CHM2311
Introduction to Structure & Bonding

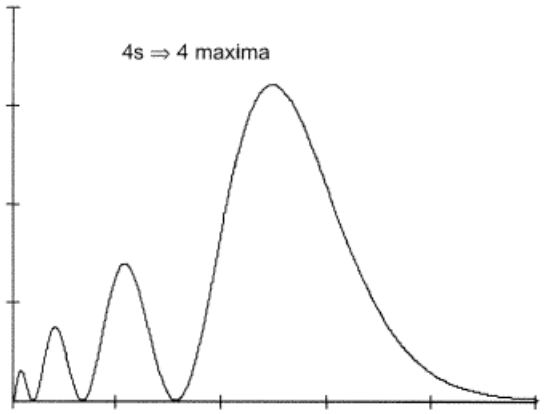
Midterm 1 Solutions

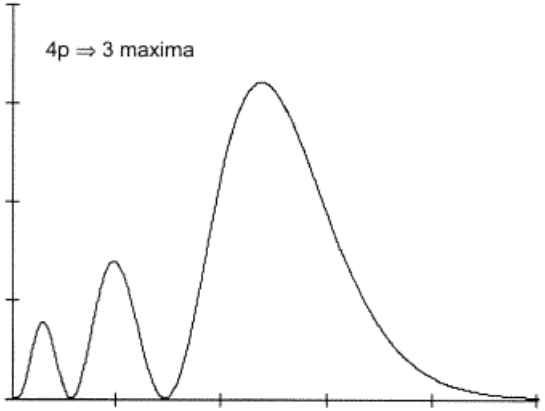
Class Average: 71.8 %

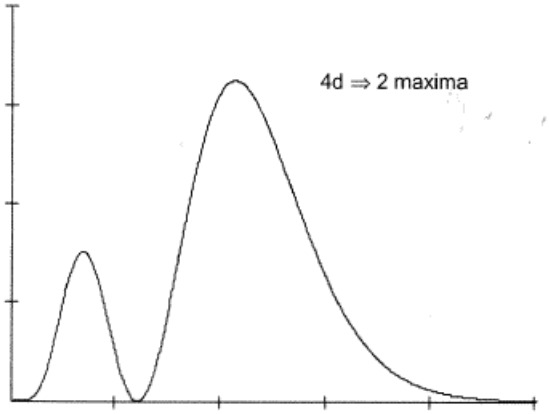
1. Indicate whether the following statements are true or false. **(6 marks)**

Statement	**True (T) or False (F)**
(a) The electron affinity of the halogens decreases with increasing Z.	F
(b) The number of radial nodes in any hydrogenic orbital is given by the expression, number = $n - l - 1$	T
(c) The wavelike character of ordinary objects such as a thrown basketball cannot be detected because their wavelengths are so short.	T
(d) In a many-electron atom, two electrons cannot occupy the same orbital.	F
(e) The following is an allowable set of quantum numbers for an electron in a hydrogen atom: $n = 4$; $l = 3$; $m_l = -3$; $m_s = +½$	T
(f) The two 1s electrons in sodium are bound more tightly than the 1s electrons in lithium.	T

2. In the space below, sketch a plot of $4\pi r^2R^2$ *vs.* r for a (i) 4s orbital, (ii) 4p orbital, (iii) 4d orbital. What is the relationship between the number of maxima and the values of *n* and *l*? (**4 marks**)







The number of maxima = $n - l$

3. (a) What is the atomic orbital designation for an electron having the quantum numbers $n = 5$, $l = 2$, $m_l = -1$, $m_s = -½$. (**1 mark**)

Answer: 5d

(b) One of the valence electrons in a ground state atom has the quantum numbers $n = 4$, $l = 1$, $m_l = 0$, $m_s = +½$. What atom could this be? (**1 mark**)

Answer: Any of the 4p block elements: Ga, Ge, As, Se, Br, Kr

4. What is the wavelength, in nm, of the electromagnetic radiation emitted when the electron in a hydrogen atom makes a transition from a 4s to a 2p orbital? (**4 marks**)

$$\textbf{Energy of light} = E_h - E_l = R_H \left(\frac{1}{n_l^2} - \frac{1}{n_h^2} \right)$$

$$E = R_H \left(\frac{1}{2^2} - \frac{1}{4^2} \right)$$

$$E = 4.08 \times 10^{-19} \text{ J}$$

$$\lambda = hc/E$$

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J} \bullet \text{s})(2.998 \times 10^{8} \text{ m/s})}{(4.08 \times 10^{-18} \text{ J})}$$

