Chemistry 410A **Exam 6** **Spring 2016**

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) put your name on your exam;
    (b) show all your work, using only the exam papers, including the back of this sheet if necessary;
    (c) specify the correct units, if any, for your final answers;
    (d) use an appropriate number of significant digits for final numerical answers;
    (e) **stop writing and close your exam immediately when time is called.**

Other notes:

- **Problem 1 (covering all of page 3) 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) Name the process (for example, "collisional relaxation") that occurs in each of the experiments described below:

      i. Benzene is excited to its $^3B_{1u}$ excited state, which emits light over a period of several seconds to return to the singlet ground state.

      ii. When the N—H stretches of alanine, $NH_2CH(CH_3)COOH$, are highly excited by infrared radiation, within a few vibrational periods excited stretching states of the C—H bonds in the CH_3 group are detected.

      iii. This one has **2** processes. Acetylene is excited by 187 nm radiation. After about 10^{-10} s, an allowed emission transition in hydrogen atom is observed. (A single vibrational period in acetylene is about 10^{-12} s.)

   (b) Estimate the following energies.

      i. The $v = 3 \rightarrow 5$ transition energy for a molecule with a vibrational constant of $1000\,\text{cm}^{-1}$.

      ii. The $J = 3 \rightarrow 5$ transition energy for a molecule with a rotational constant of $1.0\,\text{cm}^{-1}$.

   (c) The ground state vibrational constant of $^{65}\text{Cu}^{35}\text{Cl}$ is $415.3\,\text{cm}^{-1}$. Estimate the force constant in SI units (two significant digits is fine).

   (d) The interaction energy between two rotating water molecules averages to $-1.0\,\text{kJ mol}^{-1}$. If the distance between them is cut in half, what is the new interaction energy?

2. A molecule with the molecular formula N_xH_y has the following complete set of predicted vibrational constants, with the symmetry representations given:

   i) $1347\,\mathrm{cm}^{-1}$ a_u

   ii) $1360\,\mathrm{cm}^{-1}$ b_u

   iii) $1601\,\mathrm{cm}^{-1}$ a_g

   iv) $1651\,\mathrm{cm}^{-1}$ a_g

   v) $3220\,\mathrm{cm}^{-1}$ a_g

   vi) $3252\,\mathrm{cm}^{-1}$ b_u

   (a) How many atoms are in the molecule?

   (b) What is the molecular formula (in other words, what are the values of x and y)?

   (c) What is the point group of the molecule?

   (d) Draw a Lewis structure of the molecule.

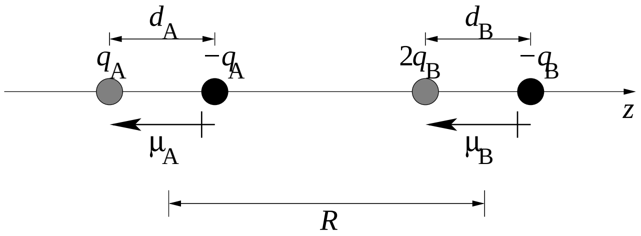
   (e) For any **three** of the modes in the list above, either label the type of motion *clearly* or sketch a picture showing the displacement arrows. The picture doesn't have to be a perfect Lewis structure, but identify which mode ($i - vi$) it represents.

3. The Morse oscillator has energy levels $E_v = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2$ where $\omega_e x_e = \omega_e^2/(4D_e)$.

   (a) Find the value of v, in terms of ω_e and D_e, at which the $v \rightarrow v+1$ transition energy becomes zero.

   (b) Find the value of E_v for this vibrational state in terms of ω_e and D_e.

4. The distribution of charges given below is the same as we used to derive the formula for $u_{2-2}(R)$, except that one of the charges on molecule B has been doubled.



Find an expression for the potential energy $u(R)$ between A and B in terms of μ_A, q_B, and R. use **either one** of the following two methods:

(a) Start by writing the interaction between these two molecules as the sum of the ion-dipole interactions between each charge on molecule B with the dipole moment of molecule A. Then simplify the result using the assumption that $R \gg d_B$.

(b) Decompose the charges on molecule B into separate monopole and dipole contributions. Then add the potential energies for the (dipole A)–(monopole B) interaction and for the (dipole A)–(dipole B) interactions.

