Lecture III: Molecular Symmetry

01-17-2020

While VSEPR model predicts molecular shapes, it is still an approximation. Atoms are not points, and if all ligands that surround the central atom are not the same, distortions result. In addition, molecules of different shapes sometimes share some properties. Analysis of molecular symmetry allows the generalization of some of these observations.

Symmetry Elements

They can be zero-, one-, and two-dimensional.

0D: center of inversion (i)

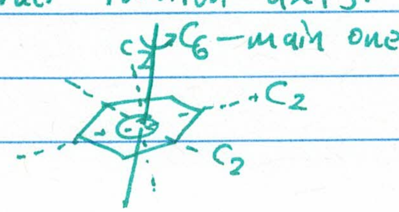
Each ~~point~~ atom of the molecule reflects through a single point into an identical atom at the same distance from the point of inversion.

1D: rotation axis (C_n)

By rotating by $360/n$ degrees around an axis, molecule will superimpose with itself.

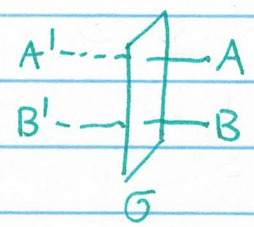
C_2, C_3, C_6 axes

Molecules can have multiple C_n axes. If there is a unique C_n axis with the highest n, it is called the main or the highest order rotation axis:



2D: plane of symmetry (σ)

Each atom in a molecule reflects through a plane into an identical atom on the other side

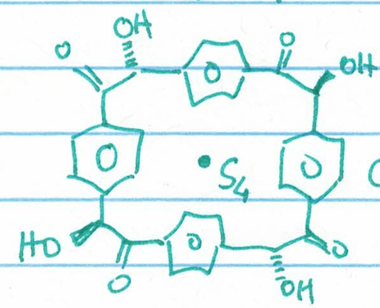


If a molecule has a unique main C_n axis, then planes of symmetry can be perpendicular to that axis (called horizontal σ_h planes) or contain that axis, in which case they are called vertical σ_v planes

Combination of 1D and 2D: improper rotation axis (S_n)

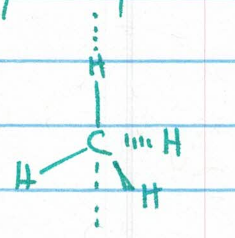
Molecule superimposes with itself if turned around an S_n axis by 360/n degrees and then reflected through a σ plane perpendicular to this axis.

example from my group:

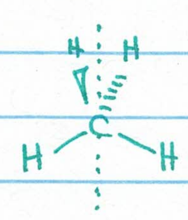


Cyclotetrabenzoin

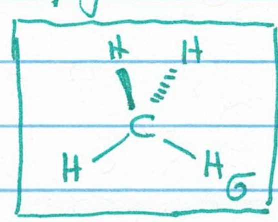
Many molecules have multiple symmetry elements, and certain symmetry elements often occur together. Let's look at methane:



C_3 axis
(there is 4 of them)

