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Appendix VIII: Point Group Symmetry

Point Groups

By finding certain key elements of symmetry, the necessary existence of others can be implied. The point group notation is a shorthand devised to express key elements. It provides a neat method of describing molecular structures.

Finding the point group:

1. Is the molecule a member of a special group? Regular tetrahedron is termed T_d. A regular octahedron is O_h. Special groups are those in which there is no more than one axis of rotation of order greater than 2, these axes not being coincident: eg., a regular tetrahedron has 4 C_3 axes.
2. Find the highest axis C_n and call it vertical.
3. If $n = 1$:
   Has molecule a centre of symmetry? If so, then C_i.
   Has molecule a plane of symmetry? If so, then C_s.
   Has molecule nothing except E? If so, then C_1, and can be described as having no symmetry.
4. If $n \geq 2$:
   Are there nC_2 axes perpendicular to C_n? If so, the molecule is termed dihedral.
5. If dihedral:
   Has the molecule a horizontal plane? If so, then D_{nh}.
   Has the molecule n vertical planes? If so, then D_{nd}.
   If neither of these, it is D_n.
6. If not dihedral:
   Does it have S_{2n} coincident with C_n? If so, the point group is S_{2n}.
7. Has the molecule a horizontal plane? If so, C_{nh}. Has it n vertical planes? If so, C_{nv}. If neither of the above, then it is C_n.

Symmetry operations

A symmetry operation of a molecule is an operation about the centre of gravity which produces a configuration indistinguishable from that of the molecule before the operation.

Using the Schönflies notation:
Identity (E) implies no alteration of atomic positions or of coordinate direction.

Axis of symmetry (C). An n-fold axis of symmetry means that the indistinguishable configurations arise after every $360/n\,^{\circ}$ of rotation about an axis. Note that after n rotations about C_n, the symmetry operation, E, has been achieved. A molecule may have a number of different axes (eg. a square has C_4, 2 C_2 through the middle of the edges, and 2 more C_2 along the diagonals) and the highest order axis (largest n) is conventionally chosen as the z-axis. (z is regarded as vertical).

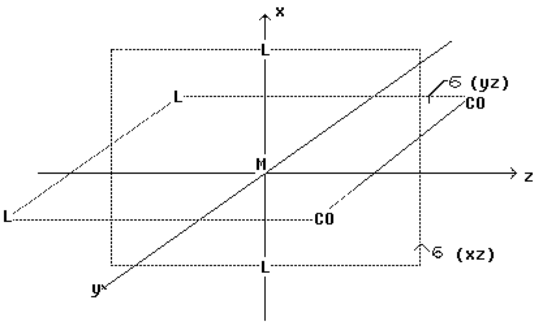
Plane of Symmetry (σ). A plane of symmetry reflects atoms from a given configuration to an indistinguishable one. Essentially the effect of a plane of symmetry operation will alter one of the cartesian coordinates defining an atom position into minus itself, leaving the other two unaltered, eg. $x,y,z \rightarrow x,y,-z$. The recognition of this is not obvious if the atom in question lies on the plane. The nature of the plane may be amplified by subscripts σ_v, σ_h and σ_d etc., where h = horizontal,(xy); d or v = vertical (there may be more than one distinct type of vertical plane).

Rotation-Reflection Axis (S_n). This is a two stage operation involving rotation about an axis 360/n degrees followed by reflection through a plane (which need not be a plane of symmetry) through the centre of gravity perpendicular to that axis. Some of the transformations achieved by performing some members of the family S_n may have been achieved by operations listed above and hence are not uniquely described in terms of S_n, eg. S_3^3 is the same as σ_h.

An operation which changes x,y,z to -x,-y,-z will belong to a family of S_n, but is singled out for description as a centre of symmetry (*i*).

The carbonyl spectrum of *cis*-$[\mathrm{M(CO)_2L_4}]$:

To deduce the number of infrared active carbonyl stretching frequencies for a molecule we must first deduce its point group. As can be seen from the figure the symmetry elements present in *cis*-$[\mathrm{M(CO)_2L_4}]$ are E (identity), $C_2(z)$ (two fold rotation axis in the z direction), σ(xz) (plane of symmetry in the xz plane) and σ(yz) (plane of symmetry in the yz plane). You can therefore verify that *cis*-$[\mathrm{M(CO)_2L_4}]$ belongs to the C_{2v} point group.



The character table for the C_{2v} point group is:

C_{2v}	E	$C_2(z)$	σ(xz)	σ(yz)			
A_1	1	1	1	1		z	xx,yy,zz
A_2	1	1	-1	-1	R_z		xy
B_1	1	-1	1	-1	R_y	x	xz
B_2	1	-1	-1	1	R_x	y	yz

We now investigate how the carbonyl groups transform under the symmetry operations of the C_{2v} point group. (As a first approximation the carbonyl stretching vibrations (υ(CO)) may be considered to be independent of other vibrations in the molecule.)

If, on carrying out a symmetry operation, the feature under consideration is totally unchanged, the effect of the symmetry operation is +1. If the feature remains in the same position in space but changes orientation, the effect will be within the range +1 or -1 (for one-dimensional species, those for which the number in the identity column is +1, the effect will always be either +1 or -1). If it is changed in its position in space, the effect is zero, but it must be interchanged with a similar item. Such features, interchangeable by any of the symmetry operations of the system, must be taken together.

Thus under the C_{2v} point group operations, the transformation of the carbonyl groups (taken together) are as follows:

E	(both CO's stay the same)	⇒	2
$C_2(z)$	(both CO's interconvert)	⇒	0
$\sigma(xz)$	(both CO's interconvert)	⇒	0
$\sigma(yz)$	(both CO's stay the same)	⇒	2

These characters form the reducible representation:

E	$C_2(z)$	$\sigma(xz)$	$\sigma(yz)$
2	0	0	2

which by inspection, may be reduced to $A_1 + B_2$

A_1	1	1	1	1
B_2	1	-1	-1	1

For a vibration to be infrared active its symmetry species must be identical to that of one of the dipole moment vectors (referred to as x, y or z in the character table). From the character table for the C_{2v} point group we can see that A_1 and B_2 transform as z and y respectively. Therefore both CO stretching vibrations are infrared active. Consequently *cis*-[$M(CO)_2L_4$] species exhibit two carbonyl stretching frequencies in the infrared spectrum.