

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 : _____ *Key* _____

Problem 1 (50 points): Shorter Answer

A) A proton is attached to a silicon surface by a bond that has a force constant of $k = 500 \text{ kg/s}^2$. 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.

For the harmonic oscillator ground state, $\langle x^2 \rangle = \frac{\hbar}{2\mu\omega} = \frac{\hbar}{2\sqrt{\mu k}}$. This translates into $\sigma_x = 7.5$

picometers. The force constant was supposed to be 5, not 500, which would have led to an uncertainty of 75 pm. (7 points)

B) Suppose you have an $^1\text{H}^19\text{F}$ molecule (bond length $R = 92 \text{ pm}$) rotating with total angular momentum J . Approximately what value of J would it take for this molecule to have as much rotational kinetic energy as a hydrogen atom in a 2p state?

For the HF molecule the energy is, $\frac{\hbar^2}{2I_{\text{HF}}} J(J+1)$, while for the Hydrogen atom the rotational

kinetic energy is $\frac{\hbar^2}{2I_{\text{elec}}} L(L+1) = \frac{\hbar^2}{I_{\text{elec}}}$. The two are equal if $\frac{2I_{\text{HF}}}{I_{\text{elec}}} = J(J+1)$.

$$I_{\text{HF}} \approx \frac{1}{2} m_p \times (9.2 \times 10^{-11})^2 = 7 \times 10^{-48} \quad I_{\text{elec}} \approx \frac{1}{2} m_e \times (5.2 \times 10^{-11})^2 = 1.2 \times 10^{-51}$$

so, $J(J+1)$ needs to be about 12,000, which will happen when J is 100 or so. The difference arises because the masses differ by a factor of 1800, so the moments of inertia are different by a similar factor. (10 points)

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} ($Z=26$)

The trend is $r_n \propto n^2/Z$. This gives $H \approx \text{Be} > \text{Fe} > \text{Ne} > \text{Na} > \text{C}$ because the corresponding values of n^2/Z come out to $1.0 \approx 1.0 > .96 > .90 > .82 > .67$. (8 points)

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?

The point midway between the atoms is $1 a_0$ away from each nucleus. Thus at this point

$$1s_A(r) = 1s_B(r) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-1} = N e^{-1}$$

Where N is the normalization constant (7.6×10^{30} in MKS units). Meanwhile, for the bonding MO,

$$P^+ = |\psi^+(r)|^2 = \left| \frac{Ne^{-1} + Ne^{-1}}{\sqrt{2(1+S)}} \right|^2 = 1.2 N^2 e^{-2}$$

and for the antibonding MO,

$$P^- = |\psi^-(r)|^2 = \left| \frac{Ne^{-1} - Ne^{-1}}{\sqrt{2(1-S)}} \right|^2 = 0$$

Thus, the electron is more likely to be at the midpoint in the bonding orbital and less so in the antibonding one. (10 points)

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

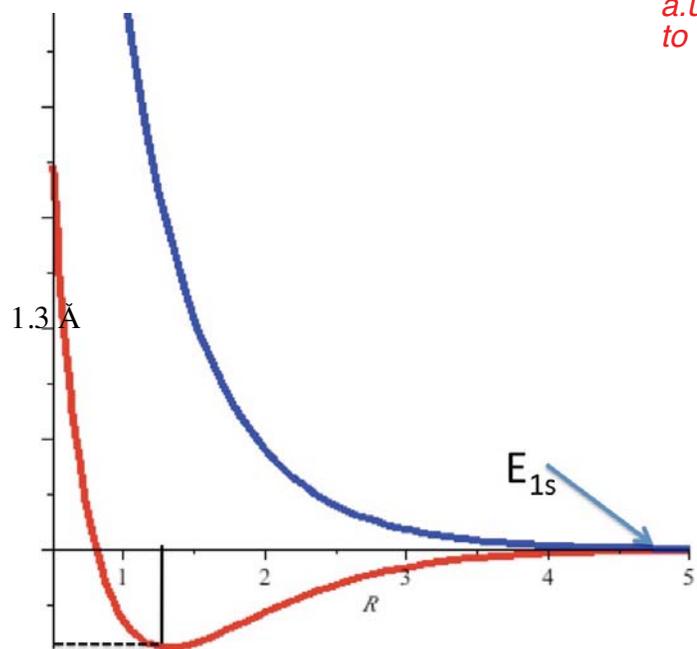
6-31G(d,p)

$$STO-3G < 3-21G < 6-31G(d,p) < TZP < QZP$$

QZP will be most accurate because it gives the most flexible description of the wavefunction. (7 points)