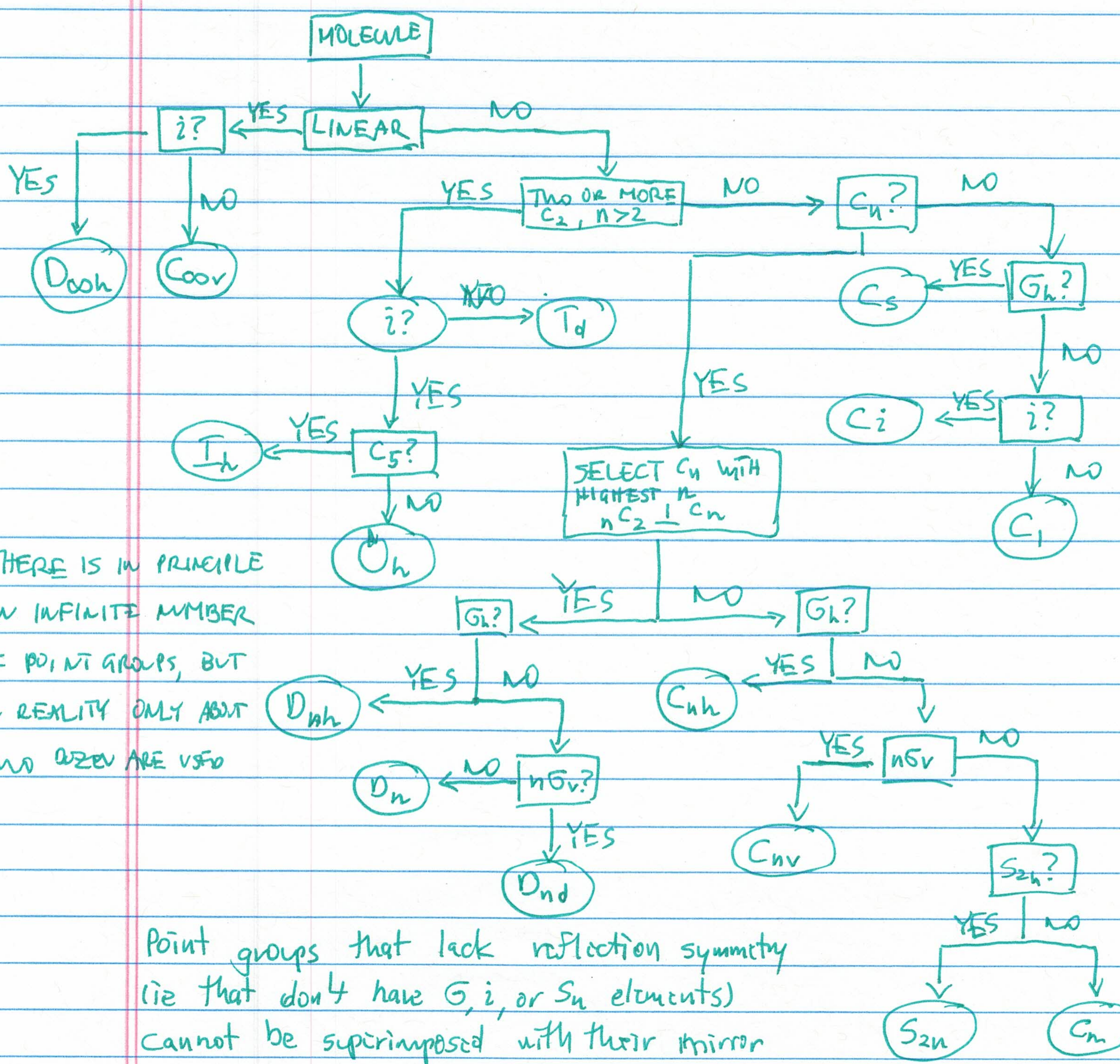


C_2 axis
(there are 3 of them)



There are six symmetry planes

Combinations of certain symmetry elements allow classification of all molecules into point groups. This chart allows easy way of figuring out a point group for a molecule:

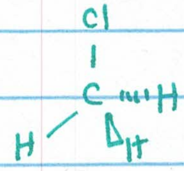


THERE IS IN PRINCIPLE AN INFINITE NUMBER OF POINT GROUPS, BUT IN REALITY ONLY ABOUT TWO DOZEN ARE USED

Point groups that lack reflection symmetry (ie that don't have σ, i, or S_n elements) cannot be superimposed with their mirror images: they are CHIRAL.

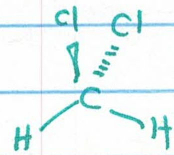
Let's practice using this chart on several exemplary molecules:

CH_3Cl



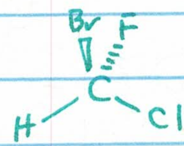
linear: NO → two or more C_2: NO → C_n: YES, n=3 → $3C_2 \perp C_3$: NO → σ_h: NO → $3\sigma_v$: YES → C_{3v}

CH_2Cl_2



linear: NO → two or more C_2: NO → C_n: YES, n=2 → $2C_2 \perp C_2$: NO → σ_h: NO → $2\sigma_v$: YES → C_{2v}

CHClBrF



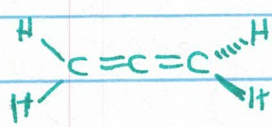
linear: NO → two or more C_2: NO → C_n: NO → σ_h: NO → i: NO → C_1

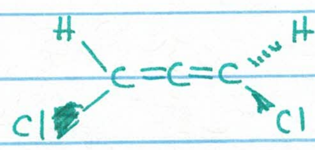
acetylene

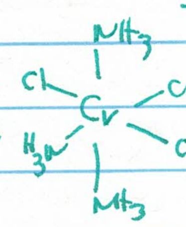
H–C≡C–H   linear: YES → i: YES → $D_{\infty h}$

two suggestions from the audience!

Homework examples:







SPEND THE REST OF THE CLASS WORKING ON EXAMPLES.