

NAME: _____ Section: _____ Student Number: _____

Spring 2015

Chemistry 2000 Midterm #1A

_____/ 55 marks

- INSTRUCTIONS:
- 1) Please read over the test carefully before beginning. You should have 5 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.
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Confidentiality Agreement:

I agree not to discuss (or in any other way divulge) the contents of this exam until after 8:00pm Mountain Time on Tuesday, February 10th, 2015. I understand that breaking this agreement would constitute academic misconduct, a serious offense with serious consequences. The minimum punishment would be a mark of 0/55 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 2015

The University of Lethbridge

Question Breakdown

Q1	/ 6
Q2	/ 4
Q3	/ 15
Q4	/ 14
Q5	/ 9
Q6	/ 3
Q7	/ 4
Total	/ 55

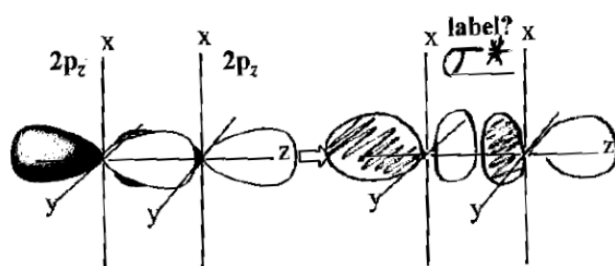
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1. Fill in each blank with the word or short phrase that best completes the sentence. [6 marks]

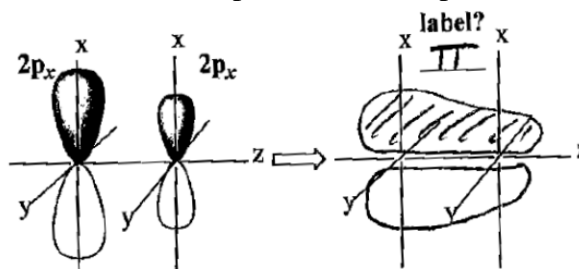
- (a) An exact solution to the Schrödinger wave equation can be derived for H_2^+ by “freezing” the separation of the two H nuclei, an approach which is known as the Born-Oppenheimer approximation.
- (b) The parameter defined in order to correlate the degree of bonding in MO theory with the number of bonds counted from a Lewis diagram is called the bond order.
- (c) Electron density in a molecule is expected to be *highest* in what location? near the nuclei (just as in atoms).
- (d) The frontier molecular orbital (FMO) that is associated with a molecule’s ability to act as a *donor* (i.e. as a Lewis base) is known by the following acronym: HOMO.
- (e) In *linear* and *planar* molecules, the sigma-pi (or σ - π) separation can be used to simplify the treatment of bonding in MO theory.
- (f) In the MO description of bonding in the molecule hydrogen fluoride (HF), the $2p_x$ and $2p_y$ orbitals of fluorine have 100% nonbonding character.

2. Draw and label the correct *shape* of the LCAO-MO for the indicated interaction. Include correct shading. [4 marks]

(a) Destructive overlap.



(b) Constructive polarized overlap.



