NAME:_____ Section:_____ Student Number:_____

Spring 2020 **Chemistry 2000 Midterm #1A** ____/65 marks

INSTRUCTIONS:
1) Please read over the test carefully before beginning. You should have 8 pages of questions, a blank "overflow" page and a periodic table page.
2) If your work is not legible, it will be given a mark of zero.
3) Marks will be deducted for incorrect information added to an otherwise correct answer.
4) Calculators are not permitted.
5) You have 90 minutes to complete this test.

Confidentiality Agreement:
I agree not to discuss (or in any other way divulge) the contents of this exam until after 8:30 pm Mountain Time on Tuesday, February 11th, 2020. I understand that breaking this agreement would constitute academic misconduct, a serious offense with serious consequences. The minimum punishment would be a mark of 0/65 on this exam and removal of the "overwrite midterm mark with final exam mark" option for my grade in this course; the maximum punishment would include expulsion from this university.

Signature: _____ Date: _____
Course: CHEM 2000 (General Chemistry II)
Semester: Spring 2020
The University of Lethbridge

Question Breakdown

Q1	/ 16
Q2	/ 7
Q3	/ 20
Q4	/ 16
Q5	/ 6

Total	/ 65

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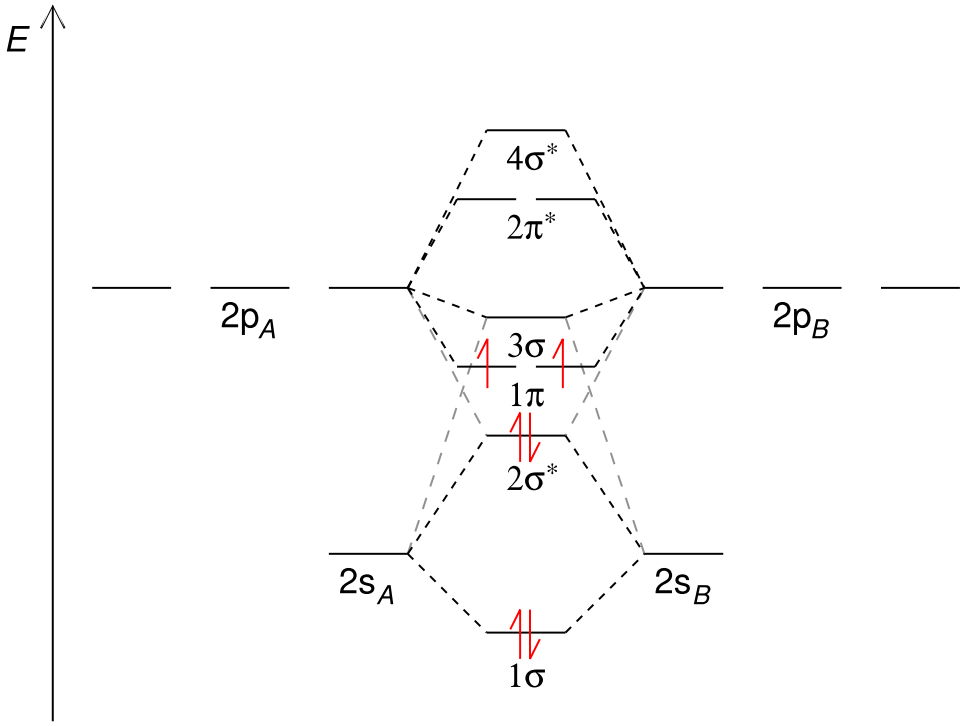
1. **[16 marks]**

(a) Develop the valence molecular orbital energy level diagram for B_2. *[7 marks]*

Your diagram must include:

- labeled molecular orbital energy levels (you don't need to draw pictures of the MOs)
- identification of each molecular orbital as bonding, nonbonding or antibonding
- electrons in the appropriate molecular orbitals

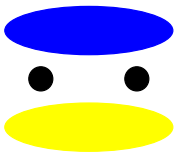


(b) Calculate the bond order for B_2 *[1 mark]*

bond order $= \frac{1}{2}(\text{bonding} - \text{antibonding}) = \frac{1}{2}(4-2) = 1$

(c) Identify and sketch the HOMO and LUMO of B_2. *[4 marks]*

HOMO: 1π LUMO: 3σ



Technically, the 1π orbitals are SOMOs (Singly Occupied Molecular Orbitals), but they are the Highest energy Occupied Molecular Orbitals, and 3σ is the Lowest energy completely Unoccupied Molecular Orbital.