F) The energy curves for the σ and σ^* states of H_2^+ are shown below. Draw the analogous curves for HeH^{2+} , labeling any important features.

that in HeH^{2+} 1) the bond is shorter and 2) the bonding and antibonding orbitals lead to different energies as $R \rightarrow \infty$. The bonding orbital leads to E_{1s} for helium (-2 a.u.), while the antibonding orbital leads to E_{1s} for hydrogen (-1/2 a.u.) (8 points)



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.

- (a) What are the energy levels available to the electron in this “molecule”?

$$E_n = \frac{n^2 h^2}{8mL^2} \quad n=1,2,3\dots \text{ (5 points)}$$

- (b) Within the electric dipole approximation, what are the selection rules for the electronic transitions in this model? Justify your answer.

The selection rule takes the form

$$0 \neq \int \psi_f^* \hat{\mu} \psi_i dr$$

The dipole operator for the electron is $\mu = e r$, which is odd. The PiB eigenstates are even when n is odd and odd when n is even. The dipole moment is odd. The only integral is only non-zero, then, if one of the functions is even and the other is odd. Thus, the selection rule is that Δn must be an odd number. (10 points)

- (c) Assuming the electron starts in the ground state of the 1D box potential, sketch the absorption spectrum for the molecule.

A correct sketch shows sharp lines at 3α , 15α , $35\alpha\dots$ where $\alpha = h^2/8mL^2$. (5 points)

- (d) How does the wavelength of the lowest energy absorption feature compare to the length of the molecule? Does this make sense?

The wavelength of the lowest absorption is $\lambda = hc/E = 8mL^2/h$. Thus, the absorption wavelength gets longer as the molecule gets longer. The L^2 dependence is incorrect, however. A better picture obtains if we realize that as the molecule gets longer, one typically has more and more π electrons, which fill up more and more of the box levels. (5 points)

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

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

- (a) Sketch V_0 and V_1 together with the energy levels available to this molecule. How will these energies change as you increase Δ ?

The surfaces are two identical parabolas displaced horizontally from one another by Δ and vertically by E_1 . The energy levels consist of a series of equally spaced vibrational states for each electronic state. Changing Δ only changes the horizontal shift and will not change the absolute energies at all. (7 points)

- (b) 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 ?

The FC transition is a vertical line from the $i=0$, $n=0$ state (or equivalently the bottom of the lower parabola) to the upper parabola. Changing Δ will change the point at which this line

strikes the upper surface. In particular, increasing Δ will increase the energy of the FC maximum absorption. (8 points)

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.

- (a) 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.

$$E = 2E_{1s} + 2E_{2s} + J_{1s1s} + 4J_{1s2s} - 2K_{1s2s} + J_{2s2s} \quad (9 \text{ points})$$

- (b) What is the ionization energy $E_{IP} = E(\text{Be}) - E(\text{Be}^+)$ 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.

$$E_{IP} = E_{2s} + 2J_{1s2s} - K_{1s2s} + J_{2s2s} \quad (9 \text{ points})$$

- (c) 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.