3. Construct an **atomic orbital – molecular orbital** interaction diagram for difluorine (F_2). [15 marks]

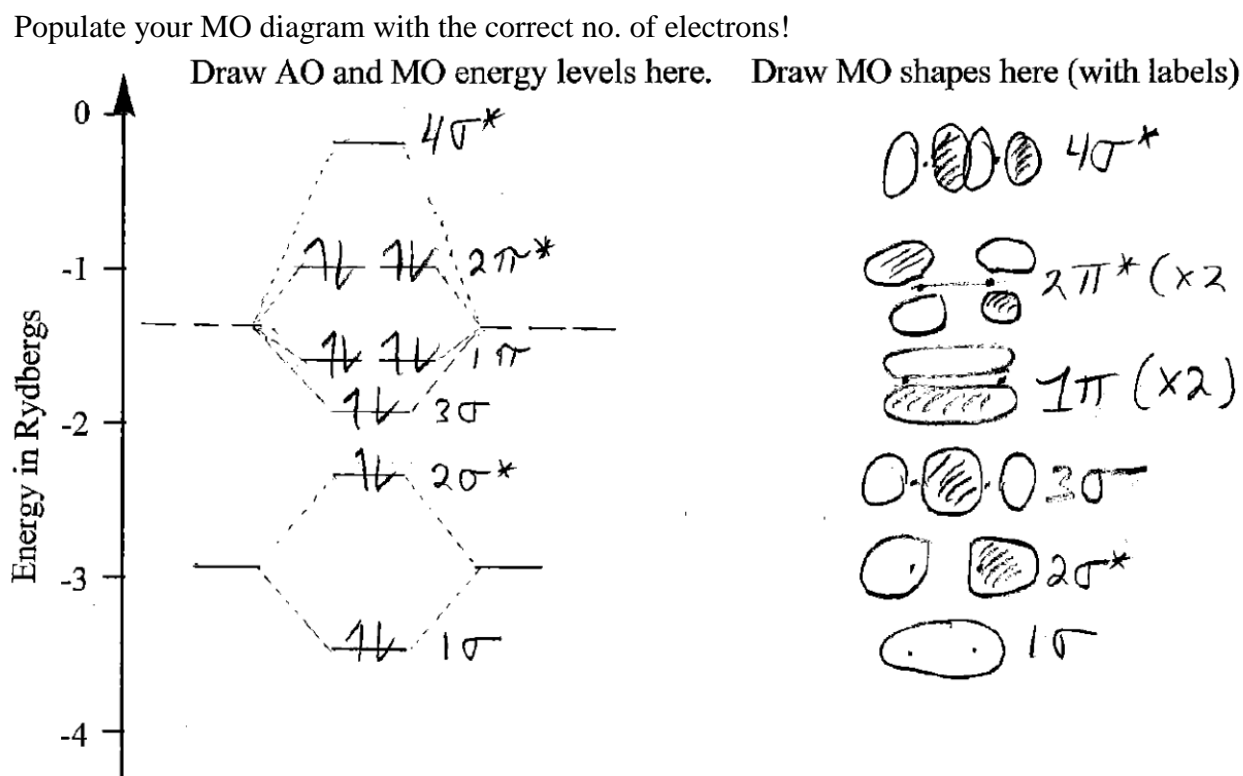
(a) Write the atomic electron configuration for a neutral atom of F and identify the valence electrons.
 $1s^2 \underline{2s^2} \underline{2p^5}$ *valence electrons are underlined*

(b) How many valence electrons does *the difluorine molecule* (F_2) possess?
 14

(c) Which valence AOs of F have σ symmetry?
 $2s$ and $2p_z$

(d) Which valence AOs of F have π symmetry?
 $2p_x$ and $2p_y$

(e) Show energy levels at left as indicated and sketch the resultant LCAO-MOs that are correct in shape and in phase (shading) at right. Be sure to label all the MOs. Make use of the provided energy scale and show both the atomic and molecular energy levels in your diagram. Where possible assign the *dominant bonding character of each MO* using the usual label markers.



(f) Determine the *bond order* in F_2 . Show your work clearly.

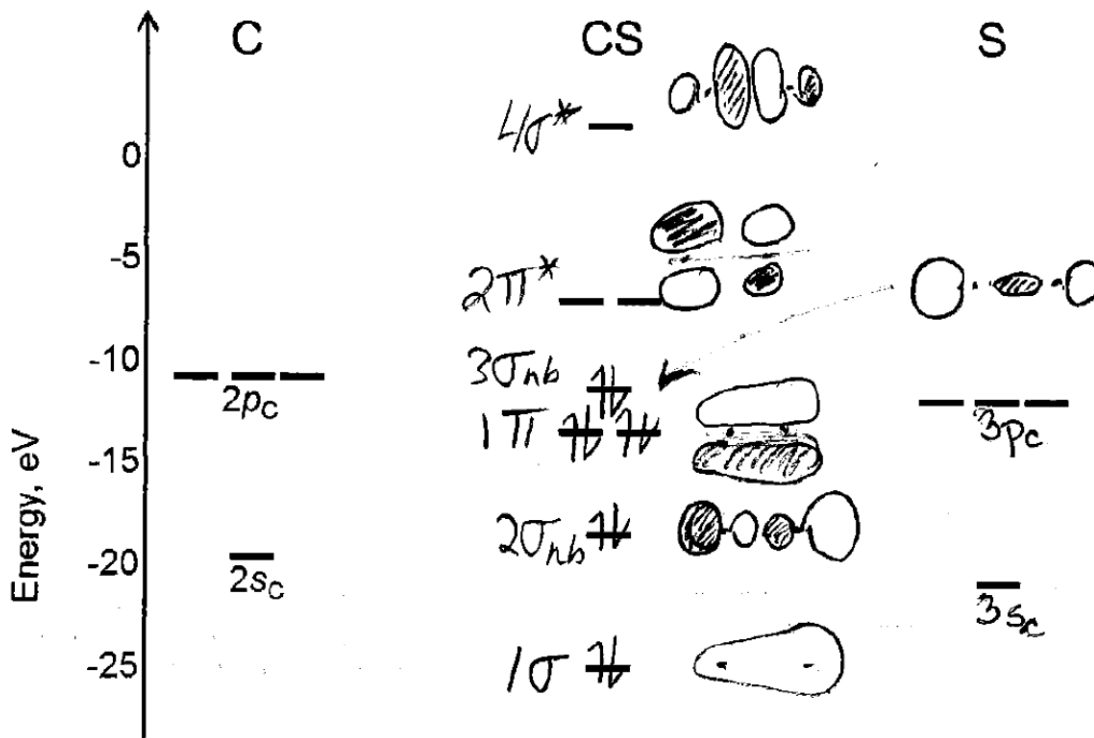
$$\text{bond order} = \frac{1}{2} (\# \text{ bonding electrons} - \# \text{ antibonding electrons}) = \frac{1}{2} (8 - 6) = 1$$

