2.8: Symmetry and Formaldehyde

These five symmetry elements are tabulated in Table 2.8.1 with their corresponding operators.

Table 2.8.1 : The five principal symmetry elements and their operators for 3D space

Symbol Elements	Description	Symbol Operator	Symbol
E	identity	$\hat{E}$	no change
C_n	n-fold axis of rotation	$\hat{C}_n$	Rotation by $360^\circ/n$leaves the molecule unchanged
σ	plane of symmetry	$\hat{\sigma}$	Reflection in the plane leaves the molecule unchanged
i	center of symmetry.	$\hat{i}$	Inversion through the center of symmetry leaves the molecule unchanged.
S_n	n-fold improper rotation	$\hat{S}_n$	The rotary reflection operation consists of rotating through an angle $360^\circ/n$about the axis, followed by reflecting in a plane perpendicular to the axis.

Every molecule has a point group associated with it, which are assigned by a set for rules (explained by Group theory). The character tables takes the point group and represents all of the symmetry that the molecule has.

Symmetry Operations

A symmetry operation is a permutation of atoms such that the molecule is transformed into a state **indistinguishable** from the starting state.

Character Tables

A character table is a two dimensional chart associated with a point group that contains the irreducible representations of each point group along with their corresponding matrix characters. It also contains the Mulliken symbols used to describe the dimensions of the irreducible representations, and the functions for symmetry symbols for the Cartesian coordinates as well as rotations about the Cartesian coordinates.

A character table can be separated into 6 different parts, namely:

1. The Point Group
2. The Symmetry Operation
3. The Mulliken Symbols
4. The Characters for the Irreducible Representations
5. The Functions for Symmetry Symbols for Cartesian Coordinates and Rotations
6. The Function for Symmetry Symbols for Square and Binary Products

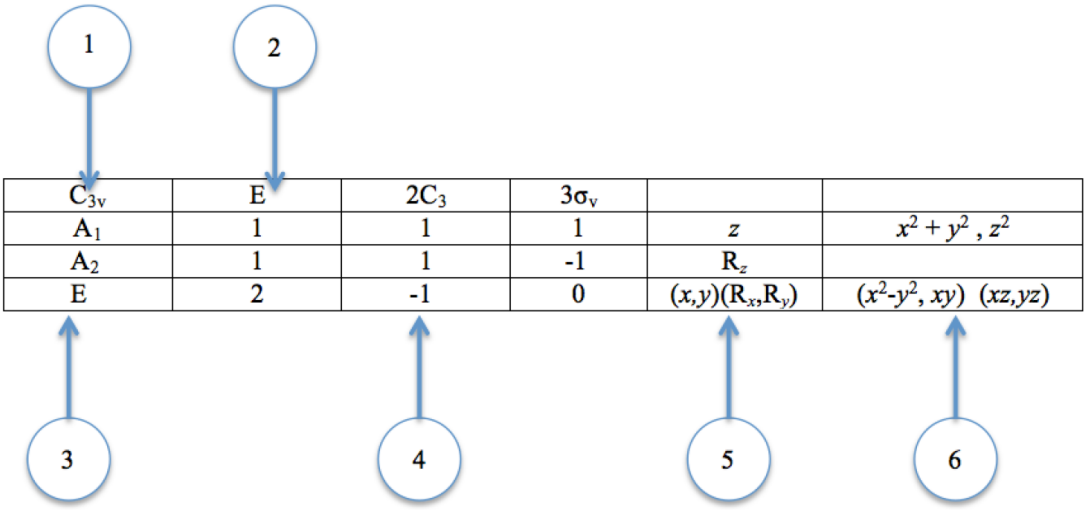

Figure 2.8.1: An example of a character table with different parts labelled

In many applications of group theory, we only need to know the characters of the representative matrices. Luckily, when each basis function transforms as a 1D **irreducible representation** (which is true in many cases of interest) there is a simple shortcut to determining the characters. All we have to do is to look at the way the individual basis functions transform under each symmetry operation.

Characters

For a given operation, step through the basis functions as follows:

i. Add 1 to the character if the basis function is unchanged by the symmetry operation (i.e. the basis function is mapped onto itself);
ii. Add -1 to the character if the basis function changes sign under the symmetry operation (i.e the basis function is mapped onto minus itself);
iii. Add 0 to the character if the basis function moves when the symmetry operation is applied (i.e the basis function is mapped onto something different from itself).

