

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Department of Chemistry
Chemistry - 5.61
Physical Chemistry

Final Examination

- (1) PRINT** your name on the cover page.
- (2)** It is suggested that you **READ THE ENTIRE EXAM** before beginning work, since you may be better prepared for some questions than others.
- (3) ANSWER ALL QUESTIONS** as completely as possible.
- (4)** The **LAST PAGES** contain information that may be useful in solving the problems on the examination. They can be torn off for easy reference.
- (5)** Return **BOTH** the **EXAM** and the **EXAM BOOKLET** with your name on both before you depart. Your exam will not be graded unless both are returned!

GOOD LUCK !!!!

1. (50 pts) _____
2. (25 pts) _____
3. (15 pts) _____
4. (25 pts+10 pts EC) _____
5. (35 pts) _____
6. (50 pts+10 pts EC) _____
- TOTAL: (200 pts) _____

Name : _____

Problem 1 (50 points): Shorter Answer

A) A proton is attached to a silicon surface by a bond that has a force constant of $k = 5.0 \text{ kg/s}^2$. Compute the uncertainty, σ_x , in the distance of the proton from the surface, assuming the bond stretch is harmonic and that the system is in its ground state.

B) Suppose you have an $^1\text{H}^{19}\text{F}$ molecule (bond length $R = 92 \text{ pm}$) rotating with total angular momentum J . **Estimate** the value of J it would take for this molecule to have as much **rotational** kinetic energy as a hydrogen atom in a $2p$ state. Your estimate need not be accurate to better than 50%. [Hint: it may be useful to first decide whether you think this will be a big or small number.]

C) The radii of hydrogenic orbitals have a systematic trend both with the charge on the nucleus (Z) and the principal quantum number (n). Use your knowledge of these trends to order the following orbitals from largest to smallest:

- i. The $1s$ state for hydrogen ($Z=1$)
- ii. The $2s$ state for Be^{+3} ($Z=4$)
- iii. The $2s$ state for C^{+5} ($Z=6$)
- iv. The $3s$ state for Ne^{+9} ($Z=10$)
- v. The $3s$ state for Na^{+10} ($Z=11$)
- vi. The $5s$ state for Fe^{+25} ($Z=26$)

D) In class we found that the molecular orbitals of H_2^+ were given by:

$$\psi^\pm = \frac{1s_A \pm 1s_B}{\sqrt{2(1 \pm S)}}$$

Assume the two nuclei are $2 a_0$ apart, in which case $S=0.6$. For each orbital, ψ^\pm , compute the probability density, P^\pm , of finding the electron exactly halfway between the two nuclei along the bond axis. Compare your result for H_2^+ to what you would find if the electron occupied one of the atomic orbitals (i.e. if $\psi = 1s_A$). For each MO, is an electron more or less likely to reside between the two nuclei as compared to an atomic orbital?

E) Order the following basis sets from smallest to largest. Which one do you expect to give the most accurate results **and why**?

3-21G

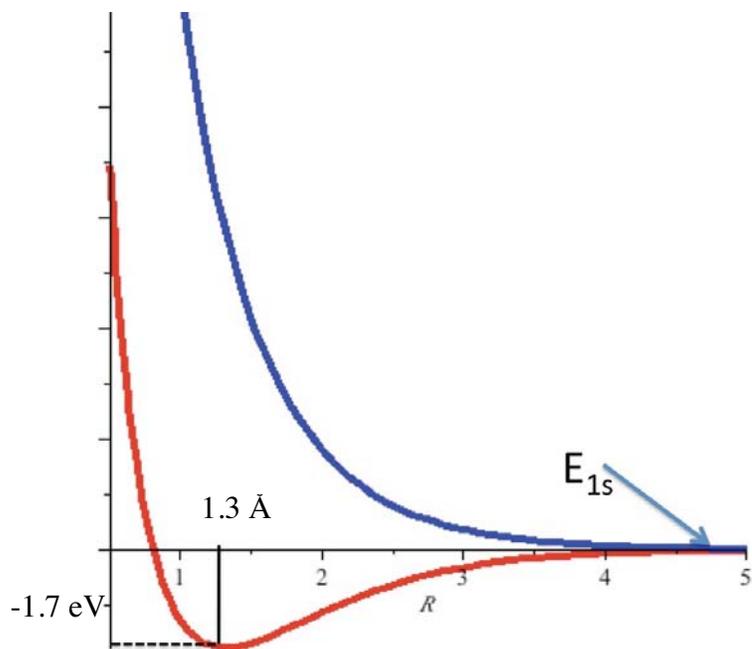
STO-3G

QZP

TZP

6-31G(d,p)

F) The energy curves for the σ and σ^* states of He_2^{+3} are shown below. Draw the analogous curves for LiH^{+3} , labeling any important features. Note that both molecules have a one electron bond.