(g) Explain clearly, with reference to the MO diagram, why the molecular ion F_2^{2-} cannot exist. What alternative form of this anion does exist and why?

To make F_2^{2-} from F_2 , two electrons must be added. They will be added to the LUMO ($4\sigma^*$) – which is an antibonding orbital. Adding two antibonding electrons reduces the bond order to 0 and therefore there is no longer a bond between the two fluorine atoms. Instead, two free F^- anions are formed, each obeying the octet rule.

4. [14 marks]

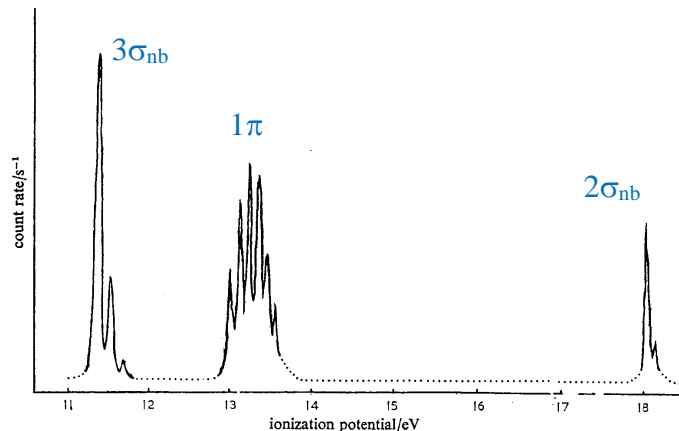
(a) ... Complete the AO-MO interaction diagram for CS...



(b) Write the valence molecular electron configuration of CS in the standard format for diatomics:



(c) Consider the UV-PES diagram for CS shown at right. Assign the ionization processes to the MO diagram by labelling the peaks with the corresponding MO labels from your diagram above.



Simplified UV-PES spectrum of carbon monosulfide (22.2 eV photons)

i. Which peak corresponds to ionization from the highest occupied molecular orbital (HOMO)? *****HOMO is 3σ_{nb}*****

peak at 11.4 eV

ii. Which peak(s) correspond to electrons ionized from bonding MOs? Explain.

peak at 13.3 eV (corresponds to 1π)

This peak shows extensive fine splitting due to vibrational energy levels, indicating a strong change in bond order after the molecule is ionized by exciting an electron out of this MO.

iii. Which peak(s) correspond to electrons ionized from non-bonding MOs? Explain.

