethene) HCCH (ethyne)

   (e) For the $v = 3$ state of a simple harmonic oscillator:

      i. Write the wavefunction in terms of the unitless coordinate y.

      ii. How many nodes does this wavefunction have?

   (f) How many vibrational modes are there in the simplest amino acid, glycine (NH_2CH_2COOH)?

2. Ground state acetylene is linear, but its lowest excited state is a triplet state with C_{2h} symmetry. Give the representations in the C_{2h} limit that correlate to the MO's listed below for the linear molecule.

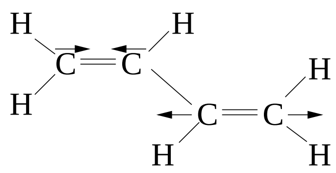
(a) C—H σ_g

(b) C—H σ_u

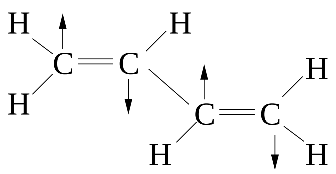
(c) C≡C σ_g

(d) C≡C π_u

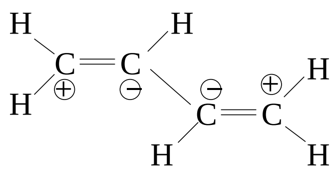
3. Give the symmetry representation for each of the vibrational modes below, and indicate whether each mode is IR-active or IR-inactive (in other words, can the mode be excited by an allowed eletctric dipole transition).



a)



b)



c)

4. The $v = 0 \rightarrow 1$ transition in CH^+ is measured at $2046.3 \mathrm{cm}^{-1}$. If the force constant is $259.0\,\mathrm{N\,m^{-1}}$, calculate the anharmonicity $\omega_e x_e$.

Fundamental Constants

Avogadro's number	$\mathcal{N}_A$	$6.0221367 \cdot 10^{23}$ mol^{-1}
Bohr radius	$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	$5.29177249 \cdot 10^{-11}$ m
Boltzmann constant	k_B	$1.380658 \cdot 10^{-23}$ J K^{-1}
electron rest mass	m_e	$9.1093897 \cdot 10^{-31}$ kg
fundamental charge	e	$1.6021773 \cdot 10^{-19}$ C
permittivity factor	$4\pi\epsilon_0$	$1.113 \cdot 10^{-10}$ C^2 J^{-1} m^{-1}
gas constant	R	8.314510 J K^{-1} mol^{-1}
	R	0.08314510 L bar K^{-1} mol^{-1}
	R	0.08206 L atm K^{-1} mol^{-1}
hartree	$E_\mathrm{h} = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$	$4.35980 \cdot 10^{-18}$ J
Planck's constant	h	$6.6260755 \cdot 10^{-34}$ J s
	$\hbar$	$1.05457266 \cdot 10^{-34}$ J s
proton rest mass	m_p	$1.6726231 \cdot 10^{-27}$ kg
neutron rest mass	m_n	$1.6749286 \cdot 10^{-27}$ kg
speed of light	c	$2.99792458 \cdot 10^{8}$ m s^{-1}

