Name_____Key_____

**Chem 370 - Spring, 2018**
**Test I**
**February 26, 2018**

1. (16 points) Fill in the symbols for the missing elements in the portion of the periodic table shown below.

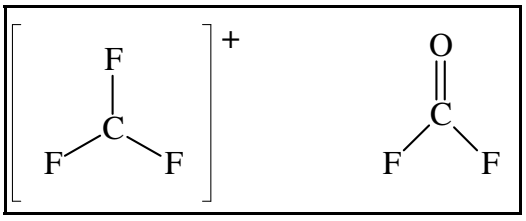
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | **B** | C |
| | | | | | | | | **Al** | **Si** |
| V | **Cr** | **Mn** | **Fe** | **Co** | **Ni** | **Cu** | **Zn** | **Ga** | **Ge** |
| **Nb** | **Mo** | **Tc** | **Ru** | **Rh** | **Pd** | **Ag** | **Cd** | **In** | **Sn** |
| **Ta** | **W** | **Re** | **Os** | **Ir** | **Pt** | **Au** | **Hg** | **Tl** | **Pb** |

2. (32 points; 4 points each part). Fill in the blanks.

a. Name the shape of each of the following molecules, based on VSEPR considerations.

$IF_7$ _pentagonal bipyramid_ $IF_5$ __square pyramid_____

b. In terms of ligand close packing (LCP) theory, briefly explain why $F_2C{=}O$ has a longer C–F bond length (131.7 pm) and smaller F–C–F angle (107.6°), compared to $CF_3^+$ (123.5 pm, 120°).




In both compounds the F···F nonbonding distance is virtually the same. But in $F_2CO$, the shorter C=O bond requires more room and pushes the two fluorine atoms away from the central carbon atom, while maintaining the same F···F nonbonding distance. This causes the C-F bonds to lengthen, and it also results in a smaller F–C–F angle.

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c. As indicated by the equation $\sum_{R_c} g_c \chi_i(R_c)\chi_j(R_c) = h\delta_{ij}$ , for a group of order $h$ the sum of the squares of the characters for any irreducible representation is equal to __$h$_, but the sum of the products of the characters for any two different irreducible representations is equal to __0__.

d. The group $D_{3h}$ has an order $h = 12$. List the four possible orders ($g$) for its subgroups (excluding $g = 1$ for the trivial subgroup $C_1$). (Do not attempt to name the subgroups.)

_____6, 4, 3, 2_____

e. Consider the $A_u$ irreducible representation of the group $C_{4h}$. Judging from the Mulliken symbol, the representation is _____symmetric____ (symmetric/antisymmetric) with respect to the $C_4$ axis, and ___antisymmetric__ (symmetric/antisymmetric) with respect to inversion.

f. Circle the correct answer among each of the following choices.

The shortest bonds: $NF_3$ $PF_3$ $AsF_3$ $NF_4^+$

The smallest bond angle: $NF_3$ $PF_3$ $AsF_3$ $NF_4^+$

g. The valence configuration of $_{27}$Co is ___$3d^7 4s^2$__, and the valence configuration of the $Co^{2+}$ ion is _____$3d^7$_____.

h. With the aid of the $D_{3h}$ character table shown on the last page, give the irreducible representations that would result from the following direct products:

$A_2'' \times A_2'' = A_1'$ $\qquad$ $A_1'' \times E' = E''$

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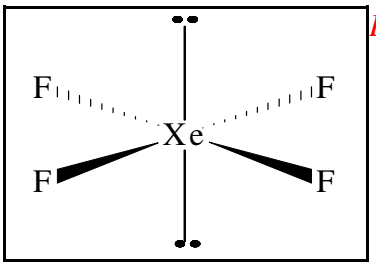
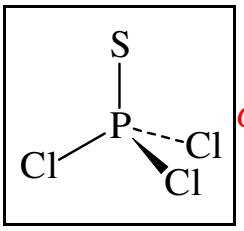
3. (20 points) Give the point group of each of the following.