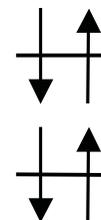
$$J_{1s1s} = 68.0 \text{ eV} \quad J_{1s2s} = 19.0 \text{ eV} \quad K_{1s2s} = 3.5 \text{ eV} \quad J_{2s2s} = 14.1 \text{ eV}$$

$$J_{1s2p} = 26.4 \text{ eV} \quad K_{1s2p} = 1.8 \text{ eV} \quad J_{2s2p} = 17.6 \text{ eV} \quad K_{2s2p} = 3.2 \text{ eV}$$

$$E_{IP} = -5.8 \text{ eV}, \text{ so the electron is somewhat too weakly bound (7 points)}$$

- (d) (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, $E_{EA} = E(\text{Be}^-) - E(\text{Be})$, for beryllium. Does your numerical result support the experimental finding that Be^- is unstable?

$$E_{EA} = E_{2p} + 2J_{1s2p} - K_{1s2p} + 2J_{2s2p} - K_{2s2p} = +35 \text{ eV}. \text{ So, yes, this is unstable. (10 points)}$$



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.

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

The Hamiltonian is

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta & 0 & \beta \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ \beta & 0 & \beta & \alpha \end{pmatrix}$$

To verify that these are eigenvectors, just compute $\mathbf{H} \cdot \mathbf{c}$ for each of the vectors above. The resulting eigenvalues are $\alpha+2\beta, \alpha, \alpha$ and $\alpha-2\beta$, respectively. (10 points)

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

The ground state energy will be $E=2E_1+2E_2=4\alpha+4\beta$. The unusual point is that the ground state is degenerate, because \mathbf{c}^1 and \mathbf{c}^2 have the same energy. (7 points)

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.

The Hamiltonian is

$$\mathbf{H} = \begin{pmatrix} \alpha & \beta + \delta & 0 & \beta - \delta \\ \beta + \delta & \alpha & \beta - \delta & 0 \\ 0 & \beta - \delta & \alpha & \beta + \delta \\ \beta - \delta & 0 & \beta + \delta & \alpha \end{pmatrix}$$

To verify that these are eigenvectors, again just compute $\mathbf{H} \cdot \mathbf{c}$ for each of the vectors above. The resulting eigenvalues are $\alpha+2\beta$, $\alpha+2\delta$, $\alpha-2\delta$ and $\alpha-2\beta$, respectively. Note that

depending on how the atoms are numbered, the \mathbf{H} changes so that $\beta-\delta$ and $\beta+\delta$ switch places. In this case, E_2 and E_3 will also be swapped relative to the answer here. (10 points)

- (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?

The ground state energy will be $E=2E_1+2E_2=4\alpha+4\beta+4\delta$. This energy is lower than the energy of the square form and suggests the molecule will want to deform into a rectangle. Thus the "antiaromatic" square form is unstable. Note that if the single-double pattern was reversed in part (c) then $E_3 < E_2$ and the correct ground state energy is $E=2E_1+2E_3=4\alpha+4\beta+4\delta$. Thus, the individual energies flip-flop, but the total stays the same, as long as we remember to occupy the lowest energy orbitals. (8 points)

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	$^1\Sigma_{g^+}$	916.64 cm ⁻¹	1.4119 Å	-----
Cl ₂	$^1\Sigma_{g^+}$	559.72 cm ⁻¹	1.9879 Å	-----
Br ₂	$^1\Sigma_{g^+}$	325.321 cm ⁻¹	2.2811 Å	-----
I ₂	$^1\Sigma_{g^+}$	214.50 cm ⁻¹	2.6663 Å	-----
At ₂	?	-----	-----	-----
H ₂	$^1\Sigma_{g^+}$	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.

(a) (5 points) Use the properties of related atoms and molecules to estimate r_e and ω_e for TAt.

$$r_e(\text{TAt}) \approx r_e(\text{HI}) + (\text{Covalent Radius}) = 1.61 + .12 = 1.73 \text{ \AA}$$

$$\omega_e(\text{HAt}) \approx 2\omega_e(\text{HI}) - \omega_e(\text{HBr}) = 1969 \text{ cm}^{-1}$$

$$\mu(\text{TAt}) = 1.007 \cdot 210 / 211.007 = 2.973$$

$$\mu(\text{TAt}) = 3.016 \cdot 210 / 213.016 = 2.973$$

$$\omega_e(\text{TAt}) \approx (1.002 / 2.973)^{1/2} \omega_e(\text{HAt}) = 1143 \text{ cm}^{-1}$$

