- There are four other C_2 axes in the place of the molecule.
- The C_2' and C_2'' axes of a planar MX_4 molecule.
- As these twofold axes are not collinear with the principal C_4 rotational axis they are distinguished by adding prime (‘) and double prime (“) to their symbols.
- Only two notations are needed for the four axes, because both C_2' axes are said to belong to the same ***class***, while the two C_2'' axes belong to a separate class.

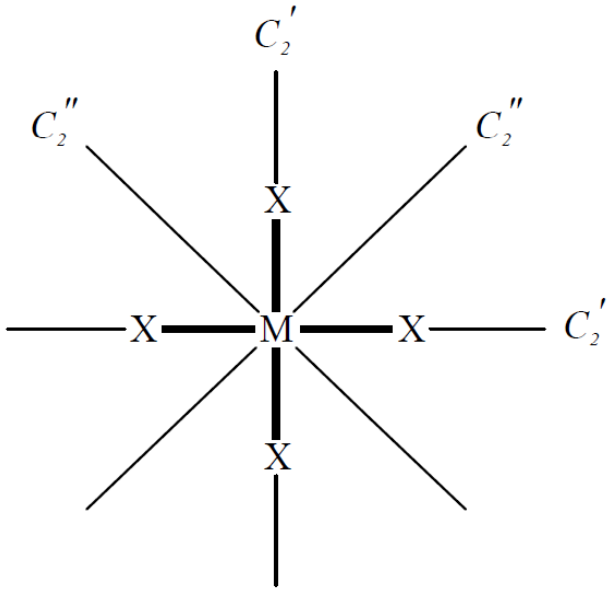
  i.e., both C_2 axes are geometrically equivalent to each other and distinct from C_2'' .

- In listing the complete set of symmetry operations for a molecule, operations of the same class are designated by a single notation preceded by a coefficient indicating the number of equivalent operations comprising the class.

  e.g. for the square planar structure here discussed, of D_{4h} symmetry, the rotational operations grouped by class are

  $2C_4$ (C_4 and C_4^3), C_2 (collinear with C_4)

  $2C_2'$, and $2C_2''$.



The C_2' and C_2'' axes of a planar MX_4 molecule.