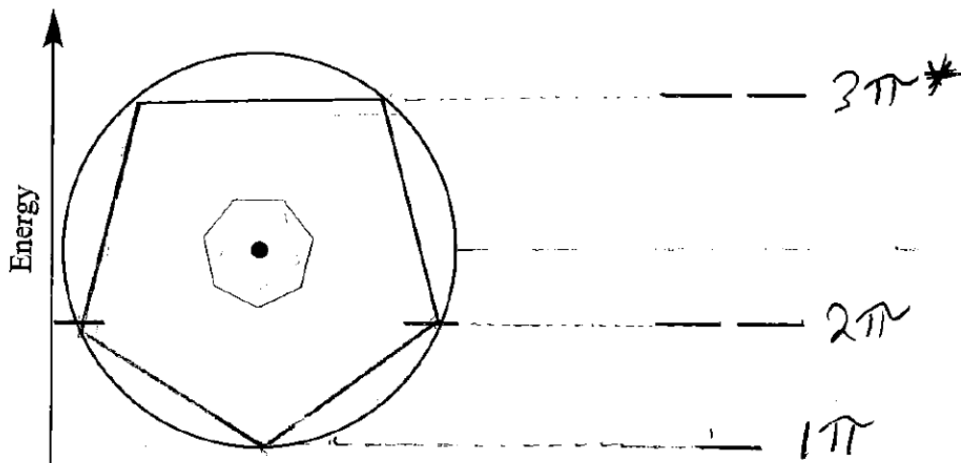
peaks at 11.4 eV and 18 eV (correspond to 2σ_{nb} and 3σ_{nb} respectively)

These peaks are sharp single peaks, indicating little change in bond order after the molecule is ionized by exciting an electron out of one of these MOs.

*****If you hadn't initially designated 2σ and 3σ as nonbonding, this part of the question provided evidence that they were, and you should have gone back to change that on your MO diagram.*****

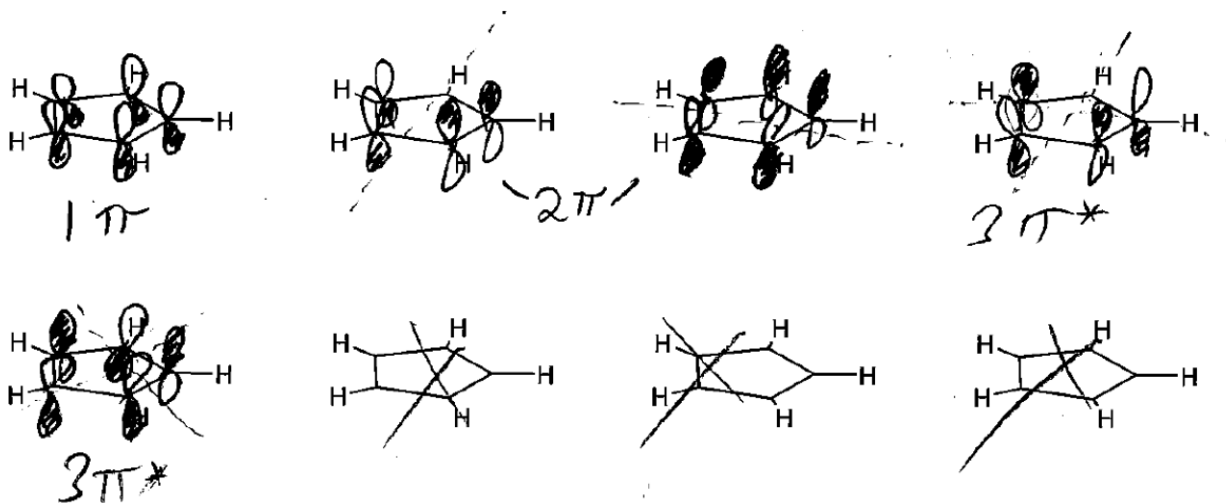
5. [9 marks]

- (a) Use the “Frost circle” approach to generate an approximate valence π -MO energy-level diagram (energy levels only!) for cyclic hydrocarbon species of the form $[\text{C}_5\text{H}_5]^x$. Be sure to label each molecular energy level on your diagram with the correct label. Indicate the *dominant* bonding character with the usual symbols. Pay attention to multiplicity of levels!



- (b) Sketch approximate orbital shapes for each of the π -MOs in your MO diagram. *Fill in as many of the rings as required to complete this project.* Clearly label each MO you decide to draw. Show the resultant \perp nodes.

It is sometimes easier just to draw the atomic p_z orbitals with the correct relative shading (phase).



- (c) Which value of “ x ” (i.e. which charge of $[\text{C}_5\text{H}_5]^x$) will provide the *optimal* π -bonding in this type of hydrocarbon? Show your work or explain your reasoning.

$$x = -1$$

To fill all three π bonding MOs requires 6 π electrons. Each carbon atom contributes one π electron, so you need one extra π electron.

