Chemistry 410A **Exam 6** **Fall 2011**

NAME:

Instructions:

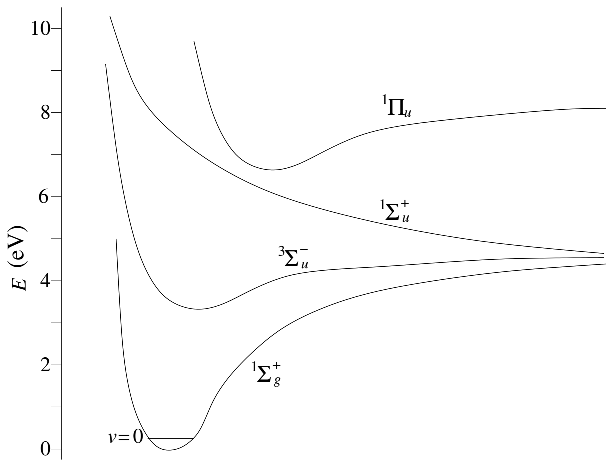
1. Keep this exam closed until instructed to begin.
2. **Please write your name on this page but not on any other page.**
3. Please silence any noisy electronic devices you have.
4. Attached sheet(s) provide potentially useful constants and equations. You may detach these from the exam.
5. To receive 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) Given the set of potential energy curves drawn below, what is the likeliest process to be induced by radiation at a photon energy of 8.0 eV, starting from the $v = 0$ state shown? Identify any of the electronic states involved.



(b) The vibrational constant of $^{14}N_2$ in the $^3\Delta_u$ excited state is 1539 cm^{-1}. Find the force constant in SI units to three significant digits.

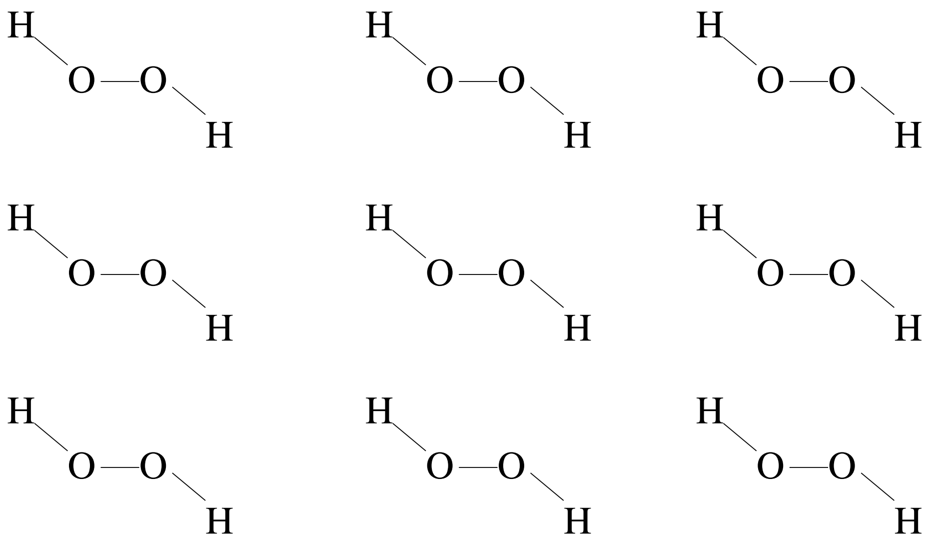
(c) Using the table of vibrational and rotational constants attached to the exam, calculate the total energy in rotation and vibration of the $v = 0, J = 10$ state of $^{12}C^{16}O$, including any corrections for which the data is available.

2. Hydrogen peroxide, HOOH, has the structure shown below.

   (a) How many vibrational modes does HOOH have?

   (b) Draw displacement arrows for each mode on the structures below. (Leave blank any extra structures I have provided)

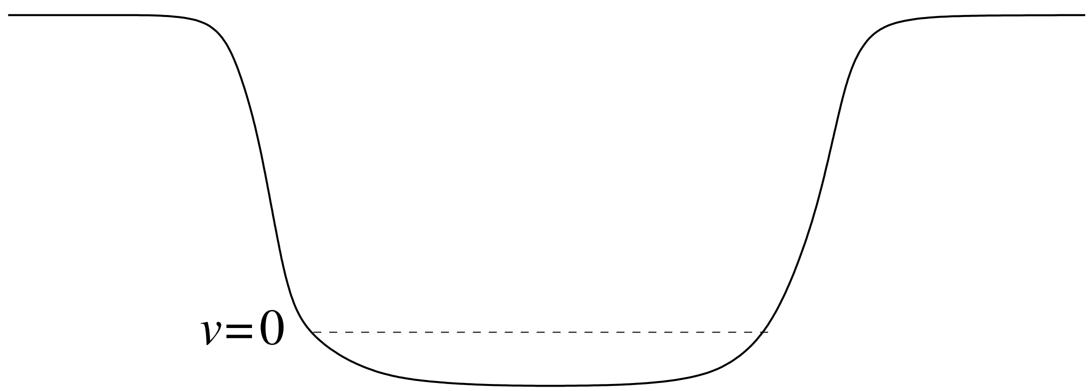
   (c) Label the representation for each mode.



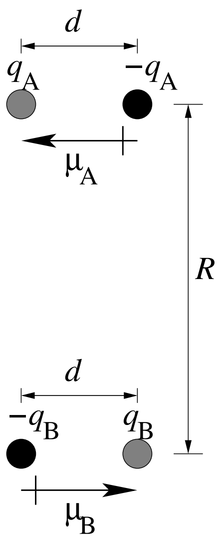
3. The Woods-Saxon potential

$$U(z) = U_0 \left[1 + \frac{1}{1 + e^{(z-a)/d}} \right]$$

   is a model for the potential energy experienced by neutrons inside a nucleus (except in three dimensions instead of one dimension as in this problem). If we label the states using the quantum number v, the $v = 0$ ground state is shown on the potential energy curve below. Sketch as accurately as you can the energy levels and wavefunctions of the $v = 1$ and $v = 2$ states.


v=0

4. We found a formula for the potential energy of interaction for two fixed dipoles that were co-aligned. Use the same approach to find the potential energy as a function of R and in terms of the dipole moments μ_A and μ_B for the case when the two dipole moments are parallel, as shown for the charges drawn below.



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

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

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

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

$$B_v = B_e \;-\; \alpha_e\left(v+\frac{1}{2}\right) \;+\; \beta_e\left(v+\frac{1}{2}\right)^2 \;+\; \ldots$$

$$B(\,\text{cm}^{-1}) = \frac{16.858}{I(\,\text{amu}\,\text{Å}^2)}$$

monopole-dipole: $$u_{1-2}(R) = -\frac{\mu_{\text{A}} q_{\text{B}}}{R^2}$$

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

dipole-dipole: $$\langle u_{2-2}\rangle_{N,\theta,\phi} = -\frac{2\mu_{\text{A}}^2\mu_{\text{B}}^2}{(4\pi\epsilon_0)^2 3k_B T R^6},$$

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

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