Unit Conversions

	K	cm^{-1}	kJ mol^{-1}	kcal mol^{-1}	erg	kJ
kHz =	$4.799 \cdot 10^{-8}$	$3.336 \cdot 10^{-8}$	$3.990 \cdot 10^{-10}$	$9.537 \cdot 10^{-11}$	$6.626 \cdot 10^{-24}$	$6.626 \cdot 10^{-34}$
MHz =	$4.799 \cdot 10^{-5}$	$3.336 \cdot 10^{-5}$	$3.990 \cdot 10^{-7}$	$9.537 \cdot 10^{-8}$	$6.626 \cdot 10^{-21}$	$6.626 \cdot 10^{-31}$
GHz =	$4.799 \cdot 10^{-2}$	$3.336 \cdot 10^{-2}$	$3.990 \cdot 10^{-4}$	$9.537 \cdot 10^{-5}$	$6.626 \cdot 10^{-18}$	$6.626 \cdot 10^{-28}$
K =	1	0.6950	$8.314 \cdot 10^{-3}$	$1.987 \cdot 10^{-3}$	$1.381 \cdot 10^{-16}$	$1.381 \cdot 10^{-26}$
cm^{-1} =	1.4388	1	$1.196 \cdot 10^{-2}$	$2.859 \cdot 10^{-3}$	$1.986 \cdot 10^{-16}$	$1.986 \cdot 10^{-26}$
kJ mol^{-1} =	$1.203 \cdot 10^{2}$	83.59	1	0.2390	$1.661 \cdot 10^{-14}$	$1.661 \cdot 10^{-24}$
kcal mol^{-1} =	$5.032 \cdot 10^{2}$	$3.498 \cdot 10^{2}$	4.184	1	$6.948 \cdot 10^{-14}$	$6.948 \cdot 10^{-24}$
eV =	$1.160 \cdot 10^{4}$	$8.066 \cdot 10^{3}$	96.49	23.06	$1.602 \cdot 10^{-12}$	$1.602 \cdot 10^{-22}$
hartree =	$3.158 \cdot 10^{5}$	$2.195 \cdot 10^{5}$	$2.625 \cdot 10^{3}$	$6.275 \cdot 10^{2}$	$4.360 \cdot 10^{-11}$	$4.360 \cdot 10^{-21}$
erg =	$7.243 \cdot 10^{15}$	$5.034 \cdot 10^{15}$	$6.022 \cdot 10^{13}$	$1.439 \cdot 10^{13}$	1	10^{-10}
J =	$7.243 \cdot 10^{22}$	$5.034 \cdot 10^{22}$	$6.022 \cdot 10^{20}$	$1.439 \cdot 10^{20}$	10^{7}	10^{-3}
dm^3 bar =	$7.243 \cdot 10^{24}$	$5.034 \cdot 10^{24}$	$6.022 \cdot 10^{22}$	$1.439 \cdot 10^{22}$	$1.000 \cdot 10^{9}$	0.1000
kJ =	$7.243 \cdot 10^{25}$	$5.034 \cdot 10^{25}$	$6.022 \cdot 10^{23}$	$1.439 \cdot 10^{23}$	10^{10}	1

distance	1 Å =	10^{-10} m	
mass	1 amu =	$1.66054 \cdot 10^{-27}$ kg	
energy	1 J =	1 kg m^2 s^{-2}	= 10^7 erg
force	1 N =	1 kg m s^{-2}	= 10^5 dyn
electrostatic charge	1 C =	1 A s	= $2.9979 \cdot 10^9$ esu
	1 D =	$3.3357 \cdot 10^{-30}$ C m	= $1 \cdot 10^{-18}$ esu cm
magnetic field strength	1 T =	1 kg s^{-2} A^{-1}	= 10^4 gauss
pressure	1 Pa =	1 N m^{-2}	= 1 kg m^{-1} s^{-2}
	1 bar =	10^5 Pa	= 0.98692 atm

v	A_v	$H_v(y)$	nodes
0	$\left(\frac{k\mu}{\hbar^2}\right)^{1/8}\left(\frac{1}{\sqrt{\pi}}\right)^{1/2}$	1	0
1	$\left(\frac{k\mu}{\hbar^2}\right)^{1/8}\left(\frac{1}{2\sqrt{\pi}}\right)^{1/2}$	$2y$	$1 : y = 0$
2	$\left(\frac{k\mu}{\hbar^2}\right)^{1/8}\left(\frac{1}{8\sqrt{\pi}}\right)^{1/2}$	$4y^2 - 2$	$2 : y = \pm 1.414$
3	$\left(\frac{k\mu}{\hbar^2}\right)^{1/8}\left(\frac{1}{48\sqrt{\pi}}\right)^{1/2}$	$8y^3 - 12y$	$3 : y = 0, \pm 1.225$
4	$\left(\frac{k\mu}{\hbar^2}\right)^{1/8}\left(\frac{1}{384\sqrt{\pi}}\right)^{1/2}$	$16y^4 - 48y^2 + 12$	$4 : y = \pm 0.525, \pm 1.651$
5	$\left(\frac{k\mu}{\hbar^2}\right)^{1/8}\left(\frac{1}{3840\sqrt{\pi}}\right)^{1/2}$	$32y^5 - 160y^3 + 120y$	$5 : y = 0, \pm 0.959, \pm 2.020$