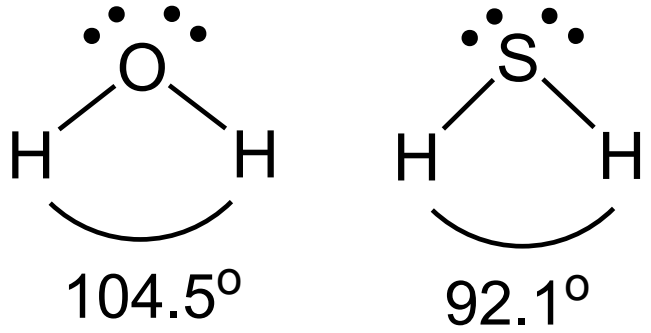
$$= 4.862 \times 10^{-7} \text{ m}$$

$$= 486 \text{ nm}$$

5. Predict and explain whether:

(a) The bond angle in H_2S should be bigger or smaller than that found in H_2O. (**2 marks)**

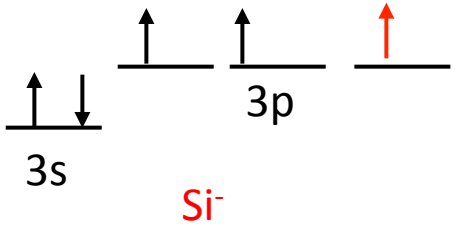
The H-S-H bond should be smaller. Sulphur is more electropositive than oxygen, more electronegative atoms draw electron density towards the central atom, causing an increase in the electron-electron repulsion and hence, larger bond angle.

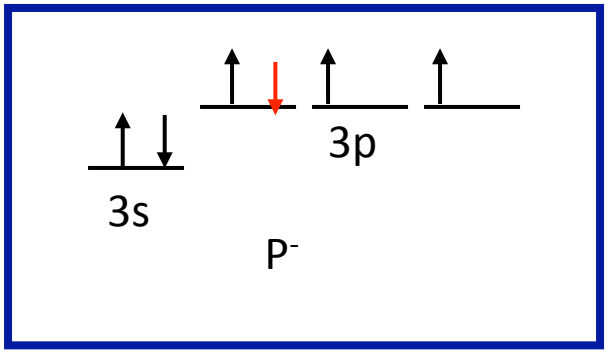


5. Predict and explain whether:

(b) Adding an electron to silicon is more or less favourable than adding an electron to phosphorus. (**2 marks)**

Adding an electron to a group 15 element is less favourable than adding an electron to a group 14 element.





Adding an electron to Si (group 14) allows it to go unpaired into the one empty 3p orbital

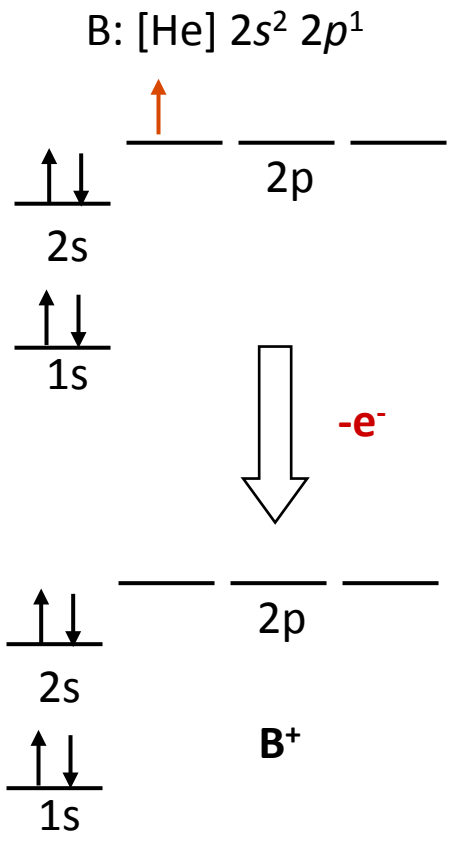
Adding an electron to P (group 15) means that it must pair up. (unfavourable e-e repulsion)

