

Chemistry 734b
Problem Set 5 Due: April 2, 2008

1.) A square planar molecule ML_4 has D_{4h} symmetry. Choosing axes so that ligand 1 lies along $+x$, ligand 2 along $+y$, ligand 3 along $-x$, and ligand 4 along $-y$, set up unit vectors on ligand 1 to represent p-orbitals such that σ_1 points towards M, π_1^\perp is perpendicular to the xy plane and pointing in the $+z$ direction, and π_1'' lies in the xy plane, pointing in the $+y$ direction. Set up similar unit vectors σ , π^\perp , π'' that form right-handed systems on ligands 2, 3, and 4. (*For a clear picture, study the notes on the ML_6 transition metal complex, but ignore the 2 ligands which are orientated in the $\pm z$ directions.*)

a) Find the characters of the representations Γ_s , Γ_p , Γ_d based on the s, p, and d orbitals on the central atom M, and give their Mulliken labels. (*Note: this information can be found in character tables.*)

b) Similarly, by observing how the unit vectors σ , π^\perp , π'' transform under (the same) typical class operators, find the characters of the representations Γ_σ , Γ_{π^\perp} , $\Gamma_{\pi''}$. Find the direct sum of irreducible representations into which these representations can be reduced and hence, tabulate possible combinations of metal and ligand orbitals.

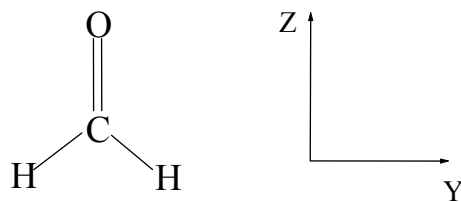
c) Finally, use the projection operator technique to find the appropriate linear combinations of σ , π^\perp and π'' orbitals which form bases for the irreducible representations found above, and make sketches of these MOs.

(Hints: a character table of the irreducible representations of D_{4h} is attached. Observe the convention that the C_2 axes that go through opposite pairs of ligand atoms are called C_2' , while those that bisect the lines joining adjacent ligand atoms are called C_2'').

Irreducible representations and characters for the D_{4h} point group.

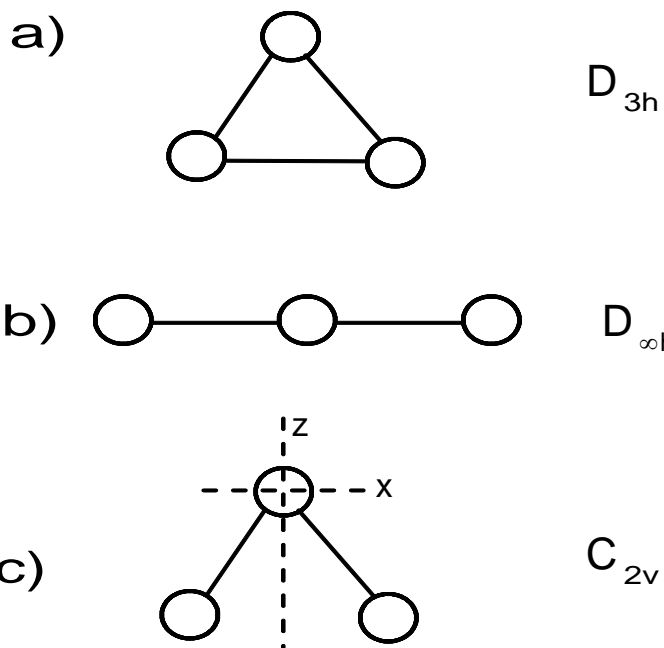
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	I	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0

2.) The first electronic transition of formaldehyde (CH_2O) is $\pi^* \leftarrow n$ (n is the non-bonding orbital on the O atom). Assume the molecule to lie in the y - z plane with the z -axis coinciding with the molecular axis, and the non-bonding orbital to be the oxygen p -orbital lying in the molecular plane pointing in the y -direction.



- What is the Mulliken symbol of the n orbital? Using the p_x orbitals on the carbon and oxygen as basis functions, find the Mulliken labels for the π and π^* excited states.
- Is this $\pi^* \leftarrow n$ electric dipole transition symmetry allowed? Fully justify your answer.
- Find the symmetries of the normal vibrations of formaldehyde.
- If the $\pi^* \leftarrow n$ transition is allowed which vibrations contribute to its fine structure, or if it is forbidden which transitions will make it allowed by vibronic interaction?

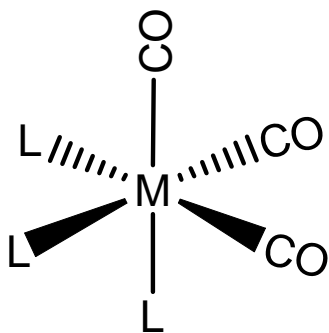
3.) a) The observed infrared spectrum of ozone (O_3) contains three fundamental bands lying at frequencies of 705 cm^{-1} , 1043 cm^{-1} , and 1110 cm^{-1} . Use this information to decide which of the following are possible structures for ozone:



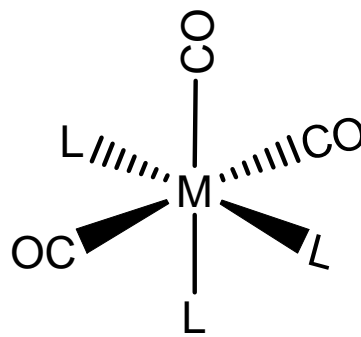
Note: Reductions in $D_{\infty h}$ must be done by inspection.

b) Based on your conclusion in part a) predict what you would expect to find in the Raman spectrum of ozone.

4.) Show how you might use IR spectroscopy in the CO stretching region to distinguish between: a) *cis* and *trans* $ML_4(CO)_2$
and
b) *fac* and *mer* $ML_3(CO)_3$



fac ML_3CO_3



mer $ML_3(CO)_3$

Note for part a) you will have to worry a bit about the point groups for linear molecules. If you have a problem, come and see me.