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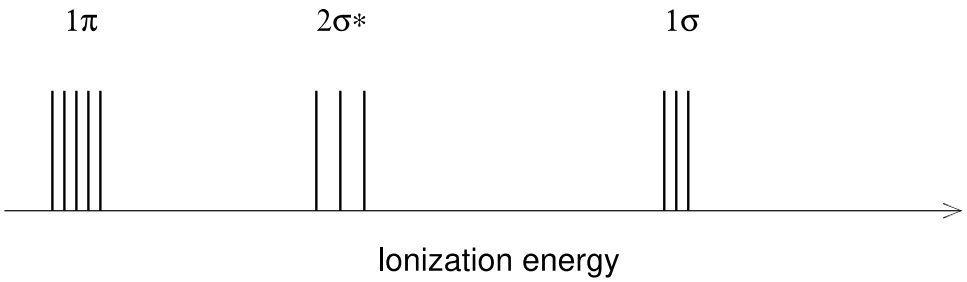
1. …*continued*

(d) Sketch the UV photoelectron spectrum of B_2. Assume that the UV photon used has enough energy to remove electrons from any of the valence orbitals. While you won't be able to put numbers on the horizontal axis, do indicate what quantity is plotted along this axis and the direction in which this quantity increases. The vibrational "frequency" of the neutral B_2 molecule is 1051.3 cm^{-1}. Indicate how the relevant feature(s) of the spectrum relate to this frequency. *[4 marks]*



The 1π and 1σ orbitals are bonding orbitals. Removing an electron from either of these will weaken the bond, and therefore decrease the vibrational spacing, i.e. a smaller spacing than 1051 cm^{-1} would be observed. The 2σ* on the other hand is an antibonding orbital. Removing an electron from this orbital would strengthen the bond, and therefore result in a spacing between the corresponding lines in the spectrum greater than 1051 cm^{-1}.

The axis may be labeled in one of two alternative ways: If labeled "kinetic energy", then it should run the other way (from the drawing above), with the 1σ at the low end and the 1π at higher electron kinetic energies. If labeled "orbital energy", since these are negative, the axis should again run "backwards" since the 1σ is at a lower (more negative) orbital energy than the 1π.
There is no way to predict the number of lines in each cluster, but there should be more than one line drawn.
The spacing between the lines should be greater in the 2σ cluster because it's antibonding.*
The intensities are not all equal in a real PES, so line height doesn't matter.

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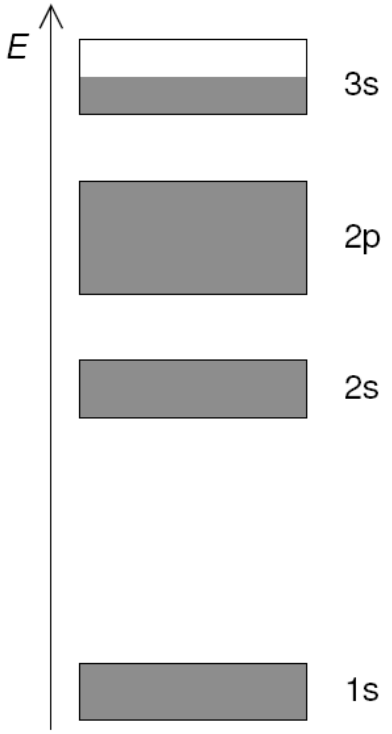
2. Consider a piece of sodium. Use the symbol *N* to represent the number of sodium atoms. **[7 marks]**

(a) Draw a band diagram for sodium. Indicate the atomic orbital(s) that contributed to the band(s) in your diagram. *[3 marks]*



It was not necessary to show any of the core bands (1s, 2s or 2p). Full marks were given for labeled band diagrams clearly showing a half full 3s band. Adding an empty 3p band overlapping the top of the 3s band was also acceptable.

(b) Indicate how many states exist in each band on your diagram. *[1 mark]*

The 3s band contains N states.

A band contains one state for each orbital from which it is made. The 3s band is made from one 3s orbital per sodium atom, and the number of sodium atoms is N.

