

## 3. ADVANCED TOPICS ON SPACE-GROUP SYMMETRY

## 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*  $\mathcal{P}_M$  of the molecule.

The group  $\mathcal{P}_M$  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<sub>2</sub>, 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  $3 \times 3$  matrices  $\mathbf{W}_i$ , referred to some predefined coordinate system.

According to their equivalence, point groups are classified into *point-group types*. Two point groups  $\mathcal{P}_{M1}$  and  $\mathcal{P}_{M2}$  belong to the same *point-group type* if, after selection of appropriate coordinate systems, the matrix groups of  $\mathcal{P}_{M1}$  and  $\mathcal{P}_{M2}$  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  $\mathcal{P}_M$* .

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  $\mathcal{P}_M$  which leave the point fixed. The site-symmetry group  $\mathcal{S}_X$  is always a subgroup of the point group of the molecule:  $\mathcal{S}_X \leq \mathcal{P}_M$ .

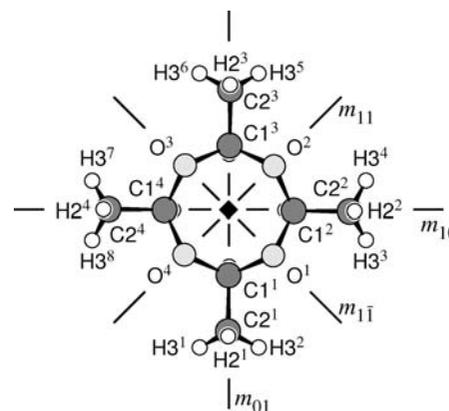
A point  $X$  is on a *general position* if its site symmetry  $\mathcal{S}_X$  consists of nothing more than the identity,  $\mathcal{S}_X = \mathcal{I}$ . Otherwise, if  $\mathcal{S}_X > \mathcal{I}$ , the point is on a *special position*.

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  $|\mathcal{P}_M|$ . If  $|\mathcal{S}_X|$  is the order of the site symmetry of a point on a special position, the multiplicity of  $X$  is  $|\mathcal{P}_M|/|\mathcal{S}_X|$ .

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  $\mathcal{P}_M$ , *i.e.* if  $\mathcal{S}_X$  and  $\mathcal{S}_Y$  are symmetry-equivalent under a symmetry operation of  $\mathcal{P}_M$ ; expressed mathematically, this is  $\mathcal{S}_Y = g\mathcal{S}_Xg^{-1}$  with  $g \in \mathcal{P}_M$ . 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<sub>3</sub>CCHO)<sub>4</sub>] has the point group  $\mathcal{P}_M = 4mm$  ( $C_{4v}$ ) of order  $|\mathcal{P}_M| = 8$ , consisting of the symmetry operations 1, 4<sup>+</sup>, 2, 4<sup>-</sup>,  $m_{10}$ ,  $m_{01}$ ,  $m_{11}$  and  $m_{\bar{1}\bar{1}}$ .



The atoms C1<sup>1</sup>...C1<sup>4</sup>, the four H atoms bonded to them (not labelled in the figure and largely hidden), C2<sup>1</sup>...C2<sup>4</sup> and H2<sup>1</sup>...H2<sup>4</sup> 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<sup>1</sup>...O<sup>4</sup> make up another orbit which belongs to a different Wyckoff position, labelled 4b, with the conjugate site symmetries  $\{1, m_{11}\}$  and  $\{1, m_{\bar{1}\bar{1}}\}$ . 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.