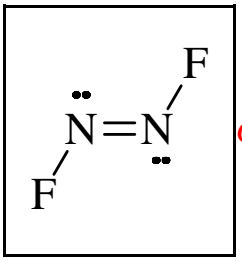
O=C=C=C=O $D_{\infty h}$



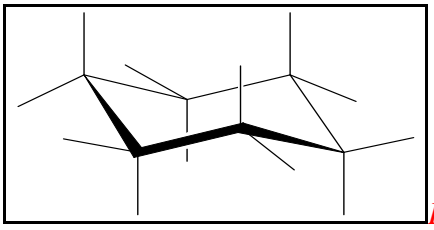
$D_{4h}$



$C_{3v}$



$C_{2h}$


$D_{3d}$

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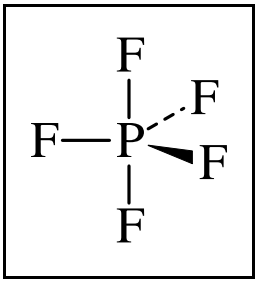
4. (32 points) Consider $PF_5$:




Determine the number of frequencies, their symmetries, and the infrared and Raman activities of the normal modes of $PF_5$. Show your work on the worksheet on page 5. A $D_{3h}$ character table is shown below the worksheet. From your work in the worksheet, write out the composition of $\Gamma_{3n}$, identify the species that comprise $\Gamma_{trans}$ and $\Gamma_{rot}$, and then indicate the symmetries of the genuine normal modes that comprise $\Gamma_{3n-6}$. When you have written out the composition of $\Gamma_{3n-6}$, you should be able to identify which species are infrared active, which species are Raman active, and which species are polarized in the Raman spectrum. Note the species and number of frequencies that may be coincident in both spectra, as well as any silent modes that would not be active in either spectrum. Once you have completed your work, summarize your results in the table below. For each category (infrared, Raman, polarized, coincidences, silent modes), give the total number of frequencies and indicate the specific numbers of frequencies of each symmetry species. **Don't forget that there are six (6) atoms in the molecule.**

| Type | Total Active Frequencies | Number of Each Symmetry Species |
|---|---|---|
| Infrared | 5 | $3E' + 2A_2''$ |
| Raman | 6 | $2A_1' + 3E' + E''$ |
| Polarized | 2 | $2A_1'$ |
| Coincidences | 3 | $3E'$ |
| Silent modes | 0 | – |

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| $D_{3h}$ | $E$ | $2C_3$ | $3C_2$ | $\sigma_h$ | $2S_3$ | $3\sigma_v$ | | |
|---|---|---|---|---|---|---|---|---|
| $N_i$ | 6 | 3 | 2 | 4 | 1 | 4 | | |
| $\chi_i$ | 3 | 0 | -1 | 1 | -2 | 1 | | |
| $\Gamma_{3n}$ | 18 | 0 | -2 | 4 | -2 | 4 | $\Sigma$ | $\Sigma/h$ |
| $A_1'$ | 18 | | -6 | 4 | -4 | 12 | 24 | 2 |
| $A_2'$ | 18 | | 6 | 4 | -4 | -12 | 12 | 1 |
| $E'$ | 36 | | 0 | 8 | 4 | 0 | 48 | 4 |
| $A_1''$ | 18 | | -6 | -4 | 4 | -12 | 0 | 0 |
| $A_2''$ | 18 | | 6 | -4 | 4 | 12 | 36 | 3 |
| $E''$ | 36 | | 0 | -8 | -4 | 0 | 24 | 2 |

| $D_{3h}$ | $E$ | $2C_3$ | $3C_2$ | $\sigma_h$ | $2S_3$ | $3\sigma_v$ | | |
|---|---|---|---|---|---|---|---|---|
| $A_1'$ | 1 | 1 | 1 | 1 | 1 | 1 | | $x^2 + y^2, z^2$ |
| $A_2'$ | 1 | 1 | −1 | 1 | 1 | −1 | $R_z$ | |
| $E'$ | 2 | −1 | 0 | 2 | −1 | 0 | $(x, y)$ | $(x^2 - y^2, xy)$ |
| $A_1''$ | 1 | 1 | 1 | −1 | −1 | −1 | | |
| $A_2''$ | 1 | 1 | −1 | −1 | −1 | 1 | $z$ | |
| $E''$ | 2 | −1 | 0 | −2 | 1 | 0 | $(R_x, R_y)$ | $(xz, yz)$ |

$\Gamma_{3n} = 2A_1' + A_2' + 4E' + 3A_2'' + 2E''$

$\Gamma_{trans} = E' + A_2''$ $\qquad$ $\Gamma_{rot} = A_2' + E''$

$\Gamma_{3n-6} = 2A_1' + 3E' + 2A_2'' + E''$

R(pol) ir, R ir R