(c) Indicate how many electrons occupy each band on your diagram. *[1 mark]*

The 3s band contains N electrons.

Each sodium atom contributes one valence electron to the 3s band, and the number of sodium atoms is N.

(d) Is sodium a conductor, semiconductor or insulator? Justify your answer with reference to your band diagram. *[2 marks]*

Conductor.

Because the 3s band is half full, there is no band gap. As such, electrons are easily excited from the occupied states to the unoccupied states of the 3s band.

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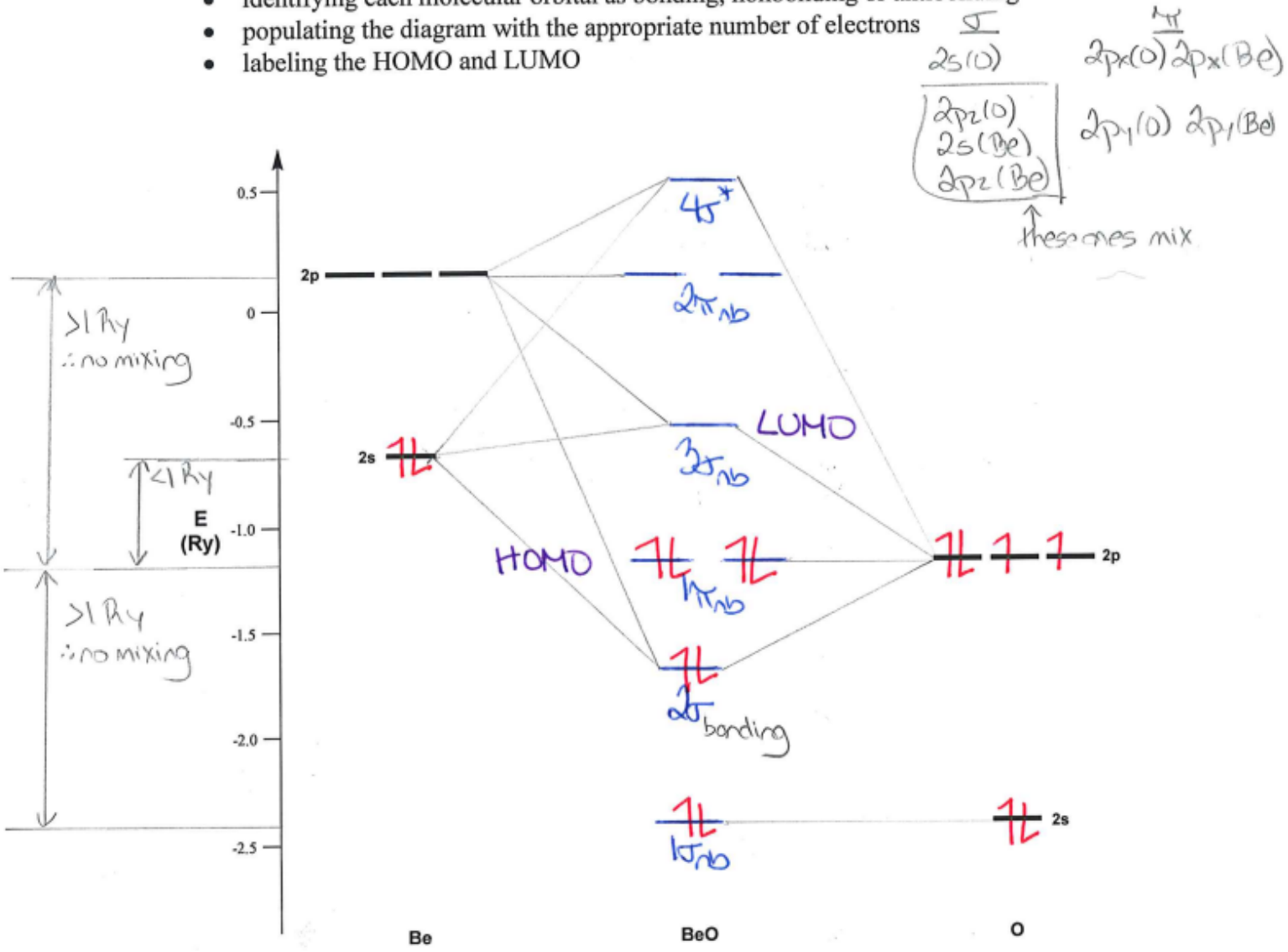
3. Consider beryllium oxide (BeO) according to molecular orbital theory. **[20 marks]**

