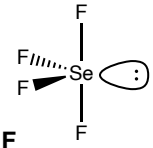
202 Symmetry and Bonding Assignment

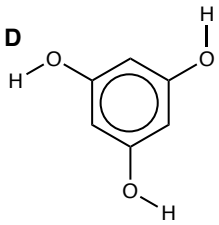
Set: 4th May. Due: **16 May 5pm**

Q1 Draw the 3D chemical structure and identify the point group of the compounds below. For each example explicitly write out the steps followed on the flow chart.

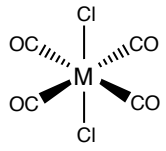
A SO_2 **B** C_2H_4 **C**



D

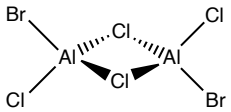


E



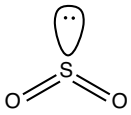
trans-$M(CO)_4Cl_2$

F

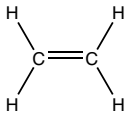


6 marks

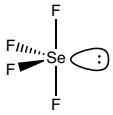
(a) SO_2
linear: no
O_h or T_d: no
C_n: yes, C_2
$2C_2$ perpendicular to C_2: no
σ_h: no
$2\sigma_v$: yes
C_{2v}



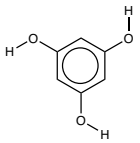
(b) C_2H_4
linear: no
O_h or T_d: no
C_n: yes, C_2
$2C_2$ perpendicular to C_2: yes
σ_h: yes
$2(\sigma_v+\sigma_d)$: yes
D_{2h}



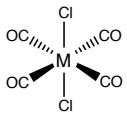
(c) SeF_5
linear: no
O_h or T_d: no
C_n: yes, C_2
$2C_2$ perpendicular to C_2: no
σ_h: no
$2\sigma_v$: yes
C_{2v}



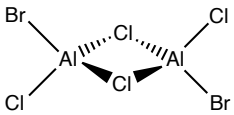
(d) tri(hydroxy)benzene
linear: no
O_h or T_d: no
C_n: yes, C_3
$3C_2$ perpendicular to C_3: no
σ_h: yes
C_{3h}



(e) trans-$M(CO)_4Cl_2$
linear: no
O_h or T_d: no
C_n: yes, C_4
$4C_2$ perpendicular to C_4: yes
σ_h: yes
$4(\sigma_v+\sigma_d)$:yes
D_{4h}



(f) trans-$Al_2Cl_4Br_2$
linear? no
O_h or T_d: no
C_n: yes, C_2
$2C_2$ perpendicular to C_2: no
σ_h: yes
C_{2h}



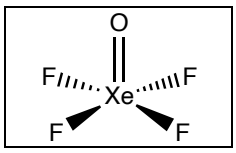
1 mark each
-1/2 no indication of n
-1/2 messy

the purpose of drawing the structures was to help students with the 3D shape, a surprising number of students did not take advantage of this.

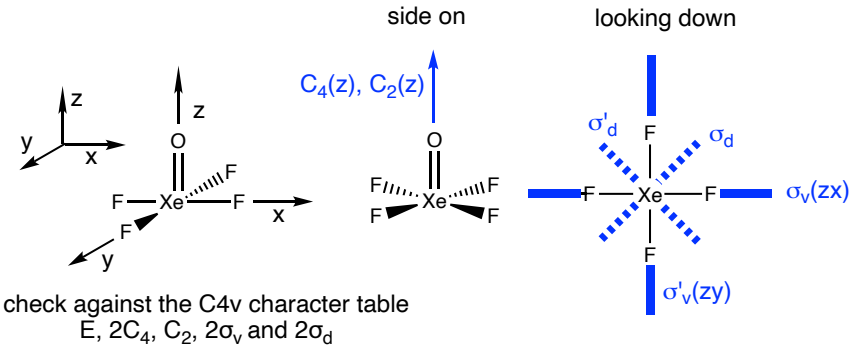
Common errors were:

- not defining n
- treating the OH in tri(hydroxy) benzene as a single unit and adding C_2 axes as a result
- treating trans-$M(CO)_4Cl_2$ as octahedral, however the 2Cl break this symmetry
- not using the image of trans-$Al_2Cl_4Br_2$ given, the Cl are out of plane, a few people incorrectly transcribed the Br!