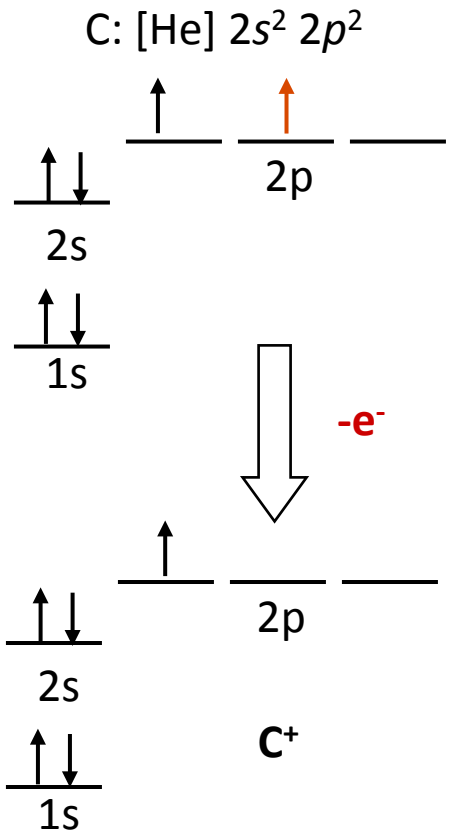
Addition of an electron to C is more favourable than addition of an electron to N

5. Predict and explain whether:

(c) The first ionization energy of B is higher or lower than C. (**2 marks)**

B has a lower first ionization energy due to smaller Z_{eff}. The larger Z_{eff} the greater the attraction to the nucleus the harder it is to remove an electron.





6. Calculate Z_{eff} for an electron in the 3d orbital of the Ti atom. (**3 marks**)

$$Z_{eff} = Z_{actual} - S$$

Determine the electron configuration of Ti:

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^2$$

Determine orbital groupings:

$(1s^2)$ $(2s^2, 2p^6)$ $(3s^2, 3p^6)$ $(3d^2)$ ~~$(4s^2\ 4p^0)$~~

Rule 2: Electrons in orbitals to the right don't shield electrons in orbitals to the left
→ the 2 electrons in 4s don't contribute to shielding

Rule 3b: Electrons in the same **nd** orbital contribute 0.35. All other electrons contribute 1.00.

$$S = (0.35 \times 1) + (1.00 \times 18) = 18.35$$

Z_{actual} = 22 because there are 22 protons (atomic number)

$$Z_{eff} = 22 - 18.35$$
$$= 3.65$$

The nuclear charge felt by an electron in the 3d orbital is 3.65

7. Provide a detailed valence electronic configuration including the number of unpaired electrons for a phosphorus atom? Is this atom paramagnetic or diamagnetic? PCl_5 is a stable compound. Using the valence electronic configuration, provide a valence bond description (including hybridization) for the bonding in this compound. (**5 marks**)

(**1 mark**) *$1s^2 2s^2 2p^6 3s^2 3p^3$ or $[Ne]3s^2 3p^3$*

(**1 mark**) *Three of the electrons in the 3p level are unpaired and thus the atom is paramagnetic*

(**3 marks**) *Using unhybridized orbitals, P can only form 3 bonds to chlorine atoms. In order to make 5 bonds we will need 5 unpaired electrons. This can be achieved by promoting one of the 3s electrons to the 3d level. Hybridization of the 3s + 3x3p + 1x3d = 5 sp^3d orbitals. These can be used to make 5 PCl bonds.*