(a) Draw the Lewis diagram for BeO. *[1 mark]*

(b) Complete the valence molecular orbital energy level diagram below by: *[9 marks]*

- drawing and labeling the molecular orbital energy levels (you don't need to draw pictures of the MOs themselves)
- identifying each molecular orbital as bonding, nonbonding or antibonding
- populating the diagram with the appropriate number of electrons
- labeling the HOMO and LUMO



(c) Write the valence orbital occupancy (electron configuration) for BeO. *[1 mark]*

$(1\sigma_{nb})^2(2\sigma)^2(1\pi_{nb})^4$

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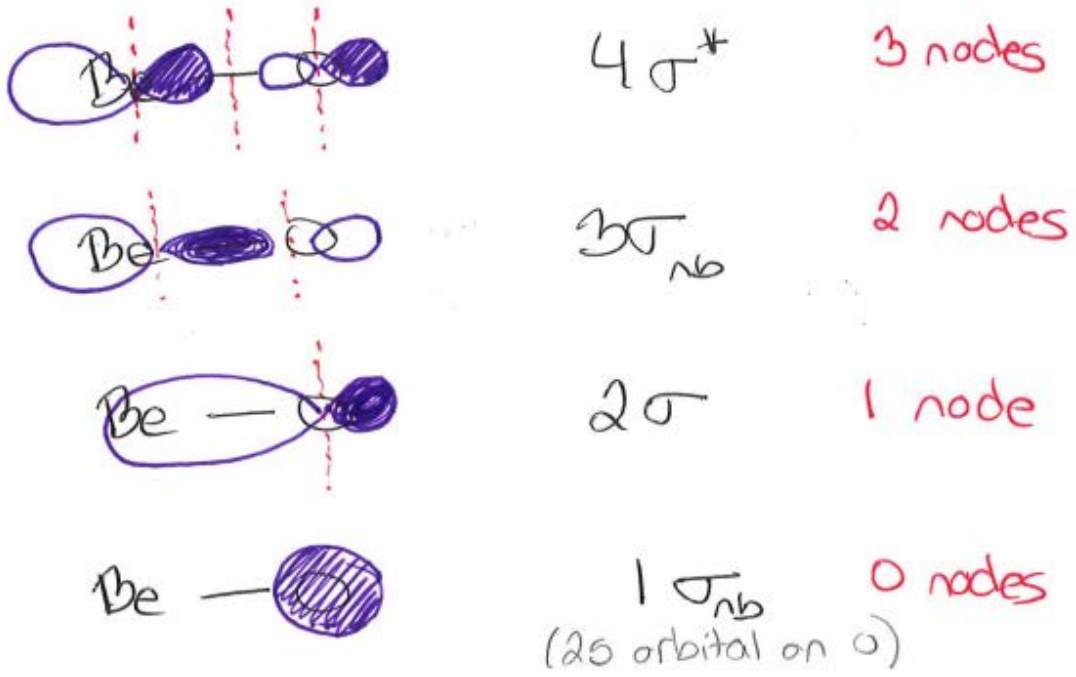
3. …*continued*

(d) Draw each of the **sigma-symmetric** valence molecular orbitals of BeO. *[4 marks]*



(e) When BeO acts as a Lewis acid, do you expect it to react at Be or at O? Justify your answer with reference to the relevant molecular orbital. *[3 marks]*

Be

Lewis acids accept electrons, so they react with their LUMO.

The LUMO of BeO is the $3\sigma_{nb}$ orbital, which is polarized toward Be (because it is closer in energy to the contributing AOs of Be than to the $2p_z$ orbital of O).

So, the Lewis base should attack the Be end of BeO.

(f) Does the bond order implied by your MO diagram agree with that predicted from your Lewis diagram? Explain briefly. *[2 marks]*

No.

The Lewis diagram suggests a bond order of 2 (double bond).

The MO diagram suggests a bond order of 1 (only one pair of bonding electrons).