(b) (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.

$$\mu(\text{TAt}) = 3.016 \cdot 210 / 213.016 = 2.973$$

$$B_e(\text{TAt}) \approx 1.6858 \times 10^{-15} / (2.973 \cdot 1.73 \cdot 1.73) = 1.89 \text{ cm}^{-1}$$

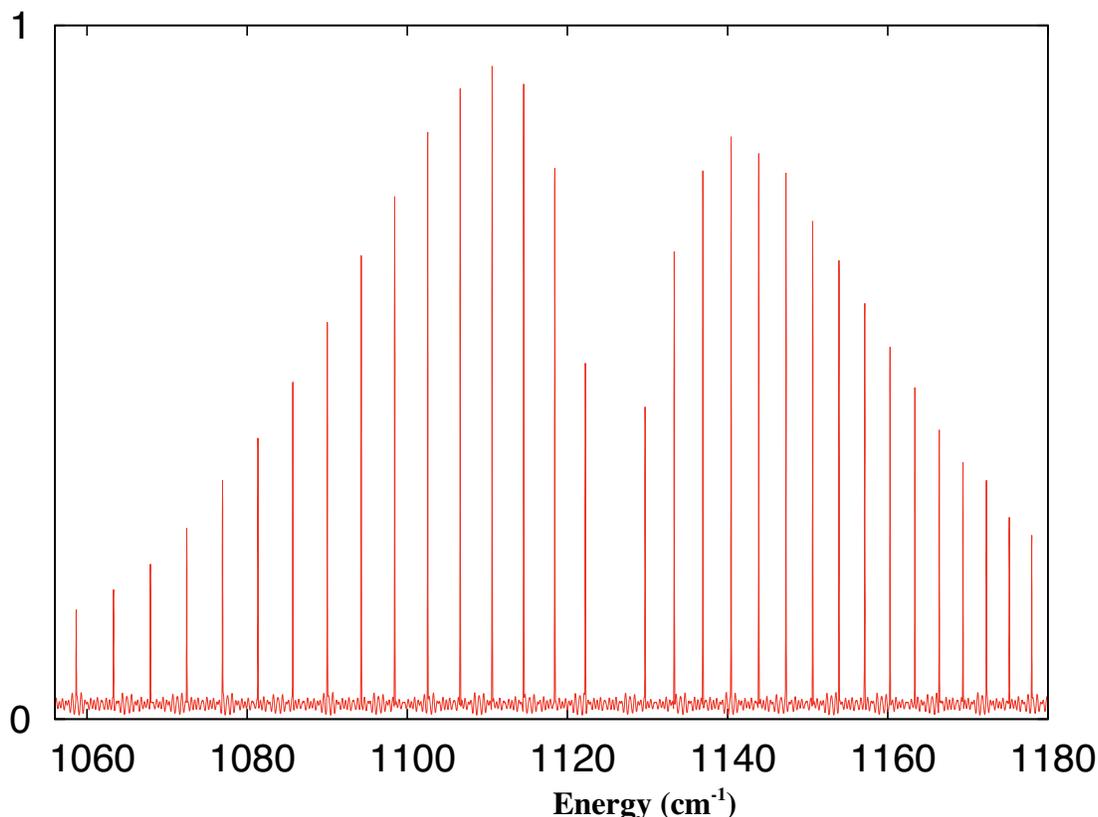
$$P \text{ Transitions: } \omega_e - 2B = 1139.22, \omega_e - 4B = 1135.44 \text{ and } \omega_e - 6B = 1131.66$$

$$R \text{ Transitions: } \omega_e + 2B = 1146.78, \omega_e + 4B = 1150.56 \text{ and } \omega_e + 6B = 1154.34$$

(c) (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?

$\mu \approx 0.1 - 0.2 \text{ D}$. The At will probably have the positive charge because the IP of At is so much lower than for H.

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

- (d) (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 .

