Molecular symmetry irrep assignment

Molecular symmetry in the [1,1,1] and [2,1] partitions is described by 1, 2 or 3 symbols. The first symbol is always a number between 1 and ∞, showing the order n or $\bar{n}$ for the main rotational axis (usually chosen to be the z axis). In the [1,1,1] partition this number is either 1 or 2. In the [2,1] partition it can be any number between 3 and ∞ while in the [3] partition it is either 2, 4 or 5. Lower case letter c is always used to describe multiples of this operation and it is useful to think of c as the "generator" of the group. One symbol implies the one generator of a cyclic group.

If it occurs, the second symbol in the [1,1,1] and [2,1] partitions *n*2 represents a 2-fold rotational at right angles to the main axis. Lower case letter u is used for this generator, doubling the order of the group to produce a dihedral group. These are the dihedral groups. In the [3] partition it is a 3-fold rotation about a line from the centre of a cube through which the main axis passes and an apex of that cube.

Groups in the [1,1,1] or [2,1] partitions with main axial orders n describe molecules that may have sets of n equivalent atoms with the irreps shown in the table below or single atoms on the molecular axis that contribute irrep A to the total. Contributions from each set of equivalent atoms in the molecule are added together to obtain a final result.

Cyclic stem irreps

n	Irrep stems	n	Irrep stems
1	A	2	A, B
3	A, E_1	4	A, B, E_1
5	A, E_1, E_2	6	A, B, E_1, E_2
7	A, E_1, E_2, E_3	8	A, B, E_1, E_2, E_3
	.....		
∞	$A, E_1, E_2, .., E_\infty$		

Inverted cyclic groups $\bar{n}$ might also have pairs of atoms on the main axis that contribute irreps A + B while the central atom contributes irrep A. That's it – irreps can be worked out on the back of an envelope.

Remaining with the [1,1,1] and [2,1] partitions, a second symbol indicates a dihedral group ($n2$, $\bar{n}2$, n$\bar{2}$) or a centred group ($ni, n2i$). If it's a dihedral group the only work required is to add subscripts 1 and 2 to the A and B symbols already obtained for the cyclic group. Equal numbers of each subscript are required unless one or more of a set of equivalent atoms lies on the horizontal rotational 2-fold axis (usually taken to be the y axis), in which case only subscripts 1 are applied. Irrep A_1 must occur once and only once for each set of equivalent atoms.

Generally the molecules of centred cyclic group simply repeats all the irreps, once with subscripts g then with u but the centre atom takes the A_g symbol. If all the atoms of the molecule lie on a mirror plane then even irreps are given a g subscript and odd ones a u subscript. The remaining possibility is a centred dihedral group and probably the best way to get these irreps is to deduce irepps fro both the dihedral and the cyclic centred groups and merge the results.

Cubic groups in the [3] partition have a very limited repertoire of irreps. Tetrahedral and octahedral Laue classes are related in a similar way to the cyclic and dihedral group of the [1,1,1] and [2,1] partitions.. Irrep stems are deduced for the tetrahedral form then, if appropriate, extended to the octahedral state.