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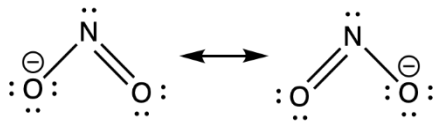
4. **[16 marks]**

(a) Draw a Lewis diagram (with resonance structures, if appropriate) of NO_2^-. *[3 marks]*

Include any non-zero formal charges on the appropriate atom(s).



(b) Use VSEPR theory to predict the shape of NO_2^-. *[1 mark]*

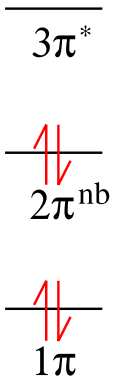
bent

(c) Develop the π MO energy level diagram of NO_2^-. *[4 marks]*

Your diagram must include:

- labeled molecular orbital energy levels
- identification of each molecular orbital as bonding, nonbonding or antibonding
- electrons in the appropriate molecular orbitals

There are four π electrons, two in the double bond, and two from a lone pair one bond away (i.e. from the –O⁻).



(d) Does the π bond order implied by your π MO diagram agree with that predicted from your Lewis diagram(s)? Explain briefly. *[2 marks]*

Total π bonding from the MO diagram: $\frac{1}{2}(\text{bonding} - \text{antibonding}) = \frac{1}{2}(2 - 0) = 1$

Since there are two N–O linkages, the π bond order is $\frac{\text{total π bonding}}{\text{number of N–O linkages}} = \frac{1}{2}$

Two ways to proceed from here:

i. The Lewis diagram has one double bond over the two N–O linkages, so the π bond order from the Lewis diagram is also ½.

ii. To get the overall bond order from an MO diagram that only includes the π bonding, we need to add the assumed σ bond order of 1, i.e. the N–O bond order from the MO diagram is $1 + \frac{1}{2} = \frac{3}{2}$. To get the overall bond order from the Lewis diagram, we average the bond orders in the two resonance structures: $\frac{1}{2}(1 + 2) = \frac{3}{2}$. Again, the two treatments agree.

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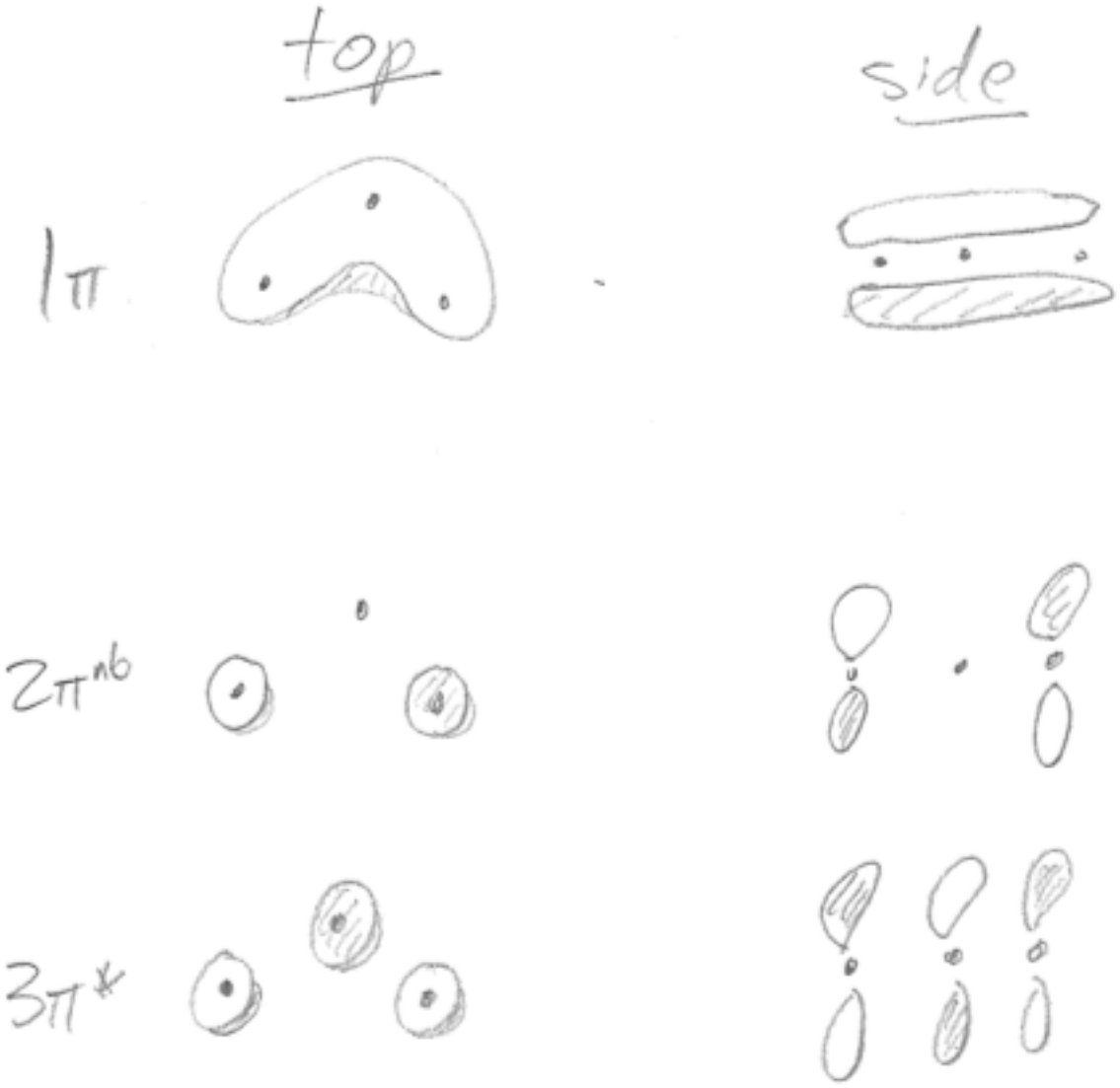
4. *…continued*