Formaldehyde

The MO's form a basis for irreducible representation of the C_{2v} **point-group** of H_2CO. Conventionally, the z-axis is along the C=O bond and the x-axis is ⊥ to place of the molecule. The symmetry operations for C_{2v} are E, C_2, $\sigma_v(xy)$ and $\sigma_{v'}(yx)$. For :

π and π^*

$$\hat{E}\pi = (+1)\pi$$

$$\hat{C}_2\pi = (-1)\pi$$

$$\hat{\sigma}_v\pi = (+1)\pi$$

$$\hat{\sigma}_{v'}\pi = (-1)\pi$$

So π and π^* transform as the B_1 irreducible representation

σ and σ^*

$$\hat{E}\sigma = (+1)\sigma$$

$$\hat{C}_2\sigma = (+1)\sigma$$

$$\hat{\sigma}_v\sigma = (+1)\sigma$$

$$\hat{\sigma}_{v'}\sigma = (+1)\sigma$$

So σ and σ^* transform as the A_1 irreducible representation

n_a

n_a also transform as B_1 it is a core electron in this orbital

n_b

$$\hat{E}n_b = (+1)n_b$$

$$\hat{C}_2 n_b = (-1)n_b$$

$$\hat{\sigma}_v n_b = (-1)n_b$$

$$\hat{\sigma}_{v'} n_b = (+1)n_b$$

So n_b transforms as the B_2 irreducible representation

Having ascertained the symmetry species of the MO's: $A_1(\sigma, \sigma^*, n_a)$; $B_1(\pi, \pi^*)$; $B_2(n)b)$, we can ask about the symmetry of the state produced by a configuration.

Direct Products of Representations

Here are listed some helpful general rules for the product of two irreducible representations. For specific combinations not listed here, one can work out the product by multiplying the characters of each irreducible representation and solving the linear combination of the irreducible representations from the point group that generates that product. Often this process is simple, especially when one or both of the irreducible representations are non-degenerate (in most cases *A* or *B*).

2. For C_2, C_3, C_6, D_3, D_6,C_{2v},C_{3v}, C_{6v},C_{2h}, C_{3h}, C_{6h}, D_{3h}, D_{6h}, D_{3d}, S_6

	A_1	A_2	B_1	B_2	E_1	E_2
A_1	A_1	A_2	B_1	B_2	E_1	E_2
A_2		A_1	B_2	B_1	E_1	E_2
B_1			A_1	A_2	E_2	E_1
B_2				A_1	E_2	E_1
E_1					$A_1 + [A_2] + E_2$	$B_1 + B_2 + E_1$
E_2						$A_1 + [A_2] + E_2$

Representation of an Electronic State

The representation of a specific quantum electronic state can be evaluated by the **direct product** of the representations of the molecular orbitals of the occupied electrons. Direct products can be extracted from the tables above. For example, the non-degenerate representations below

$$A \times A = A$$

$$B \times B = A$$

$$A \times B = B$$

Remember that the ground state valence electronic configuration of formaldehyde is:

$$n_a^2 \sigma^2 \pi^2 n_b^2 (\pi^*)^0 (\sigma^*)^0$$

so the representation of the ground-state is

$$\Gamma = (B_1 \times B_1)(A_1 \times A_1)(B_1 \times B_1)(B_2 \times B_2) \tag{2.8.1}$$

This can be simplified using the direct product tables

$$\Gamma = (A_1)(A_1)(A_1)(A_1)$$

so the ground state has a representation of A_1. We can make a general "rule" from this. This is a **“closed shell”** configuration and corresponds to a state with all molecular orbitals *doubly* occupied or *empty* and must be a singlet state! Since there are no odd electrons in the orbitals in the ground state, the configuration has a ${}^1A_1$ symmetry (totally symmetry).

Rule: Simpler Calculation

The symmetry representation of an electronic state is the direct product of the symmetry representations of each of the odd electrons orbitals. Since doubly filled orbitals do not contribute since their products are always totally symmetry:

$$B_1 \times B_1 = A_1$$

$$A_2 \times A_2 = A_1$$

etc.

There are no odd electrons in the orbitals in the ground state. Possible excited state symmetry includes:

$$n_b \rightarrow \pi^* \text{ or } {}^1\left(n_b, \pi^*\right)$$

and pay attention to only the unpair electrons give the following representation

Notation

- We use lower case representations for designating 1e- orbitals.
- We use capital case representation for designated are electronic states

$$\Gamma = b_2 \times b_1 = A_2$$

The electronic state symmetry is thus ${}^1A_2$. Conventionally, the $n_b \rightarrow \pi^*$ transition, in terms of states, is described as

$${}^1A_2 \leftarrow {}^1A_1$$

or

$${}^1A_2\left(n, \pi^*\right) \leftarrow {}^1A_1$$

Higher energy state is conventionally places on the left hand side and the arrow points in the direction of the transition.

Example 2.8.1

The ${}^1\left(\pi, \pi^*\right)$ state has the symmetry of

$$\mathrm{b_1} \times \mathrm{b_1} = \mathrm{a_1}$$

thus this transition is designated

$${}^1A_1\left(\pi, \pi^*\right) \leftarrow {}^1A_1$$

and this transition moves electron density from the O to the C, this is because

$$\pi = a\left(2p_x^C\right) + b\left(2p_x^o\right)$$

$b > a$ since O is more electronegative

$$\pi^* = b'\left(2p_x^C\right) + a'\left(p_x^O\right)$$

$b' > a'$ since for orthogonality with π.

Now, the ${}^1A_2 \leftarrow {}^1A_1$ transition also moves electron density from the O to the C. (For a similar argument).

References

- https://chem.libretexts.org/Bookshel...aracter_Tables
- http://www1.udel.edu/pchem/C444/Lect.../Lecture31.pdf