Problem 2 (25 points): *Spectrum of a Particle in a 1D Box*

The absorption spectrum of a conjugated molecule of length L can be approximated as an electron trapped in a 1D box of the same length. Thus, the electron feels a potential

$$V(x) = \begin{cases} 0 & \text{if } 0 \leq x \leq L \\ \infty & \text{otherwise} \end{cases}$$

In this problem, we will use this model to make a simple picture of the electronic absorption spectrum of a conjugated molecule.

- What are the energy levels available to the electron in this “molecule”?
- Within the electric dipole approximation, what are the selection rules for the electronic transitions in this model? Justify your answer.
- Assuming the electron starts in the ground state of the 1D box potential, sketch the absorption spectrum for the molecule.
- How does the wavelength of the lowest energy absorption feature compare to the length of the molecule? Does this make sense?

Problem 3 (15 points): *Shifted Harmonic Oscillators and Franck-Condon*

Very often, the bond length of a diatomic molecule changes when we electronically excite the system. Thus, if the vibrational potential energy of the ground state is approximately harmonic

$$V_0(x) = \frac{1}{2}kx^2$$

the potential in the 1st excited state is approximately given by

$$V_1(x) = E_1 + \frac{1}{2}k(x - \Delta)^2.$$

- Sketch V_0 and V_1 together with the energy levels available to this molecule. How will these energies change as you increase Δ ?
- On your sketch, draw a line indicating the maximum intensity absorption transition within the Franck-Condon approximation. How will the energy of this transition change as you increase Δ ?

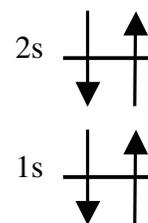
Problem 4 (25 points+10 points extra credit): *Beryllium Atom*

The ground state of the beryllium atom can be represented by the stick diagram at right.

- What is the ground state energy of beryllium in the independent particle model? Please express your answer in terms of hydrogen atom orbital energies and *spatial* Coulomb (J) and Exchange (K) integrals.
- What is the ionization energy $E_{\text{IE}} = E(\text{Be}) - E(\text{Be}^+)$ of Beryllium in the independent particle model (IPM)? Again, please give your answer in terms of hydrogen atom energies and *spatial* Coulomb (J) and Exchange (K) integrals.
- Given the following values of Coulomb and Exchange integrals assign a numerical value to the IPM ionization energy of Be. Compare your result to the experimental value of -9.3 eV.

$$\begin{array}{llll} J_{1s1s} = 68.0 \text{ eV} & J_{1s2s} = 19.0 \text{ eV} & K_{1s2s} = 3.5 \text{ eV} & J_{2s2s} = 14.1 \text{ eV} \\ J_{1s2p} = 26.4 \text{ eV} & K_{1s2p} = 1.8 \text{ eV} & J_{2s2p} = 17.6 \text{ eV} & K_{2s2p} = 3.2 \text{ eV} \end{array}$$

- (Extra Credit) Experimentally it is known that Be^- is unstable – it always falls apart into Be plus an electron. Use the IPM to compute the electron affinity, $E_{\text{EA}} = E(\text{Be}^-) - E(\text{Be})$, for beryllium. Does your numerical result support the experimental finding that Be^- is unstable?



Problem 5 (35 points) Qualitative MO Picture of Cyclobutadiene

As you may have been taught, aromaticity follows the $4n+2$ rule: systems with $4n+2$ π -electrons (i.e. 6,10,14 ... electrons) are aromatic while those with $4n$ π -electrons (i.e. 4,8,12 ...) are not. In class, we treated the simple example of benzene as an example of aromaticity. In this problem we will look at cyclobutadiene as an example of *anti*-aromaticity.