Q2 XeF_4O is a square pyramidal molecule that belongs to the C_{4v} point group. Draw all the symmetry elements of this point group on a diagram(s) of the molecule. Clearly identify the axial system.



4 marks



check against the C4v character table
E, $2C_4$, C_2, $2\sigma_v$ and $2\sigma_d$

2 all C_n and all σ

1 for clear diagrams

1 axis information in labels

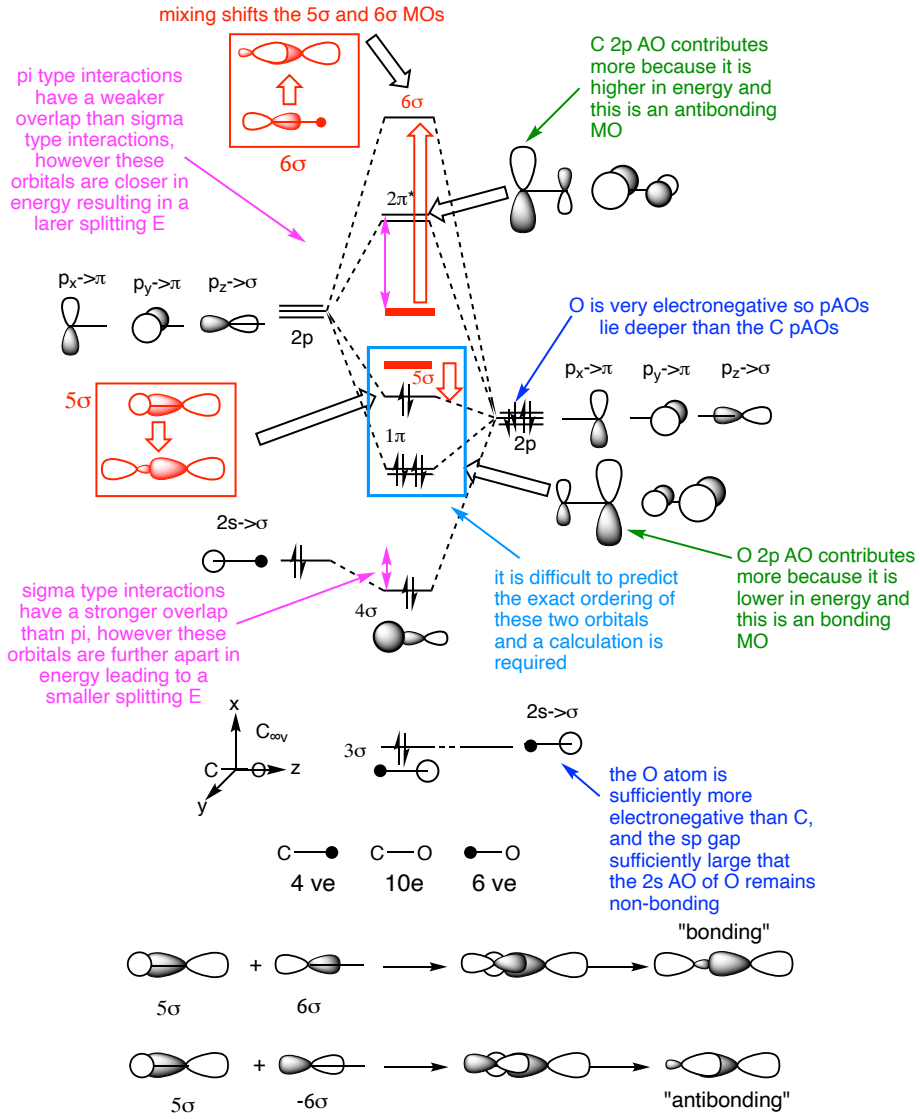
surprisingly poor performance, especially as this is essentially given in Figures 11,12, 13 of Lecture 1 in the notes!

Things to watch out for are:

- the axis definition and the molecule alignment MUST be consistent
- define BOTH $C_4(z)$ and $C_2(z)$ on the same axis
- make sure you add the axis descriptions to the correct mirror planes, σ_v along bonds, σ_d between bonds!

Q3 Draw the MO diagram for CO, include at least 3 annotations on your diagram. In a separate figure show how the mixed MO orbitals are formed.

