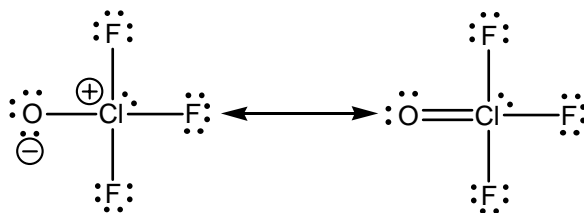


**Take-Home Quiz 1**  
**CHEM 325**  
**Spring 2009**

Name: \_\_\_\_\_

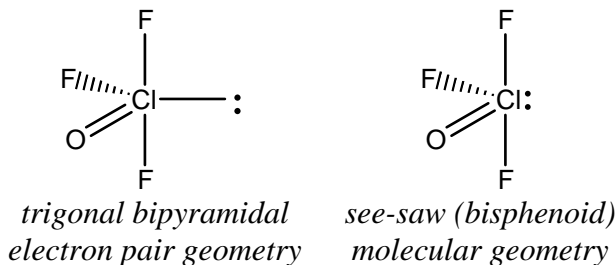
1a. (5 Points) Draw the Lewis dot structure of the compound  $\text{ClF}_3\text{O}$ . Show any contributing resonance structures.

**There are 34 valence electrons to place. Cl, being the least electronegative atom is the central atom. The two resonance structures that contribute the most to the resonance hybrid description of this molecule are shown below, with the one on the right making the largest contribution because it has no formal charge (note the expanded octet on Cl in this structure). Structures with double bonds to F are not shown because these would place a positive formal charge on F, the most electronegative atom in the molecule, which would not be energetically favorable according to the Electroneutrality Principle.**



b. (3 Points) Using VSEPR theory, convert the Lewis dot structure of  $\text{ClF}_3\text{O}$  to a molecular structure. Indicate any bond angle that deviates from the ideal predicted by VSEPR. Give its approximate value and explain why it is not ideal.

**The Cl has five regions of electron density around it (it doesn't matter which resonance structure you choose), and therefore we have a trigonal bipyramidal electron pair geometry. This gives a see-saw (bisphenoid or diphenoid) molecular shape.**

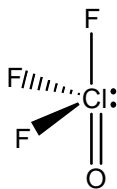


**In VSEPR theory the presence of the lone pair may be inferred by the void in the coordination sphere that it leaves and by its effects on the remaining bonding pairs. The increased lone pair-bonding pair repulsion should push the fluorines and the oxygen away from the position of the lone pair. This should make the**

$F_{\text{axial}}\text{-Cl-}F_{\text{equatorial}}$  and the  $\text{O-Cl-}F_{\text{axial}}$  bond angles all be less than  $90^\circ$ . For the same reason the  $F_{\text{equatorial}}\text{-Cl-O}$  bond angle will be less than  $120^\circ$  and the  $F_{\text{axial}}\text{-Cl-}F_{\text{axial}}$  angle will be less than  $180^\circ$  (or greater than  $180^\circ$ , depending on how you defined it).

We would expect the effects to be larger (smaller angles) when two fluorines are involved because the high electronegativity of F will pull electron density out of the bond, allowing for these atoms to get closer together because bonding pair-bonding pair repulsions would be less. The increased lone pair-bonding pair repulsion for the  $\text{Cl=O}$  (because the larger electron density in the double bond) should further decrease the  $F_{\text{equatorial}}\text{-Cl-O}$  bond angle.

The VESPR structure that is shown was drawn putting the more electron-rich  $\text{Cl=O}$  in an equatorial position to minimize the lone pair-bonding pair and bonding pair-bonding pair repulsions. However, the structure shown below was all accepted. Note that in reality there is an intramolecular rearrangement that moves the O between the equatorial and axial positions so rapidly that the two structures cannot be distinguished.



c. (2 Points) What is the hybridization of the Cl in  $\text{ClF}_3\text{O}$ ? What is the hybridization of O?

Since the Cl has five areas of electron density about it, it would be  $sp^3d$  hybridized in valence bond theory. The oxygen is problematic because it has either three areas of electron density (and therefore  $sp^2$  hybridized) or four areas of electron density (making it  $sp^3$  hybridized). The best way to think about this is to have it be  $sp^2$  hybridized with the lone pair in the p orbital not used for hybridization and then have this pair of electrons donated to the Cl to form the double bond.

2a. (10 Points) Determine the irreducible representations spanned by the direct product  $E_g \times E_u$  in  $D_{4h}$  using the Great Orthogonality Theorem.

$D_{4h}$	E	$2 C_4$	$C_2$	$2 C_2'$	$2 C_2''$	i	$2 S_4$	$\sigma_h$	$2 \sigma_v$	$2 \sigma_d$
$E_g$	2	0	-2	0	0	2	0	-2	0	0
$E_u$	2	0	-2	0	0	-2	0	2	0	0
$E_g \times E_u$	4	0	4	0	0	-4	0	-4	0	0

We do not need to consider any function with g symmetry (see below).

Using the Great Orthogonality Theorem (with the order of the group equal to 16) gives the following (note that  $C_4$ ,  $C_2'$ ,  $C_2''$ ,  $S_4$ ,  $\sigma_v$  and  $\sigma_d$  are omitted because the character under these operations for the reducible representation is 0, and thus they will always contribute 0 in the Great Orthogonality Theorem).

$$a_{A_{1u}} = \left(\frac{1}{16}\right)((1)(1)(4) + (1)(1)(4) + (1)(-1)(-4) + (1)(-1)(-4)) = 1$$

$$a_{A_{2u}} = \left(\frac{1}{16}\right)((1)(1)(4) + (1)(1)(4) + (1)(-1)(-4) + (1)(-1)(-4)) = 1$$

$$a_{B_{1u}} = \left(\frac{1}{16}\right)((1)(1)(4) + (1)(1)(4) + (1)(-1)(-4) + (1)(-1)(-4)) = 1$$

$$a_{B_{2u}} = \left(\frac{1}{16}\right)((1)(1)(4) + (1)(1)(4) + (1)(-1)(-4) + (1)(-1)(-4)) = 1$$

**We don't need to continue at this point since the sum of the characters under E (the identity operation) is 4, which is what the reducible representation had. You can check that adding these four irreducible representations together gives the reducible representation.**

**Therefore,  $E_g \times E_u = A_{1u} + A_{2u} + B_{1u} + B_{2u}$ .**

b. (4 Points) Using  $D_{4h}$  as an example, explain why the direct product between an irreducible representation with  $g$  symmetry and one with  $u$  symmetry can never yield a result with  $g$  symmetry. Hint: what does it give?

**The difference between the  $g$  and  $u$  designations is the symmetry with respect to inversion. Functions with  $u$  symmetry all have a negative character with respect to inversion, while  $g$  functions all have a positive character. Whenever a function with a negative character is multiplied by a function with a positive character for any operation, the result must always have a negative character with respect to inversion. Thus, multiplying an irreducible representation with  $g$  symmetry by one with  $u$  symmetry will always give a function with  $u$  symmetry..**