- (a) First, let us assume cyclobutadiene is a perfect square (as on the left). Apply the standard Hückel MO treatment to determine the MOs in cyclobutadiene. Specifically, show that the MOs below are eigenvectors and determine their eigenvalues.

$$\mathbf{c}^1 = \frac{1}{2} \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix} \quad \mathbf{c}^2 = \frac{1}{2} \begin{pmatrix} 1 \\ 1 \\ -1 \\ -1 \end{pmatrix} \quad \mathbf{c}^3 = \frac{1}{2} \begin{pmatrix} 1 \\ -1 \\ -1 \\ 1 \end{pmatrix} \quad \mathbf{c}^4 = \frac{1}{2} \begin{pmatrix} 1 \\ -1 \\ 1 \\ -1 \end{pmatrix}$$

- (b) Compute the ground state energy of cyclobutadiene within the Hückel approximation. Is there anything unusual about your ground state?

Now, let us assume that the C-C bonds are **not** all the same length. Rather assume there are two short “double” bonds and two long “single” bonds, as on the right above. Since the bond lengths are not the same, we must modify our Hückel prescription: the off-diagonal matrix elements should be larger for the shorter bonds and smaller for the longer ones. Assume therefore that there are two different β values in your Hückel calculation: one for “single” bonds ($\beta_s = \beta - \delta$) and one for double bonds ($\beta_d = \beta + \delta$). Note that α , β and δ are all negative constants with units of energy.

- (c) Build a modified Hückel Hamiltonian that reflects the alternating single/double bond pattern. Show that the eigenvectors are unchanged from part (a) and compute their eigenvalues.
- (d) Compute the ground state energy of the rectangular version of cyclobutadiene. Is this energy lower or higher than the ground state energy of the square structure? What does this say about aromaticity in cyclobutadiene?

Problem 6 (50 points +10 points extra credit) IR Spectroscopy Under a Deadline

You have a contract with the Army Research Office (ARO) to determine the equilibrium bond length (r_e), vibrational frequency (ω_e), and electric dipole moment (μ_{el}) of the electronic ground state of TAt (tritium astatide). Your contract terminates tomorrow and you must write a final report. Last night, on your desperate final attempt to record the vibration-rotation spectrum of TAt in an electric field of 100,000 Volts/cm, you obtained a spectrum unlike any you had observed previously. You suspect that this spectrum is that of the TAt $v = 1 \leftarrow v = 0$ transition, but you have no additional scheduled experimental time on the hyper-IPECAC facility which is the only Astatine source ($^{210}\text{At}_{85}$ has a half life of 8.3 hours) in the world capable of generating the At flux needed for your experiment. Therefore you must write your final report to ARO without doing any further experiments to verify whether your spectrum is that of TAt or some other molecule. The likely other molecules include At_2 , T_2 , HAt, DAt, HT, and DT (you may ignore all other possibilities here). Your continued funding by ARO depends on the timely submittal of your report, but your career depends on its correctness.

One of your research assistants has provided you with the following possibly useful information:

Atomic Weight	H	1.00782	Ionization Potentials	H	109,677.581 cm ⁻¹
	D	2.01410		F	140,553.5 cm ⁻¹
	T	3.01605		Cl	104,991 cm ⁻¹
	At	210.		Br	95,550 cm ⁻¹
				I	84,340 cm ⁻¹
				At	_____

“Covalent Radius”	H	0.32 Å	“Ionic Radius”	H ⁻	2.08 Å
	F	0.72 Å		F ⁻	1.36 Å
	Cl	0.99 Å		Cl ⁻	1.81 Å
	Br	1.14 Å		Br ⁻	1.95 Å
	I	1.33 Å		I ⁻	2.16 Å
	At	1.45 Å		At ⁻	_____

<u>Ground State</u>		<u>ω_e</u>	<u>R_e</u>	<u>μ_{el}</u>
HF	$^1\Sigma$	4138.32 cm ⁻¹	0.9168 Å	1.8262 D
HCl	$^1\Sigma$	2990.95 cm ⁻¹	1.2746 Å	1.1085 D
HBr	$^1\Sigma$	2648.98 cm ⁻¹	1.4144 Å	0.8265 D
HI	$^1\Sigma$	2309.01 cm ⁻¹	1.6092 Å	0.4477 D
HAt	?	-----	-----	-----
F ₂	$^1\Sigma_r$	916.64 cm ⁻¹	1.4119 Å	-----
Cl ₂	$^1\Sigma_r$	559.72 cm ⁻¹	1.9879 Å	-----
Br ₂	$^1\Sigma_r$	325.321 cm ⁻¹	2.2811 Å	-----
I ₂	$^1\Sigma_r$	214.50 cm ⁻¹	2.6663 Å	-----
At ₂	?	-----	-----	-----
H ₂	$^1\Sigma_r$	4401.21 cm ⁻¹	0.7414 Å	-----