General Relationships for C_n

$$C_n^{\,n} = E$$

$$C_{2n}^{\,n} = C_2 \qquad (n = 2, 4, 6, 8\ldots\text{etc.})$$

$$C_n^{\,m} = C_{n/m} \qquad (n/m = 2, 3, 4, 5\ldots\text{etc.})$$

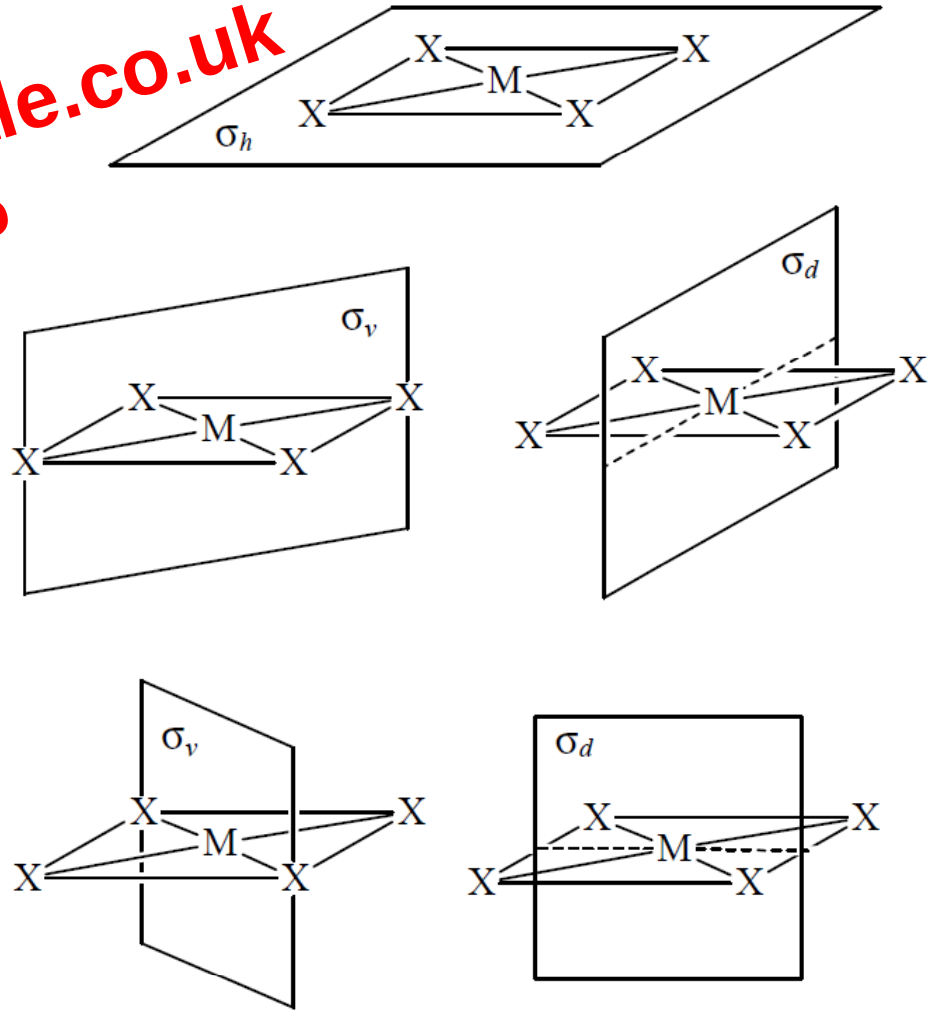
$$C_n^{\,n-1} = C_{n-1}$$

$$C_n^{\,n+m} = C_n^{\,m} \qquad (m < n)$$

- *Every n-fold rotational axis has n–1 associated operations (excluding $C_n^{\,n} = E$).*
- Remember, the rotational operation $C_n^{\,m}$ *is* preferably identified as the simpler $C_{n/m}$ operation where *m/n* is an integer value.

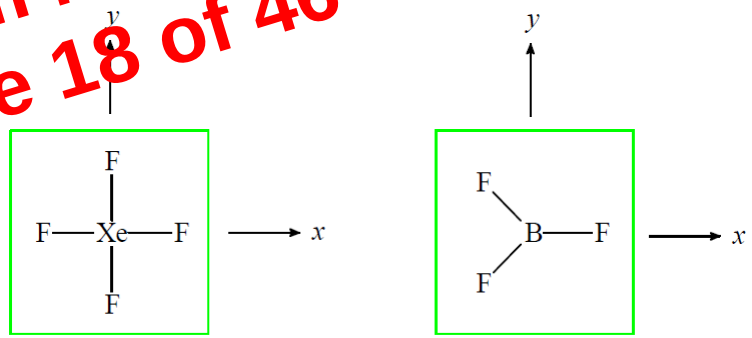
Horizontal, Vertical, and Dihedral Mirror Planes

- A σ_h plane is defined as perpendicular to the principal axis of rotation.
- If no principal axis of rotation exists, σ_v is defined as the plane of the molecule.
- σ_v and σ_d planes are defined so as to contain a principal axis of rotation and to be perpendicular to a σ_h plane.
- When both σ_v and σ_d planes occur in the same system, the distinction between the types is made by defining σ_v to contain the greater number of atoms or to contain a principal axis of a reference Cartesian coordinate system (x or y axis).
- Any σ_d planes typically will contain bond angle bisectors.
- The five mirror planes of a square planar molecule MX_4 are grouped into three classes (σ_h , $2\sigma_v$, $2\sigma_d$).

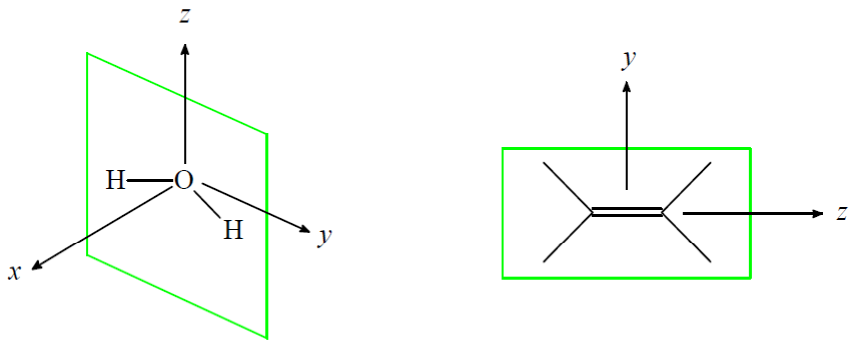


Defining the Coordinate System *(contd.)*

3. For planar molecules, if the *z* axis as defined above is perpendicular to the molecular plane, the *x* axis lies in the plane of the molecule and passes through the greatest number of atoms.

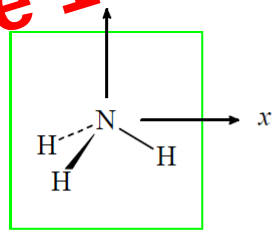


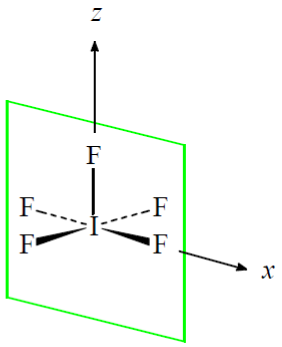
If the z axis lies in the plane of the molecule, then the *x* axis stands perpendicular to the plane.