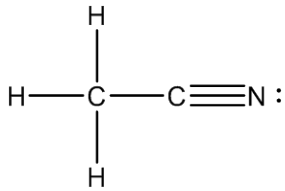
An alternative way to look at this is that the sigma skeleton requires 20 electrons. To fill all three π bonding MOs requires 6 π electrons, meaning that the species would have a total of 26 valence electrons. Neutral C_5H_5 has 25 valence electrons so C_5H_5^- has 26 valence electrons.

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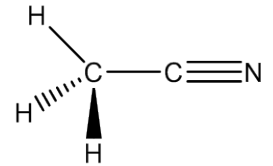
6. Use Valence Bond theory to consider the bonding in acetonitrile (CH_3CN). [3 marks]

(a) Draw the best Lewis structure for CH_3CN .

The three larger atoms are connected C-C-N with three H attached to the terminal C.



which has the shape:



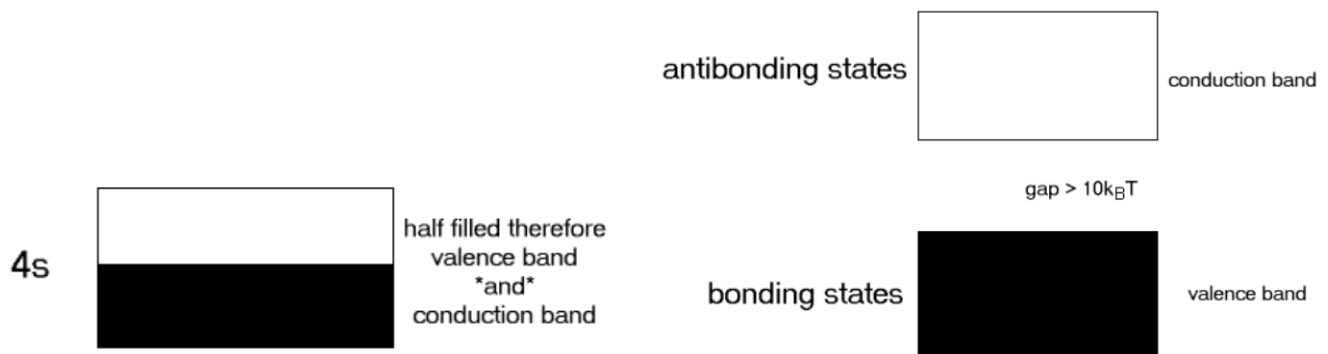
(b) What is the hybridization of each of the following atoms in CH_3CN :

C (of CH_3) = sp^3 C (of CN) = sp

7. Please answer (a) and (b) side by side so that the relative scales are obvious. [4 marks]

(a) Draw the band structure of potassium

(b) Draw the band structure of silicon.



These diagrams show the valence band and conduction band for each element.

Core bands are not shown.

(c) One of these two elements is an insulator. Which one? Explain your choice.

Silicon

Potassium is definitely **not** an insulator! It is an excellent conductor as evidenced by the valence band and conduction band being the same band (allowing electrons to move readily from the valence band to conduction band).

Therefore, silicon must be the insulator. It has an energy gap between the valence band and conduction band that must be large enough ($>10k_B \cdot T$) to make it an insulator.

1.0079 H 1																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) Uut 113	(289) Ff 114	(288) Uup 115	(293) Lv 116	(294) Uus 117	(294) Uuo 118

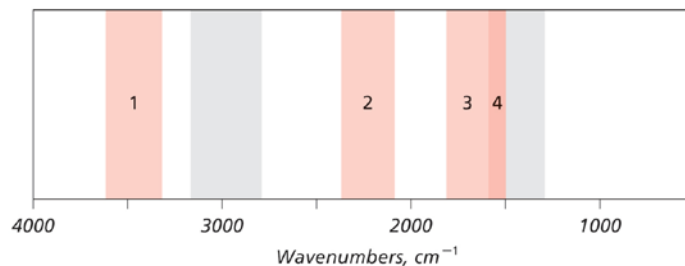
138.906 La 57	140.115 Ce 58	140.908 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.965 Eu 63	157.25 Gd 64	158.925 Tb 65	162.50 Dy 66	164.930 Ho 67	167.26 Er 68	168.934 Tm 69	173.04 Yb 70	174.967 Lu 71
227.028 Ac 89	232.038 Th 90	231.036 Pa 91	238.029 U 92	(240) Np 93	(243) Pu 94	(247) Am 95	(247) Cm 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 2014)

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
		3s	3p
S		-1.54	-0.86

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