10 marks



2 marks AO relative position, AO symmetry
3 marks MO energies, shape, relative size
3 marks annotations
2 marks mixing

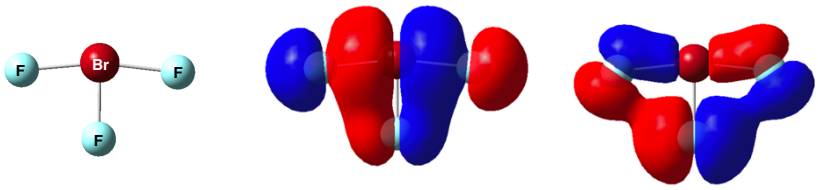
in general a poor performance, evidence of simply copying Fig 20 of Lecture 2 without understanding. A very similar question with answer given in the on-line tutorial of Lecture 4.

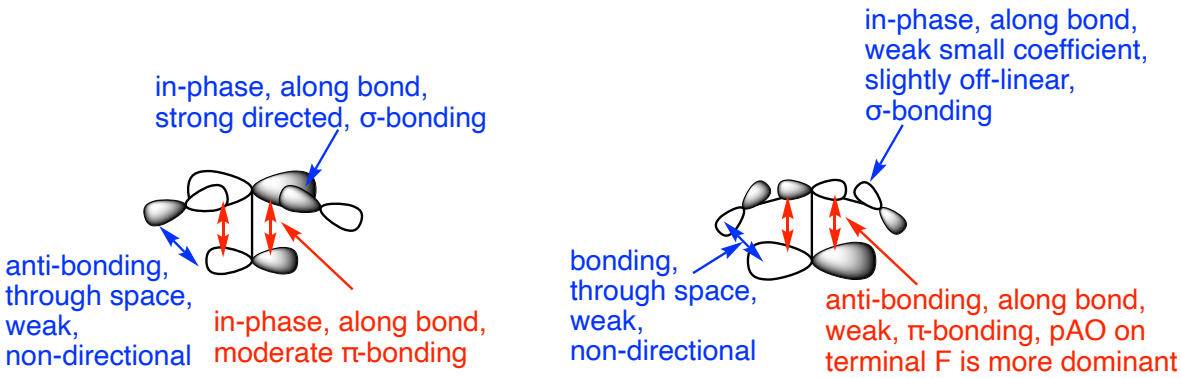
Key problem areas:

- the symmetry is $C_{\infty v}$ not $D_{\infty h}$, this impacted significantly on which orbitals mix
- not leaving O 2sAO non-interacting CO was explicitly covered in a Lecture 4 in-class problem AND also *in the self-study problems, Q4*
- not altering the size of the AO contributions to reflect the AO contribution/energy
- random expansion and contraction of C-O distance
- not following instruction to provide *annotations* ie short explanations (NOT descriptions) with arrows to the entity being explained, or providing only very basic annotations that don't explain more complex features of the diagram
- not understanding the *mixing* is a technical term and *applies only to MOs* not the AOs which are used to build the first-stage diagram
- very messy diagrams, for an assignment for which you have time a clean, carefully drawn diagram is important

Q4 Draw LCAOs for the computed MOs shown below. On your diagrams **annotate** features important for evaluating the orbital bonding character.

5 marks





2 marks 1 for each LCOAs

3 marks for 3 annotations *(must relate to bonding character)*

Annotations need to include reference to:
bonding/antibonding
through bond, through space where distance dependence should be noted
strength: distance, coefficient
sp-type, sigma or pi and directional/non-directional orbitals

in general a very poor performance, especially as specific examples of expected format of answers given in Lecture 6: in-class problems P3 and P4 and self-study problems Q3 and Q4.

Key problem areas:

- not drawing in the slight bend in the "equatorial" Br-F bonds, or giving too much of a bend
- not observing the MOs and giving the AOs the right size relative to each other (important!)
- drawing pAOs as vertical or horizontal when they are obviously slightly rotated
- not referring to EACH of the components above
- saying π-interactions are through space when they are through bond
- saying interactions are "directional" when they are not!
- missing identifying σ and π (directed or side-on are acceptable) where appropriate
- nodes on atoms are not as important to bonding, statements of this accepted for reduced marks
- describing the bonding character overall, this is not what was asked for (re-read the question)