(e) Draw the π MOs. Show both a top view and a side view for each π MO. Label each picture so that it is clear which π MO it shows. *[6 marks]*

Dots mark the locations of the nuclei. (The pictures are really hard to interpret without those.) Showing the bottom lobe peeking out from under the top lobe in the top view isn't essential, although then the side view becomes all the more important to figure out what is in your head.



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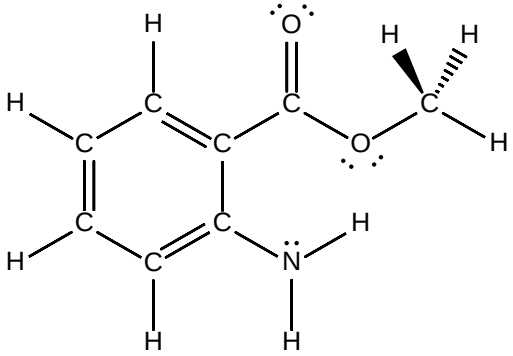
5. The following is a graphic of methyl anthranilate, a compound that occurs naturally in grapes and gives them some of the characteristic grape aroma and flavor. It is the main flavoring agent in grape Kool-Aid. **[6 marks]**



The following questions are to be answered using valence-bond theory.

(a) What is the hybridization of the nitrogen atom? *[1 mark]*

sp^3

(b) What is the hybridization of the carbon atoms in the ring? *[1 mark]*

sp^2

(c) How would valence-bond theory describe the bonding in the C=O group of this molecule? Make sure to provide the description of both the sigma and pi bonds. *[4 marks]*

σ bond: C(sp^2)–O(2p) *[O($2p_x$) or O($2p_y$) is also correct]*
π bond: C(2p)–O(2p) *[C($2p_z$)–O($2p_z$) is also correct]*

