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3.2.4. Molecular symmetry

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3.2.4.1. Introduction

In this section, by 'molecule' we mean a separate set of closely bonded atoms; this definition includes molecular ions. The term 'molecule' as used here also includes molecular aggregates held together by hydrogen bonds or other important molecular interactions. We consider only the symmetry of isolated molecules, *i.e.* we act as if the molecule had no surroundings or a completely isotropic surrounding (even if it is a molecular ion that in reality has nearby counter ions), and we do not consider any vibrational distortions. Of course, in crystals the surroundings are not isotropic; their anisotropy is reflected in the site symmetry of the molecule. The site symmetry of the molecule in the crystal may not be higher than the molecular symmetry, and, in most cases, it is lower, *i.e.* it is a subgroup of the point group of the isolated molecule. From experience we know that the actual deviation of the molecular symmetry in crystals as compared to the symmetry in an isotropic surrounding is usually unimportant; generally, only conformation angles are affected significantly.

According to the statistical data for organic molecules (molecules having C—C or C—H bonds), the point group 1 is the most frequent (70.9%), followed by $\bar{1}$ (8.1%), 2 (7.5%), m (6.5%), $2/m$ (2.1%) and $mm2$ (1.7%); all others are <1% (Pidcock *et al.*, 2003). In crystals, the site symmetry of organic molecules is 1 with a frequency of 80.7%, followed by $\bar{1}$ (~11%). Centrosymmetric molecules ($\bar{1}$ and higher centrosymmetric point groups) almost always crystallize in centrosymmetric space groups (99%) and lie on centrosymmetric sites ($\bar{1}$ and higher) with a frequency of 97% (Pidcock *et al.*, 2003; Müller, 1978).

Since all real molecules are objects of three-dimensional space, we consider only three-dimensional symmetry groups. This choice also applies to so-called 'zero-', 'one-' and 'two-dimensional' molecules; these misleading terms are sometimes used for, respectively, finite molecules, polymeric chain molecules and polymeric layer molecules. For chemists who use these terms, the 'dimensionality' mostly refers to the linkage by covalent bonds; for physicists, 'dimensionality' may refer to some other anisotropic property, *e.g.* conductivity.

3.2.4.2. Definitions

The set of all isometries that map a molecule onto itself is its *molecular symmetry*. Its symmetry operations form a group which is the *point group* $\mathcal{P}_{\rm M}$ *of the molecule*.

The group $\mathcal{P}_{\rm M}$ is finite if the molecule consists of a finite number of atoms and is mapped onto itself by a finite number of isometries. However, the group is infinite for linear molecules like HCl and CO_2, because of the infinite order of the molecular axis. For the symmetry of polymeric molecules see below (Section 3.2.4.4).

All symmetry operations of a finite molecule leave its centre of mass unchanged. If this point is chosen as the origin, all symmetry operations can be represented by 3×3 matrices $\boldsymbol{W}_i$, referred to some predefined coordinate system.

According to their equivalence, point groups are classified into *point-group types*. Two point groups $\mathcal{P}_{\rm M1}$ and $\mathcal{P}_{\rm M2}$ belong to the same *point-group type* if, after selection of appropriate coordinate systems, the matrix groups of $\mathcal{P}_{\rm M1}$ and $\mathcal{P}_{\rm M2}$ coincide. Why point groups and point-group types have to be distinguished is shown in the following example of metaldehyde; however, for most molecules the distinction is usually of only minor importance.

In Section 1.1.7 a general definition is given for an *orbit* under the action of a group. Applied to molecules, we formulate this definition in the following way:

The set of points symmetry-equivalent to a point X of a molecule is the *orbit of X under* $\mathcal{P}_{\rm M}$.

A point X in a molecule has a definite *site symmetry* $\mathcal{S}_X$ (site-symmetry group). It consists of all those symmetry operations of the point group $\mathcal{P}_{\rm M}$ which leave the point fixed. The site-symmetry group $\mathcal{S}_X$ is always a subgroup of the point group of the molecule: $\mathcal{S}_X \leq \mathcal{P}_{\rm M}$.

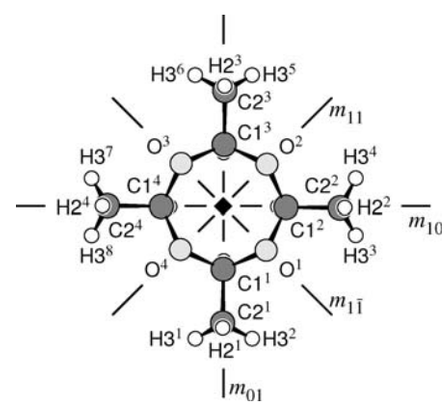
A point X is on a *general position* if its site symmetry $\mathcal{S}_X$ consists of nothing more than the identity, $\mathcal{S}_X = \mathcal{I}$. Otherwise, if $\mathcal{S}_X > \mathcal{I}$, the point is on a *special position*.