$$y\ H_v(y) = vH_{v-1}(y) + \frac{1}{2}H_{v+1}(y) \qquad y\ \eta_v(y) = A_v\left[v\frac{\eta_{v-1}(y)}{A_{v-1}} + \frac{1}{2}\frac{\eta_{v+1}(y)}{A_{v+1}}\right]$$

$$\frac{dH_v(y)}{dy} = vH_{v-1}(y) - \frac{1}{2}H_{v+1}(y) \qquad \frac{d\eta_v(y)}{dy} = A_v\left[v\frac{\eta_{v-1}(y)}{A_{v-1}} - \frac{1}{2}\frac{\eta_{v+1}(y)}{A_{v+1}}\right]$$

Selected vibrational and rotational constants.

Molecule	μ (amu)	R_e (Å)	B_e (cm^{-1})	α_e (cm^{-1})	D (10^{-6} cm^{-1})	ω_e (cm^{-1})
^{1}H^{1}H	0.50	0.742	60.8536	3.0622	46660	4401.21
^{1}H^{2}D	0.67	0.742	45.6378	1.9500		3811.92
^{2}D^{2}D	1.01	0.742	30.442	1.0623		3118.46
^{1}H^{19}F	0.96	0.917	20.9557	0.798	2150	4138.32
^{1}H^{35}Cl	0.98	1.275	10.5934	0.3702	532	2990.95
^{1}H^{79}Br	1.00	1.414	8.3511	0.226	372	2649.67
^{1}H^{127}I	1.00	1.609	3.2535	0.0608	526	2309.60
^{2}D^{19}F	1.82	0.917	11.0000	0.2907	585	2998.19
^{12}C^{16}O	6.86	1.128	1.9313	1.7507	6	2169.82
^{14}N^{14}N	7.00	1.098	1.9987	0.0171	6	2358.07
^{14}N^{16}O$^+$	7.47	1.063	1.9982	0.0190		2377.48
^{14}N^{16}O	7.47	1.151	1.7043	0.0173	−37	1904.41
^{14}N^{16}O$^-$	7.47	1.286	1.427			1372
^{16}O^{16}O	8.00	1.207	1.4457	0.0158	5	1580.36
^{19}F^{19}F	9.50	1.418	0.8828			891.2
^{35}Cl^{35}Cl	17.48	1.988	0.2441	0.0017	0.2	560.50
^{79}Br^{79}Br	39.46	2.67	0.0821	0.0003	0.02	325.29
^{127}I^{79}Br	48.66	2.470	0.0559	0.0002	0.008	268.71
^{127}I^{127}I	63.45	2.664	0.0374	0.0001	−0.005	214.52
^{23}Na^{23}Na	11.49	3.077	0.1548	0.0009	0.7	159.13
^{133}Cs^{133}Cs	66.45	4.47	0.0127	0.00003	0.005	42.02

vibration

$$\eta_v(R) = A_v H_v(y) e^{-(R-R_e)^2/(2c^2)}, \qquad c = \left(\frac{\hbar^2}{k\mu}\right)^{1/4}$$

$$E_{\text{vib}} = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x_e\left(v + \frac{1}{2}\right)^2 + \ ...$$

$$\omega_e = \hbar\sqrt{\frac{k}{\mu}}$$

$$\omega_e\,(\,\text{cm}^{-1}) = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = 130.28\sqrt{\frac{k\,(\,\text{N}\,\text{m}^{-1})}{\mu\,(\,\text{amu})}}$$