Chem 1000 Standard Periodic Table

1												13	14	15	16	17	18
1.0079 **H** 1	**2**																4.0026 **He** 2
6.941 **Li** 3	9.0122 **Be** 4											10.811 **B** 5	12.011 **C** 6	14.0067 **N** 7	15.9994 **O** 8	18.9984 **F** 9	20.1797 **Ne** 10
22.9898 **Na** 11	24.3050 **Mg** 12	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	26.9815 **Al** 13	28.0855 **Si** 14	30.9738 **P** 15	32.066 **S** 16	35.4527 **Cl** 17	39.948 **Ar** 18
39.0983 **K** 19	40.078 **Ca** 20	44.9559 **Sc** 21	47.88 **Ti** 22	50.9415 **V** 23	51.9961 **Cr** 24	54.9380 **Mn** 25	55.847 **Fe** 26	58.9332 **Co** 27	58.693 **Ni** 28	63.546 **Cu** 29	65.39 **Zn** 30	69.723 **Ga** 31	72.61 **Ge** 32	74.9216 **As** 33	78.96 **Se** 34	79.904 **Br** 35	83.80 **Kr** 36
85.4678 **Rb** 37	87.62 **Sr** 38	88.9059 **Y** 39	91.224 **Zr** 40	92.9064 **Nb** 41	95.94 **Mo** 42	(98) **Tc** 43	101.07 **Ru** 44	102.906 **Rh** 45	106.42 **Pd** 46	107.868 **Ag** 47	112.411 **Cd** 48	114.82 **In** 49	118.710 **Sn** 50	121.757 **Sb** 51	127.60 **Te** 52	126.905 **I** 53	131.29 **Xe** 54
132.905 **Cs** 55	137.327 **Ba** 56	**La-Lu**	178.49 **Hf** 72	180.948 **Ta** 73	183.85 **W** 74	186.207 **Re** 75	190.2 **Os** 76	192.22 **Ir** 77	195.08 **Pt** 78	196.967 **Au** 79	200.59 **Hg** 80	204.383 **Tl** 81	207.19 **Pb** 82	208.980 **Bi** 83	(210) **Po** 84	(210) **At** 85	(222) **Rn** 86
(223) **Fr** 87	226.025 **Ra** 88	**Ac-Lr**	(265) **Rf** 104	(268) **Db** 105	(271) **Sg** 106	(270) **Bh** 107	(277) **Hs** 108	(276) **Mt** 109	(281) **Ds** 110	(280) **Rg** 111	(285) **Cn** 112	(284) **Nh** 113	(289) **Fl** 114	(288) **Mc** 115	(293) **Lv** 116	(294) **Ts** 117	(294) **Og** 118

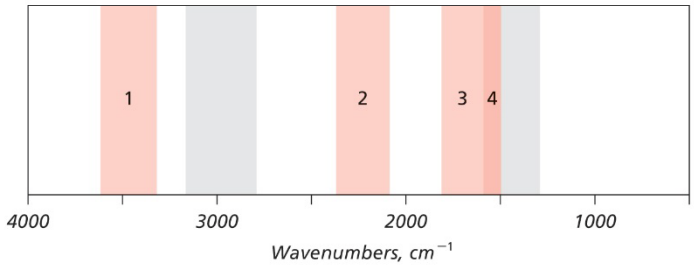
138.906 **La** 57	140.115 **Ce** 58	140.908 **Pr** 59	144.24 **Nd** 60	(145) **Pm** 61	150.36 **Sm** 62	151.965 **Eu** 63	157.25 **Gd** 64	158.925 **Tb** 65	162.50 **Dy** 66	164.930 **Ho** 67	167.26 **Er** 68	168.934 **Tm** 69	173.04 **Yb** 70	174.967 **Lu** 71
227.028 **Ac** 89	232.038 **Th** 90	231.036 **Pa** 91	238.029 **U** 92	237.048 **Np** 93	(240) **Pu** 94	(243) **Am** 95	(247) **Cm** 96	(247) **Bk** 97	(251) **Cf** 98	(252) **Es** 99	(257) **Fm** 100	(258) **Md** 101	(259) **No** 102	(262) **Lr** 103

Developed by Prof. R. T. Boeré (updated 2016)

Table of atomic orbital energies. All energies are in Ry.

	1s	2s	2p
H	-1.00		
He	-1.81		
Li	-4.77	-0.40	
Be	-8.9	-0.69	
B	-14.5	-1.03	-0.42
C	-21.6	-1.43	-0.79
N	-30.0	-1.88	-0.95
O	-39.9	-2.38	-1.17
F	-51.2	-2.95	-1.37
Ne	-64.0	-3.56	-1.59

All energies are from J.C. Slater, *Physical Review* (1955) **98**, 1039-1045.



Region	Frequency range, (cm^{-1})	Bond types	Functional groups
1	3500 – 3200	O—H N—H	Alcohol, phenol Amine, amide
2	2300 – 2100	C≡C C≡N	Alkyne Nitrile
3	1800 – 1650	C═O	Aldehyde Amide Anhydride (2 bands) Carboxylic acid Acid chloride Ester
4	1650 – 1500	C═C C═C C═N N═O	Alkene Arene Imine Nitro compound