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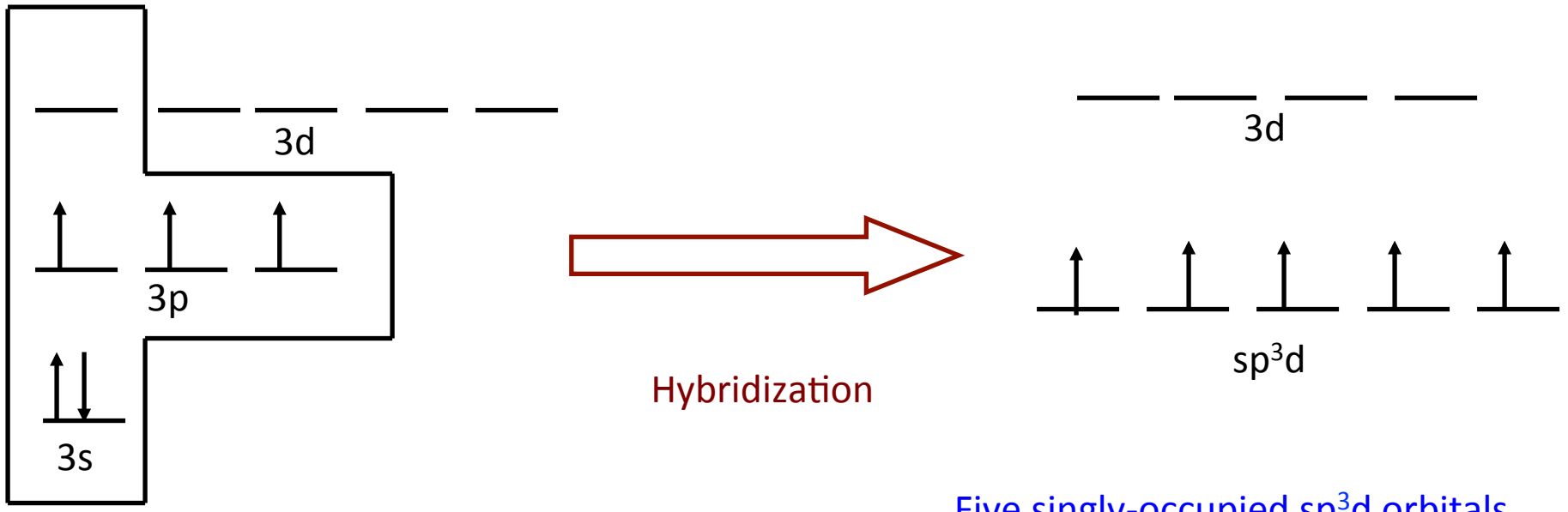
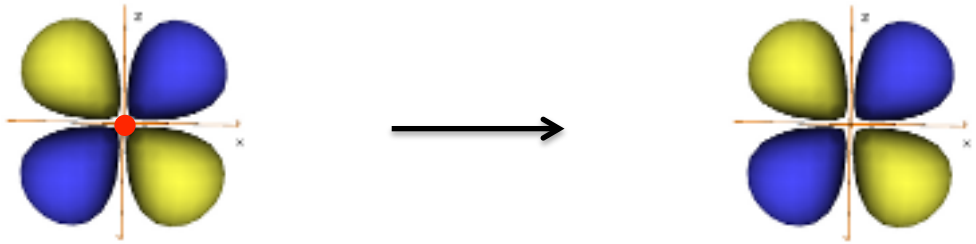


Using unhybridized orbitals, P can only form three bonds to chlorine atoms.

Five singly-occupied sp^3d orbitals can now be used to make five P-Cl bonds

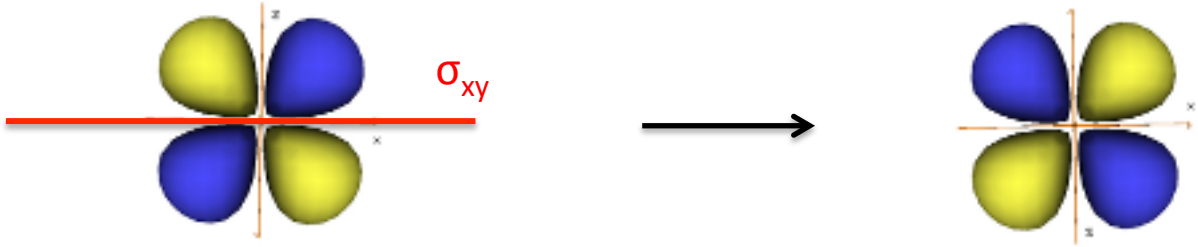
8. Is the $3d_{xz}$ atomic orbital:

(a) Symmetric or antisymmetric with respect to inversion? Explain with a diagram. (**1 mark**)



symmetric with respect to inversion

(b) Symmetric or antisymmetric with respect to reflection in the xy plane (e.g., σ_{xy})? Explain with a diagram. (**1 mark**)



antisymmetric with respect to reflection in the xy plane

(c) How many angular nodes does the $3d_{xz}$ orbital have? (**1 mark**)