Some useful conversion formulas (B_e is in cm⁻¹ if μ is in atomic mass units and r_e is in cm):

$$\text{Reduced Mass: } \mu(XY) = \frac{M_X M_Y}{M_X + M_Y} \quad \omega_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (\text{cm}^{-1})$$

$$B_e = \frac{1.6858 \times 10^{-15}}{\mu r_e^2} \quad (\text{cm}^{-1})$$

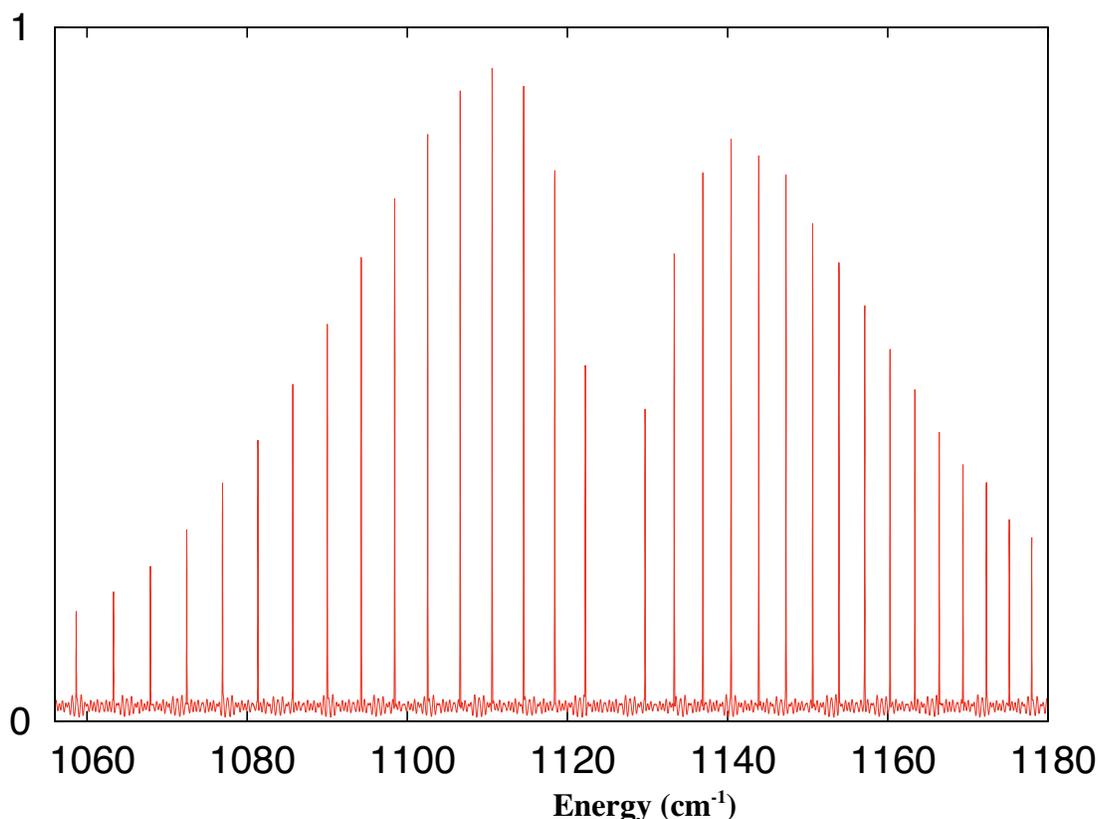
In the absence of the electric field, the vibrational rotational energy is given by:

$$E_{v,J}/hc = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + [B_e - \alpha_e(v + 1/2)]J(J + 1). \quad (\text{cm}^{-1})$$

Before analyzing your spectrum and writing your report to ARO, it would be a good idea to make some predictions about the spectroscopic properties of TAt.

- (5 points) Use the properties of related atoms and molecules to estimate r_e and ω_e for TAt.
- (5 points) Compute B_e from your estimated r_e . Let $\alpha_e \approx 0$ and $\omega_e x_e \approx 0$ and calculate the frequencies (in cm^{-1}) of the 3 lowest-J transitions in the P and R branches of the $v = 1 \leftarrow v = 0$ rotation-vibration band.
- (5 points) Estimate the electric dipole moment, μ_{el} , for TAt. Do you expect the T or the At to have a net positive charge? Why?

