Irreducible Representation (IR) Symmetry Labels

The symbols to the far left of the character table are part of "Mulliken notation" defined in an article by R.S. Mulliken, *J Chem. Phys.,* **1955**, 23, p1997

The notes presented here are derived from material in "Symmetry and Group Theory in Chemistry" by Mark Ladd, Horwood Publishing, Chichester, 1998, p89-91

A, B, E and T Symbols

A is used when the IR is symmetric under C_n or S_n for the highest n in the group, in addition A is used if there are 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

E doubly degenerate

T triply degenerate

For example:

C_2	E	C_2
A	1	1
B	1	-1

The u and g Subscripts

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 sign is – under i then the subscript is u (*ungerade* = odd), if the sign is + 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

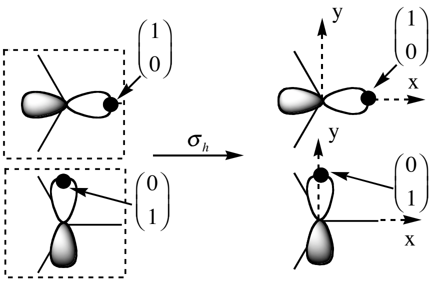
The Primes

If the point group contains the operator σ_h but no i, the IR labels are singly primed if the character is +1 under σ_h and doubly primed otherwise. A similar assignment applies to the components of the degenerate representations

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 degenerate IR (A and B) subscripts 1 and 2 relate to the symmetric (1) or antisymmetric (-1) characters respectively, in relation to a C_2 axis *perpendicular* to the principle C_n axis, or in the absence of this element, to a σ_v plane.

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 of 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 $D_{\infty h}$. These are infinite groups and the above named conventions do not hold, moreover the reduction of reducible representations does not work for infinite groups.

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 addition there are also coincident with the principle axis (C∞) additional axes: C_2, C_3, C_4, C_5 …C∞. As a rationalisation for the 2 in $2C_\infty^\Phi$ considet theat we count only unique opperations and many of these overlap whith a C_n of lower n, eg $C_4^2 = C_2^1$ and thus there are only 2 unique operations for each axis, eg C_n^1, C_n^{-1}. Thus for an infinite rotation there will be two unique operations $C_\infty^\Phi, C_\infty^{-\Phi}$.

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
...	...		...	...