Chemistry 410A **Exam 6** **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) When $^{12}C^{32}S$ is excited from its $X^1\Sigma^+$ ground state to the $A^1\Sigma^+$ excited state, the bond length increases from 1.535 Å to 1.944 Å. The ground state rotational constant is $0.8200\,\mathrm{cm}^{-1}$. Find the rotational constant in the A excited state.

   (b) Identify the strongest bonding interaction you would expect for each pair of atoms and/or molecules listed below. Be specific; *i.e.*, "monopole-monopole."

      i. Ar and Ar

      ii. HF and Kr

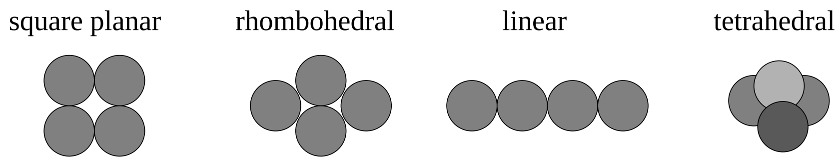
      iii. Na^+ and N_2

      iv. NH_3 and Cl^-

      v. HI and NH_3

   (c) Estimate the dispersion energy in kJ/mol between two naphthalene molecules ($\alpha = 17.5\,\text{Å}^3$, $\Delta E \approx 8\,\mathrm{eV}$) at a separation of 6.5 Å.

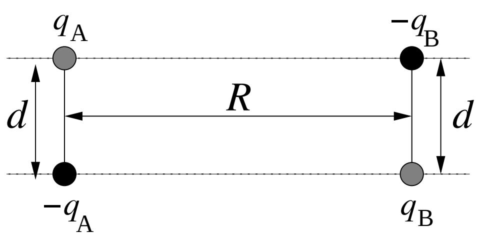
   (d) Four geometries for the Ar_4 cluster are sketched below. Number them from 1 to 4 in order of decreasing stability, so that 1 is the **most stable** and 4 is the **least stable**.



2. A student compares two rovibrational spectra: one for the $v = 0 \rightarrow 1$ transition of $^{12}\mathrm{C}^{16}\mathrm{O}$ and one for the $v' - 1 \rightarrow v'$ transition of $^{14}\mathrm{N}^{16}\mathrm{O}^+$. Surprisingly, the spacing between the $R(0)$ and $R(1)$ lines in both spectra are equal to within $0.01\,\mathrm{cm}^{-1}$. Use this fact and the data below to find the upper state v' of the $^{14}\mathrm{N}^{16}\mathrm{O}^+$ transition.

molecule	B_e	α_e
$^{14}\mathrm{N}^{16}\mathrm{O}^+$	$1.9982\,\mathrm{cm}^{-1}$	$0.0190\,\mathrm{cm}^{-1}$
$^{12}\mathrm{C}^{16}\mathrm{O}$	$1.9313\,\mathrm{cm}^{-1}$	$0.0175\,\mathrm{cm}^{-1}$

3. We derived Eq. 9.14 for the dipole-dipole interaction energy under the assumption that the two dipoles lay along the same axis. Use the same method to derive a formula in terms of μ_A, μ_B, and R for two polar molecules with their dipoles aligned **in parallel** as shown below.



4. Find the potential energy due to dispersion between two electrons trapped in one-dimensional boxes of length a and separated by a distance R, under the same approximations we used to obtain our (more general) expression for the dispersion energy. Do *not* assume we know the polarizabilities of the boxes. Leave explicit any integrals you encounter, but you do not need to evaluate them.

particle in a 1-D box:

$$\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \qquad E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

vibration

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

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

rotation

$$E_{\mathrm{rot}} = B_e J(J+1) - \alpha_e J(J+1)(v+1/2)$$

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

$$\Delta E[R(J'')] = \omega_e - 2v'\omega_e x_e + 2(J''+1)B_e - (J''+1)(J''+2v'+1)\alpha_e$$

$$\Delta E[P(J'')] = \omega_e - 2v'\omega_e x_e - 2J''B_e - J''(J''-2v')\alpha_e$$

monopole-dipole:

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

dipole-dipole:

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

dipole-dipole:

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

dipole-induced dipole:

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

dispersion:

$$u_{\mathrm{disp}}(R) \approx \frac{e^4}{(4\pi\epsilon_0)^2R^6}\frac{\left[\int \psi_{\mathrm{A1}}\; z_{\mathrm{A}}\; \psi_{\mathrm{A2}}\; dz_{\mathrm{A}}\right]^2 \left[\int \psi_{\mathrm{B1}}\; z_{\mathrm{B}}\; \psi_{\mathrm{B2}}\; dz_{\mathrm{B}}\right]^2}{(E_{\mathrm{A1}}+E_{\mathrm{B1}}) - (E_{\mathrm{A2}}+E_{\mathrm{B2}})}$$

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

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	$E_\text{h} = \frac{m_e e^4}{(4\pi\epsilon_0)^2\hbar^2}$	$4.35980 \cdot 10^{-18}$ 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