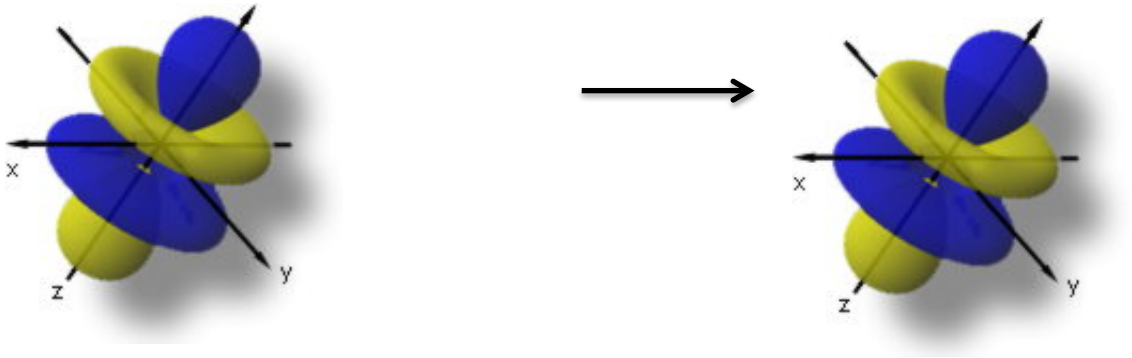
Answer: 2

(d) How many radial nodes does the $3d_{xz}$ orbital have? (**1 mark**)

Answer: 0

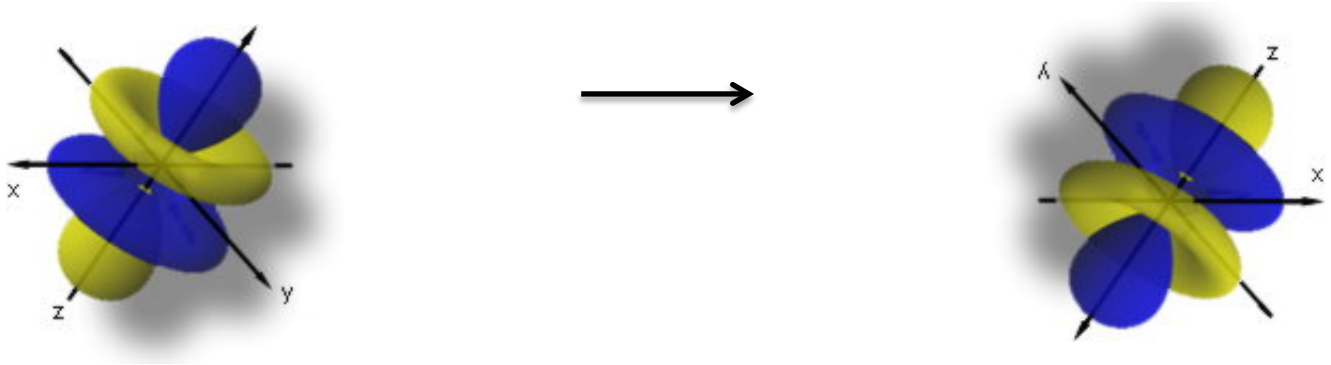
9. Is the f_{z3} atomic orbital:

(a) Symmetric or antisymmetric with respect to a principle C_2 (z) axis? (**1 mark**)



symmetric

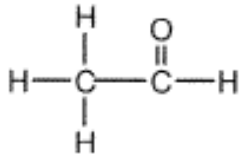
(b) Symmetric or antisymmetric with respect to a C_2' (x) axis. (**1 mark**)



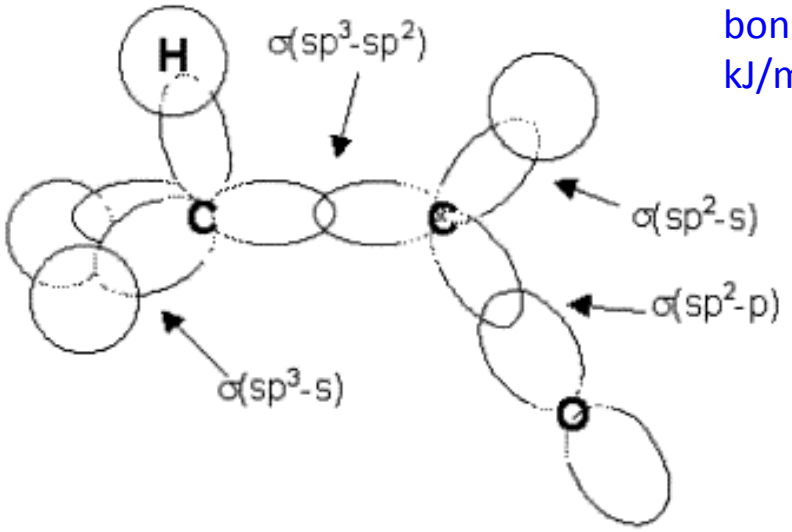
antisymmetric

10. Draw and label the valence bond representation of acetaldehyde (CH_3CHO). Be sure to include bond type and hybridization in your drawing. Which of the two bonds C-C or C-O is likely to be weaker? Explain. **(8 marks)**