The *multiplicity* of a point X in a molecule is equal to the number of points which are symmetry-equivalent to this point, *i.e.* the number of points in its orbit. If the point is on a general position, its multiplicity is equal to the group order $|\mathcal{P}_{\rm M}|$. If $|\mathcal{S}_X|$ is the order of the site symmetry of a point on a special position, the multiplicity of X is $|\mathcal{P}_{\rm M}|/|\mathcal{S}_X|$.

Two points X and Y of a molecule belong to the same *Wyckoff position* if the site-symmetry groups $\mathcal{S}_X$ and $\mathcal{S}_Y$ are conjugate subgroups of $\mathcal{P}_{\rm M}$, *i.e.* if $\mathcal{S}_X$ and $\mathcal{S}_Y$ are symmetry-equivalent under a symmetry operation of $\mathcal{P}_{\rm M}$; expressed mathematically, this is $\mathcal{S}_Y = g\mathcal{S}_X g^{-1}$ with $g \in \mathcal{P}_{\rm M}$. The special case $\mathcal{S}_X = \mathcal{S}_Y$ is included.

Example

A molecule of metaldehyde [tetrameric acetaldehyde, 2,4,6,8-tetramethyl-1,3,5,7-tetraoxacyclooctane, $(H_3CCHO)_4$] has the point group $\mathcal{P}_{\rm M} = 4mm$ (C_{4v}) of order $|\mathcal{P}_{\rm M}| = 8$, consisting of the symmetry operations 1, 4^+, 2, 4^-, m_{10}, m_{01}, m_{11} and $m_{1\bar{1}}$.



The atoms $C1^1 \ldots C1^4$, the four H atoms bonded to them (not labelled in the figure and largely hidden), $C2^1 \ldots C2^4$ and $H2^1 \ldots H2^4$ make up four sets of symmetry-equivalent atoms and thus form four orbits. All these atoms are placed on the mirror planes m_{10} and m_{01}; their site-symmetry groups are $\{1, m_{10}\}$ or $\{1, m_{01}\}$. $\{1, m_{10}\}$ and $\{1, m_{01}\}$ are conjugate subgroups of $4mm$ because they are equivalent by a fourfold rotation, *i.e.* $\{1, m_{01}\} = 4^+\{1, m_{10}\}4^-$. All of these atoms belong to *one* Wyckoff position, labelled $4c$ in Table 3.2.3.2. The symmetry-equivalent atoms $O^1 \ldots O^4$ make up another orbit which belongs to a different Wyckoff position, labelled $4b$, with the conjugate site symmetries $\{1, m_{11}\}$ and $\{1, m_{1\bar{1}}\}$. Although the site symmetries of both $4b$ and $4c$ consist of the identity and one reflection, they are not conjugate because there is no symmetry operation of $4mm$ that relates them. The subgroups $\{1, m_{10}\}$ and $\{1, m_{11}\}$ are different point groups of the same point-group type.

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These four site-symmetry groups all have order 2. Accordingly, the multiplicity for each of the atoms discussed above is 8/2 = 4. The atoms $H3^1 \ldots H3^8$, however, are on a general position, their site symmetry is 1 and their multiplicity corresponds to the order 8 of the point group $4mm$. Their orbit belongs to the Wyckoff position $8d$. The Wyckoff position $1a$ on the fourfold rotation axis is not occupied.

3.2.4.3. Tables of the point groups

In Table 3.2.3.2 all crystallographic point groups are listed, *i.e.* all point groups with axes of orders 1, 2, 3, 4 and 6. As described in Section 3.2.1.2.3, the tables also contain the crystal forms which refer to the faces of crystals. As far as molecular symmetry is concerned, only the first four columns and the names of the polyhedra (point forms) in the fifth column given in italics are of interest.

The polyhedra listed in the fifth column result when the points of one orbit of the corresponding Wyckoff position are connected by lines. As for their names, see the remarks on 'point forms' in Sections 3.2.1.2.3 and 3.2.1.2.4.

In Table 3.2.3.2 each point group is headed by its short and, if it differs, full Hermann–Mauguin symbol and by its Schoenflies symbol. Each of the subsequent entries corresponds to one Wyckoff position, in order of increasing site symmetry. The last Wyckoff position of the list is always the one with the highest site symmetry and a multiplicity of 1. The sequence of the coordinate triplets follows the sequence as for the symmorphic space groups.

The columns of Table 3.2.3.2 contain the following data:

Column 1: The multiplicity, *i.e.* the number of equivalent points.

Column 2: The Wyckoff letter, which is an alphabetical label. For all point groups with a 'floating' origin, *i.e.*, where the origin is not fixed on a unique point of highest symmetry, the last entry is the Wyckoff letter a. For point groups with a fixed origin, the unique origin point has the highest site symmetry and has the letter o (for origin).

Column 3: The site symmetry, given as an 'oriented point-group symbol' (*cf.* Section 2.1.3.12).