In the absence of anharmonicity, you just need the first P transition (P_1 at 1122.24) and the first R transition (R_1 at 1129.70). The vibrational frequency is the average of the two:

$$(P_1 + R_1)/2 = (\omega_e - 2B + \omega_e + 2B)/2 = \omega_e$$

So $\omega_e = 1125.97 \text{ cm}^{-1}$. Meanwhile B is related to the difference

$$(R_1 - P_1)/4 = (\omega_e + 2B - \omega_e - 2B)/4 = B_e$$

So $B_e = 1.87 \text{ cm}^{-1}$.

To obtain the anharmonic terms, we need to assign the next few transitions in the rotational spectrum: P_2 at 1118.42, P_3 at 1114.54, R_2 at 1133.34 and R_3 at 1136.92. We find:

$$(P_1 + R_1)/2 = (\omega_e - 2\omega_e x_e - 2B + \omega_e - 2\omega_e x_e + 2B)/2 = \omega_e - 2\omega_e x_e = 1125.97 \text{ cm}^{-1}$$

Meanwhile, a little more playing around isolates α_e

$$(R_1 - R_2 - P_3 + P_2)/10 = \alpha_e = .03 \text{ cm}^{-1}$$

and $B_e - \alpha_e/2$

$$(R_1 - P_1)/4 = (\omega_e + 2B_e - \alpha_e - \omega_e - 2B_e + \alpha_e)/4 = B_e - \alpha_e/2 \rightarrow B_e = 1.895 \text{ cm}^{-1}$$

In either case, these numbers match reasonably well with our predictions above for the vibrational frequency and rotational constant, so yes this could be TAt.

- (e) (5 points) Which of the molecules At_2 , T_2 , 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.

Only molecules whose dipole changes as the bond length changes will have an IR spectrum. Thus HAt, DAt will certainly have spectra. At_2 and T_2 will definitely not. HT and DT are interesting cases. The dipole will always be almost zero, but because of the different zero point distributions of H, D and T the nuclear charge distribution will not quite have the same center of charge as the electrons. So there can be a small dipole moment, and a very weak IR spectrum.

- (e) (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 vibrational frequencies are way off: $\omega_e(\text{HAt})=1984 \text{ cm}^{-1}$, $\omega_e(\text{DAt})=1403 \text{ cm}^{-1}$, $\omega_e(\text{HT})=3593 \text{ cm}^{-1}$, $\omega_e(\text{DT})=2840 \text{ cm}^{-1}$. Because our frequency is 1126 cm^{-1} we can rule all of these out.

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:

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

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

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

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

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).

The second order energy is

$$\sum_{J', M'_J} \left| \frac{\int \phi_{J, M_J}^* \hat{H}^{Stark} \phi_{J', M'_J} d\tau}{E_J - E_{J'}} \right|^2$$

The integral formulas above collapse the sum to two terms: one with $J'=J+1$ and the other with $J'=J-1$:

$$\frac{\left| \int \phi_{J, M_J}^* \hat{H}^{Stark} \phi_{J+1, M_J} d\tau \right|^2}{E_J - E_{J+1}} + \frac{\left| \int \phi_{J, M_J}^* \hat{H}^{Stark} \phi_{J-1, M_J} d\tau \right|^2}{E_J - E_{J-1}}$$

For $M_J=0$ this gives

$$E_{10} = (f\mu\varepsilon)^2 / (10 B)$$

While for $M_J=\pm 1$ we get

$$E_{10} = -(f\mu\varepsilon)^2 / (20 B)$$

Thus the $M_J=\pm 1$ states shift down and the $M_J=0$ state shifts up, as expected.

- (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} ?

The splitting is $3(f\mu\varepsilon)^2 / (20 B)$. Plugging in the numbers, the dipole comes to $\mu = .20$ Debye, right in line with our expectations. The sign of the dipole cannot be determined by the Stark effect, as it only depends on μ^2 . Hence, chemical intuition must play a role here. Note that the Stark effect gets weaker as J increases and there are more M_J levels that must be split so that the electric field has little effect on the higher lines.

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