Acetaldehyde is CH_3CHO. The Lewis structure is



sigma bonds:



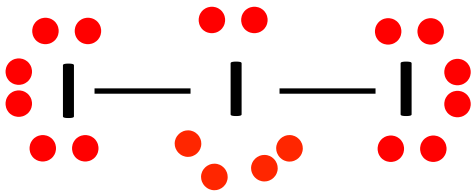
One of the carbons is sp^3 hybridized and the other is sp^2. The bond between the two carbons is a σ bond. The double bond between C and O consists of a σ and π bond. The π bond is formed by the unhybridized p-orbital on the sp^2-hybridized carbon and p-orbital on O. The p-orbitals on C and O are perpendicular to the plane of the page. The C-C bond is expected to be weaker than C=O as it consists only of one σ bond (no π bond). The bond energies are 348 kJ/mol and 802 kJ/mol, respectively

11. (14 marks; 1 mark per blank; *no partial credit*) For the following molecules:

i. Draw the Lewis structure
ii. Indicate any non-zero formal charges in the Lewis structure
iii. Determine the VSEPR geometry and shape of the molecule
iv. Draw the three-dimensional representation of the molecule
v. Determine whether the molecule is polar or non-polar
vi. Give the hybridization of the central atom

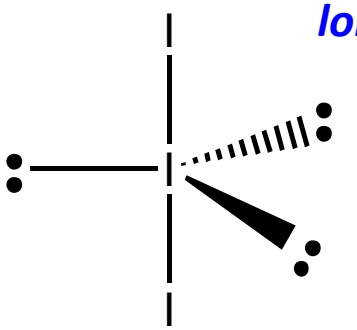
(a) I_3^-

Lewis Structure:



3D Drawing:

iodine atoms are axial
lone pairs are equatorial



Geometry: trigonal bipyramidal **Shape:** linear

Polarity: nonpolar **Hybridization**: sp^3d

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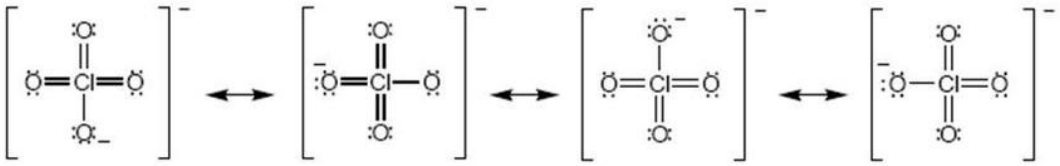
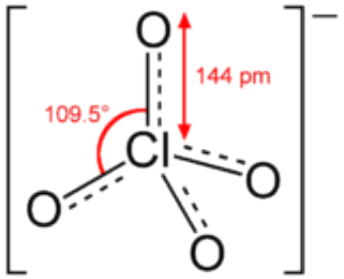
(b) ClO_4^-

Lewis Structure:



3D Drawing:



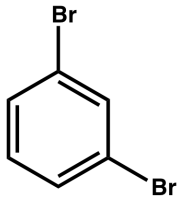
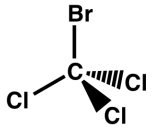
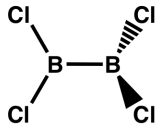
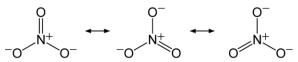
Geometry: tetrahedral

Shape: tetrahedral

Polarity: nonpolar

Hybridization: sp^3

12. (2 marks each) For the following molecules or ions, indicate highest rotation axis and if there is a plane of reflection.

	Compound	Rotation/Reflection label
Example	BF_3	C_3, σ_h
(a)	N_3^-	C_∞, σ_h
(b)		C_2, σ_v
(c)		C_3, σ_v
(d)		C_2, σ_v
(e)	NO_3^- 	C_3, σ_h