Column 4: Coordinates x, y, z of equivalent points.

Column 5: The name of the polyhedron (point form) spanned by the set of symmetry-equivalent points with the coordinates from column 4 is given in italics. The names given in roman type refer to crystal forms described in Section 3.2.1.2.3 and have no importance for molecules. In some cases, a Wyckoff position has several entries in columns 5 and 6, with several polyhedron names. All but the first one correspond to orbits of the same Wyckoff position where some special values have been assigned to one or more of the variable coordinates, *e.g.* $z = 0$, with the consequence that the eigensymmetries of these orbits are higher than the symmetry of the generating point group (non-characteristic orbits, *cf.* Section 1.4.4.4).

Since there is no lattice, point groups of molecules, unlike point groups of crystals, have no 'natural' coordinate system. It is common for coordinates of atoms in molecules to refer to a Cartesian xyz coordinate system; with the exception of trigonal and hexagonal point groups, the coordinates given in Table 3.2.3.2 can be taken as Cartesian coordinates with arbitrary unit length. For point groups with a floating origin, the origin 0, 0, 0 has to be assigned to an arbitrarily chosen point of the Wyckoff position $1a$. The following conventions are used for the orientation of the coordinate axes:

Triclinic system: arbitrary orientation of the axes.

Monoclinic system: unique axis either y or z, as specified. The other two directions arbitrary but normal to the unique axis.

Orthorhombic system: Axes x, y and z along the symmetry directions.

Tetragonal system: z along the fourfold symmetry axis, x along the symmetry direction mentioned in the second position of the Hermann–Mauguin symbol. In the case of one-digit Hermann–Mauguin symbols the x direction is arbitrary within the plane normal to the unique axis. The axis y is normal to both x and z.

Trigonal and hexagonal systems: z along the unique symmetry axis, x along the symmetry direction mentioned second in the Hermann–Mauguin symbol. In the case of one-digit Hermann–Mauguin symbols the x direction is arbitrary within the plane normal to the unique axis. The axis y is also normal to z. *Note*: The coordinates given in Table 3.2.3.2 do not refer to a Cartesian, but to a symmetry-adapted coordinate system. For the hexagonal point groups and the trigonal point groups marked 'hexagonal axes' there is an angle of 120° between the x and y axes. These coordinates can be converted to a Cartesian system according to $x - \frac{1}{2}y, \frac{1}{2}\sqrt{3}y, z$. Coordinates that refer to 'rhombohedral axes' are not suited for separate molecules.

Cubic system: x, y and z along the symmetry directions described by the first position of the Hermann–Mauguin symbol.

For the trigonal and hexagonal systems, the following pairs of point-group types are distinguished in Table 3.2.3.2: 321 & 312, $3m1$ & $31m$, $\bar{3}m1$ & $\bar{3}1m$ and $\bar{6}m2$ & $\bar{6}2m$. In fact, each of these pairs represents only one molecular point-group type, the difference being only the arbitrarily chosen direction of the x axis. The members of each pair can be interconverted by turning the coordinate system by 30° about the z axis (referred to hexagonal axes). The same applies to the tetragonal pair $\bar{4}2m$ & $\bar{4}m2$, the turning angle being then 45°.

The terms triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal and cubic designate the crystal systems, *i.e.* the point groups of crystal lattices. As far as point groups of molecules are concerned, these terms only have the meaning of a classification by analogy with the crystal classes. For those who are accustomed to using Schoenflies symbols, it may seem odd to term the point groups $C_{3h} = S_3 = \bar{6}$ and $D_{3h} = \bar{6}2m$ hexagonal rather than trigonal, because the Schoenflies symbolism relies on rotoreflection operations rather than rotoinversion operations. In fact, some properties of C_{3h} and D_{3h} are rather more 'trigonal' than 'hexagonal'; for example, they have only one kind of degenerate irreducible representation (E), rather than two (E_1 and E_2) as do the other hexagonal point groups.

For the sake of treating molecular symmetries in the most uniform way, some recommendations for the preferred directions of the coordinate axes have been proposed (Joint Commission for Spectroscopy, 1955). These recommendations include:

(1) If any specifications are being made that depend on the choice of the axes (*e.g.* certain irreducible representations), the choice should explicitly be stated.

(2) For planar molecules with one three- or higher-fold axis (z axis): x axis through the greater number of atoms. For planar molecules with $mm2$ (C_{2v}) or mmm (D_{2h}) symmetry: x axis perpendicular to the plane of the molecule.

Molecular symmetry is not restricted to the crystallographic point groups. No detailed tables are given for noncrystallographic point groups, but the symbols for them can be found in Table 3.2.1.6. For the two icosahedral point groups see Section 3.2.1.4.2 and Table 3.2.3.3.

Certain physical properties depend on symmetry. In particular, a molecule can have a dipole moment only if it is polar, *i.e.* if it

references