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

harmonic osc.

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

$$E_v = \omega_e\left(v+\tfrac{1}{2}\right)$$

vibration

$$E_{\rm vib} = \omega_e\left(v+\tfrac{1}{2}\right) - \omega_e x_e\left(v+\tfrac{1}{2}\right)^2 + \omega_e y_e\left(v+\tfrac{1}{2}\right)^3 + \ldots$$

$$\omega_e = \hbar\sqrt{\frac{k}{\mu}} \qquad \omega_e\,(\,{\rm cm}^{-1}) = 130.28\sqrt{\frac{k\,(\,{\rm N\,m}^{-1})}{\mu\,(\,{\rm amu})}}$$

Morse potential

$$U_{\rm M}(R) = D_e\left\{\left[1\ -\ e^{-\beta(R-R_e)}\right]^2\ -\ 1\right\}, \qquad \beta \approx \sqrt{\frac{k}{2D_e}}$$

$$E_{{\rm M},v} = \omega_e\left(v+\tfrac{1}{2}\right) - \omega_e x_e\left(v+\tfrac{1}{2}\right)^2$$

rotation

$$E_{\rm rot} = B_v J(J+1)\ -\ D_v[J(J+1)]^2\ +\ \ldots$$

$$B(\,{\rm cm}^{-1}) = \frac{16.858}{I(\,{\rm amu}\,\mathring{\rm A}^2)} = \frac{16.858}{\mu(\,{\rm amu})\ \left[R(\,\mathring{\rm A})\right]^2}\ \text{ for diatomics}$$

monopole-dipole:

$$u_{1-2}(R) = -\frac{\mu_{\rm A} q_{\rm B}}{R^2}$$

dipole-dipole:

$$u_{2-2}(R) = -\frac{2\mu_{\rm A}\mu_{\rm B}}{(4\pi\epsilon_0)R^3}$$

dipole-dipole:

$$\langle u_{2-2}\rangle_{N,\theta,\phi} = -\frac{2\mu_{\rm A}^2\mu_{\rm B}^2}{(4\pi\epsilon_0)^2 3k_{\rm B}TR^6},$$

Molecule	μ (amu)	R_e (Å)	B_e (cm^{-1})	α_e (cm^{-1})	D (10^{-6} cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})
^{1}H^{1}H	0.50	0.742	60.8536	3.0622	46660	4401.21	121.34
^{1}H^{2}D	0.67	0.742	45.6378	1.9500		3811.92	90.71
^{2}D^{2}D	1.01	0.742	30.442	1.0623		3118.46	117.91
^{1}H^{19}F	0.96	0.917	20.9557	0.798	2150	4138.32	89.88
^{1}H^{35}Cl	0.98	1.275	10.5934	0.3702	532	2990.95	52.82
^{1}H^{79}Br	1.00	1.414	8.3511	0.226	372	2649.67	45.21
^{1}H^{127}I	1.00	1.609	3.2535	0.0608	526	2309.60	39.36
^{2}D^{19}F	1.82	0.917	11.0000	0.2907	585	2998.19	45.76
^{12}C^{16}O	6.86	1.128	1.9313	0.0175	6	2169.82	13.29
^{14}N^{14}N	7.00	1.098	1.9987	0.0171	6	2358.07	14.19
^{14}N^{16}O$^+$	7.47	1.063	1.9982	0.0190		2377.48	16.45
^{14}N^{16}O	7.47	1.151	1.7043	0.0173	−37	1904.41	14.19
^{14}N^{16}O$^-$	7.47	1.286	1.427			1372	8
^{16}O^{16}O	8.00	1.207	1.4457	0.0158	5	1580.36	12.07
^{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	2.90
^{79}Br^{79}Br	39.46	2.67	0.0821	0.0003	0.02	325.29	1.07
^{127}I^{79}Br	48.66	2.470	0.0559	0.0002	0.008	268.71	0.83
^{127}I^{127}I	63.45	2.664	0.0374	0.0001	−0.005	214.52	0.61
^{23}Na^{23}Na	11.49	3.077	0.1548	0.0009	0.7	159.13	0.73
^{133}Cs^{133}Cs	66.45	4.47	0.0127	0.00003	0.005	42.02	0.08