Chemistry 410A **Exam 6** **Spring 2008**

NAME:

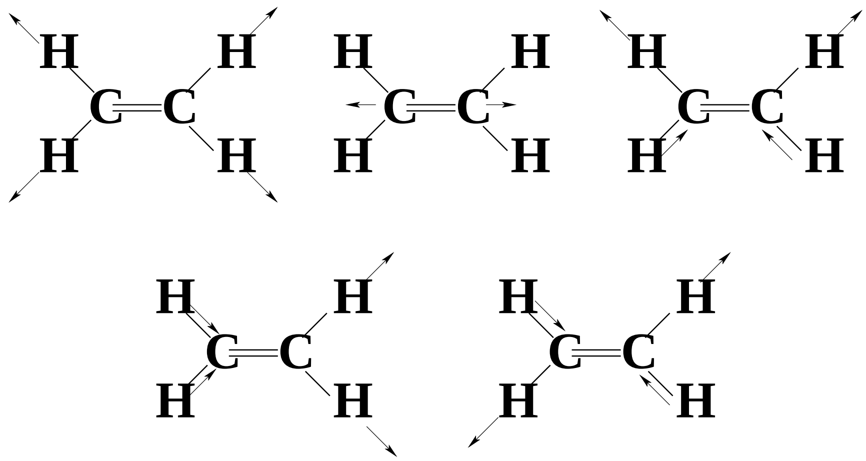
Instructions:

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

Other notes:

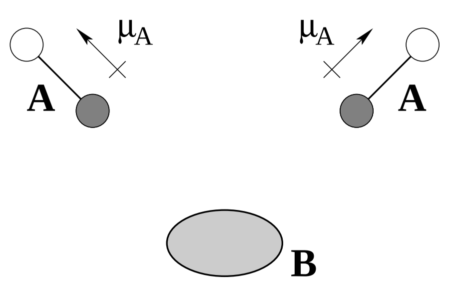
- **Your 4 best scores of the 5 problems will constitute your total score.**
- Partial credit is available for all problems, so try each problem and do not erase any of your work.
- Each question is worth 25 points, but they are not intended to be equally easy.

1. The five stretching modes of ethene are illustrated below. Circle the pictures that correspond to modes that are *infrared active* (*i.e.*, that can be excited according to electric dipole selection rules) and draw a rectangle around any that are *Raman active*.



2. The rotational constant of $^{12}C^{16}O_2$ is given in Table 8.2 as 0.390 Å. Use this to find the C=O bond length in CO_2.

3. For the arrangement of molecules shown below, write an expression for the total *force* on non-polar molecule B, having polarizability α_B, due to its interaction with two molecules A each with dipole moment μ_A. The distance between A and B is R for both interactions, and the two AB axes form an angle of 90°. Neglect any repulsive forces.



4. The Lennard-Jones potential that we introduced is prpoerly called the Lennard-Jones **6-12** potential, because the general form is used for other powers of R as well. For example, in the AMBER molecular mechanics program, hydrogen bonding is represented using a Lennard-Jones **10-12** potential:

$$u_{\mathrm{HB}}(R) = \epsilon_{\mathrm{HB}} \left[\left(\frac{R_e}{R} \right)^{12} - 2 \left(\frac{R_e}{R} \right)^{10} \right].$$

Find the value of R where $u_{\mathrm{HB}}(R) \;=\; 0$ in terms of R_e.

5. The icosohedral or cuboctahedral geometries of a close-packed X_{13} cluster complete a coordination shell around the central X atom. Estimate the cluster size N of a close-packed cluster X_N that exactly completes *two* shells around the central atom.

vibration $$\hat{H}_{\rm vib} = -\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R}$$

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

Morse potential $$E_{\rm elec}(R) = D_e\left\{\left[1 - e^{-\beta(R-R_e)}\right]^2 - 1\right\}$$

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

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

$$I_x = \sum_i m_i(y_i^2+z_i^2) \;(\; = \mu R^2 \quad \text{for diatomic})$$

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

dipole-induced dipole: $$u_{2-2^*}(R) = -\frac{4\mu_{\rm A}^2\alpha}{(4\pi\epsilon_0)R^6}$$

dispersion: $$u_{\rm disp}(R) \approx -\frac{\alpha^2\Delta E}{(4\pi\epsilon_0)^2\; 2R^6}$$

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

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