You record the infrared spectrum below for what (you hope) is TAt:



You identify the following lines from the spectrum (all in cm^{-1}):

1058.66, 1063.32, 1067.92, 1072.46, 1076.93, 1081.35, 1085.71, 1090.01, 1094.25, 1098.43,
 1102.55, 1106.61, 1110.60, 1114.54, 1118.42, 1122.24, 1129.70, 1133.34, 1136.92, 1140.44,
 1143.89, 1147.29, 1150.63, 1153.91, 1157.13, 1160.29, 1163.39, 1166.43, 1169.40, 1172.32,
 1175.18, 1177.98

- (10 points+10 points extra credit) Assign a few lines of the rotation-vibration spectrum. Two or three lines each in the R and P branches will be sufficient. Assume $\alpha_e \approx 0$ and $\omega_e x_e \approx 0$ and use

your assigned lines to determine ω_e and B_e . Could this be TAt? For extra credit, you may instead assume $\alpha_e \neq 0$ and $\omega_e x_e \neq 0$ and use your assigned lines to compute $\omega_e - 2\omega_e x_e$, B_e and α_e .

- (e) (5 points) Which of the molecules At₂, T₂ HAt, DAt, HT, and DT are expected to have electric dipole allowed rotation-vibration spectra? If you are undecided about HT and DT, state the reasons for and against.
- (f) (5 points) Compute the minimum necessary spectroscopic information that could be useful in showing that your observed spectrum is not due to any of the molecules from part (e) which have allowed rotation-vibration spectra. Could this spectrum be from any of the other likely candidates?

The $v = 1 \leftarrow v = 0$ spectrum consists of a series of absorption lines following the selection rule $\Delta J = \pm 1$ (R and P branches). In the absence of an external electric field, all $2J + 1$ M_J components of each J-level are exactly degenerate and the spectrum consists of simple R and P lines. When a 10^5 V/cm electric field is applied, a new term is added to the Hamiltonian:

$$\hat{\mathbf{H}}^{\text{Stark}} = \boldsymbol{\varepsilon} \cdot \boldsymbol{\mu}$$

If this field lies along the laboratory z-direction, the M_J -degeneracy is lifted. The **only non-zero** integrals involving the Stark-effect Hamiltonian are

$$\int \phi_{J,M_J}^* \hat{\mathbf{H}}^{\text{Stark}} \phi_{J-1,M_J} d\tau = \mathbf{H}_{J,M;J-1,M}^{\text{Stark}} = f \mu_{el} \varepsilon_z \left[\frac{J^2 - M^2}{4J^2 - 1} \right]^{1/2}$$

$$\int \phi_{J,M_J}^* \hat{\mathbf{H}}^{\text{Stark}} \phi_{J+1,M_J} d\tau = \mathbf{H}_{J,M;J+1,M}^{\text{Stark}} = f \mu_{el} \varepsilon_z \left[\frac{(J+1)^2 - M^2}{(2J+1)(2J+3)} \right]^{1/2}$$

where f is a constant whose value depends on the units used. If μ_{el} is in Debye (D), ε_z is in Volts/cm, and $\mathbf{H}_{JM;J\pm 1,M}^{\text{Stark}}$ is desired in cm^{-1} , the conversion factor is $f = 1.6794 \times 10^{-5} [(\text{V/cm})\text{D}]^{-1}$.

At $E = 10^5$ V/cm, the lines at 1129.70 and 1122.24 cm^{-1} split into two components separated by $9.0 \times 10^{-3} \text{ cm}^{-1}$. The lines at 1133.34 and 1118.42 cm^{-1} broaden slightly, but no splitting is resolvable. The electric field has no perceptible effect on all of the remaining lines.

- (g) (10 points) Calculate the Stark splitting for a generic diatomic molecule in $J = 1$. The $M_J = 0$ component is pushed down by $J = 2, M_J = 0$ and pushed up by $J = 0, M_J = 0$. The $M_J = +1$ and $M_J = -1$ levels are both pushed down the same amount by $J = 2, M_J = 1$, and $M_J = -1$, but there are no $J = 0, M_J = \pm 1$ levels to push them up. Use second order perturbation theory to express the energy shifts in terms of μ_{el} and B_e (specifically, μ_{el}^2/B times some J-dependent factors).
- (h) (5 points) Interpret the observed Stark effect and use it to estimate μ_{el} . Does the Stark effect determine the sign of μ_{el} ?

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