Irreducible Representation (IR) Symmetry Labels

- The symbols to the far left of the character table are part of "Mulliken notation" defined in the article by R.S. Mulliken, *J Chem. Phys.,* **1955**, 23, p1997
- these symbols are determined by considering whether or not a representation is **symmetric (positive character) or antisymmetric (negative character)** with respect to a set of symmetry operations.
- singly degenerate symbols (1 x 1 matrix)
  - A is used when the IR is symmetric under C_n or S_n for the highest n in the group
  - A is also used if there is no C_n or S_n
  - B is used when the IR is antisymmetric under C_n or S_n for the highest n in the group

For example:

C_2	E	C_2
A	1	1
B	1	-1

- multiply degenerate symbols (n x n matrix)
  - E doubly degenerate (and is not the same as E for the identity operation!)
  - T triply degenerate
  - G has degeneracy of 4
  - H has degeneracy of 5
- The u and g subscripts (the comments made here will make more sense after the next lecture!)
  - simply put g indicates a representation that is symmetric with respect to inversion and u a representation that is antisymmetric with respect to inversion
  - A more complete and mathematical description is as follows: A centrosymmetric group G_i is the direct product of two groups G and C_i or G and i. u and g are determined from the characters that are NOT in BOTH G_i and G, if the character is negative under i then the subscript is u (*ungerade*=odd), if the character is odd under i then the subscript is g (*gerade*=even)

For example:

$$D_3 \otimes i = D_{3d}$$

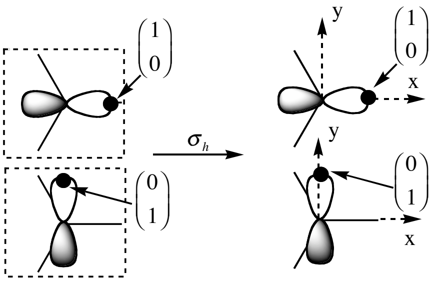
		E	$2C_3$	$3C_2'$	i	$2S_2$	$3\sigma_d$
D_3	A_2	1	1	-1			
D_{3d}	A_{2g}	1	1	-1	1	1	-1
	A_{2u}	1	1	-1	-1	-1	1

- The Primes
  - If the point group contains the operator σ_h but no i, a single prime indicates a representation that is symmetric with respect to a σ_h plane and a double prime a representation that is antisymmetric with respect to σ_h
  - Be careful with degenerate representations, as the assignment applies to the components and not the whole representation, for example see E' of D_{3h} below.

For example:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	(T_x, T_y)
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	T_z
E''	2	-1	0	2	1	0	

E' has components (say p_x and p_y) that are symmetric under σ_h:



$$\sigma_h \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

- The 1 and 2 as Subscripts
  - For non-degenerate representations (A and B) a subscript of 1 indicates the representation is symmetric with respect to a C_2 axis perpendicular to the principle C_n axis, or in the absence of this element, to a σ_v plane. A subscript of 2 indictes the representation is antisymmetric.
  - For multidimensional representations, the subscripts 1, 2 … are added to distinguish between non-equivalent irreducible representations that are not separated under the above rules.

For example:

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	(T_x, T_y)
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	T_z
E''	2	-1	0	2	1	0	

- Complex Characters ε
  - For a number of groups complex characters arise where ε=exp(i2π/n) where e can be regarded as an operator that rotates a vector by 2π/n anticlockwise in the complex plane or an Argand diagram. The two IR with complex characters are normally bracketed. Such point groups are not often encountered with molecules.

For example:

C_3	E	C_3^1	C_3^2
A	1	1	1
E	1	ε	ε*
	1	ε*	ε

- Linear Groups
  - Linear groups have an infinity subscript, eg $C_{\infty v}$ and $D_{\infty h}$. The symbol C_∞^ϕ indicates a rotation by an angle (ϕ) of any value, including infinitesimal. An infinite number of rotations is therefore possible, and an infinite number of vertical mirror planes $\infty\sigma_v$. In these groups Greek symbols are often used rather than the Mulliken notation. In addition, the primes are not used, and are replaced with + or – signs superscript to the Greek symbol, they still however refer to the sign under σ_v. The degenerate components do not follow the rules given for the other point groups.

For example:

$C_{\infty v}$	E	$2C_\infty^\phi \cdots$		$\infty\sigma_v$
$A_1=\Sigma^+$	1	1	...	1
$A_2=\Sigma^-$	1	1	...	-1
$E_1=\Pi$	2	2cosϕ	...	0
$E_2=\Delta$	2	2cos2ϕ	...	0
$E_3=\Phi$	2	2cos3ϕ	...	0
...	...		...	...