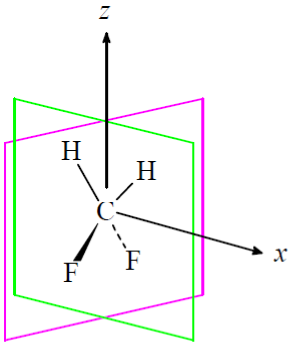
Defining the Coordinate System *(contd.)*

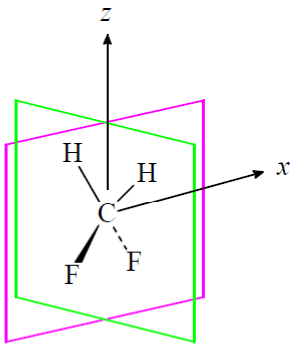
4. For non-planar molecules, once the *z* axis has been defined, the *x* axis is usually chosen so that the *xz* plane contains as many atoms as possible. If there are two or more such planes containing identical sets of atoms, any one may be taken as the *xz* plane.





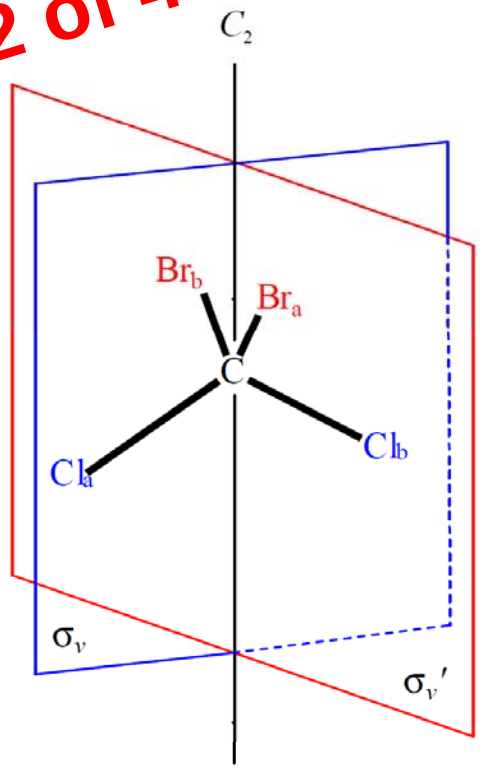
Where a decision about the orientation of the *x* axis cannot be made on this basis, the distinction between *x* and *y* is usually not important or is not generally fixed by convention.





- We will now consider the complete set of symmetry operations for a particular molecule and determine all the binary combinations of the symmetry operations it possesses.
- The symmetry elements of the CBr_2Cl_2 molecule are shown below. This molecule has a tetrahedral geometry

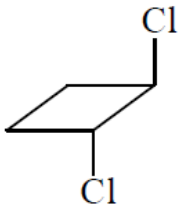
  Note: tetrahedral geometry does not automatically imply tetrahedral symmetry !



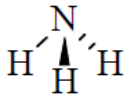
- The complete set of symmetry operations are E, C_2 , σ_v , σ_v'

- To the rotations of the corresponding C_n groups the family of C_{nv} groups adds n vertical mirror planes, which intersect at the C_n axis.
- The point group $C_{\infty v}$, which has a infinite-fold C_∞ rotational axis, is an important member of this family. It is the point group of all non-centrosymmetric linear molecules.

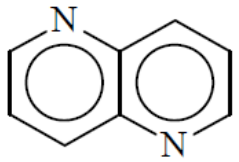
  e.g., H-Cl, C≡O.
- To generate any of the C_{nh} groups, we need only add a horizontal mirror plane to the series of C_n rotations of the appropriate cyclic C_n group.
- Since $C_n\sigma_h = S_n$ and $C_2\sigma_h = S_2 = i$, these groups also have n-fold improper axes when $n > 2$, and they are centrosymmetric when n is even.
- The S_{2n} series are not common.



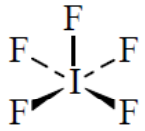
C_2



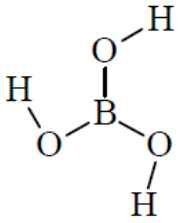
C_{3v}



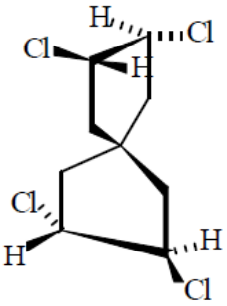
C_{2h}



C_{4v}



C_{3h}



S_4