

## Molecular-Distortion Analysis with Cartesian Symmetry Coordinates

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### Abstract

A general method for the analysis of molecular distortion using Cartesian symmetry coordinates is proposed. The method is characterized by explicit definition of the spatial disposition of the reference structure and by the use of  $3N-6(5)$  symmetry coordinates which represent real modifications of the molecular structure, thus avoiding problems of redundancy. The method is applied to  $ML_4(T_d)$  and  $ML_6(O_h)$  type molecules.

### 1. Introduction

Group theory has only in recent years been applied to the analysis and description of molecular distortions. It is particular relevance to the study of solid-state matter, where one frequently encounters molecular systems which show structural deviations from a geometrical configuration of higher symmetry (Baur, 1974).

Of particular interest is the method of analysis proposed by Murray-Rust, Bürgi & Dunitz (1978*a,b*, 1979), where molecular distortion is described in terms of symmetry coordinates relative to a reference structure which is of higher symmetry. The main advantage of this method lies in the fact that each of the terms represents a partial distortion retaining some of the symmetry elements of the reference configuration. Furthermore, with this procedure we can define the concept of approximate symmetry in a quantitative way.

It is known that symmetry coordinates can be expressed in terms of internal parameters, *i.e.* bond distances and angles, or in terms of atomic Cartesian displacements. The Murray-Rust procedure uses symmetry coordinates which are related to the internal parameters. In this paper we propose a general method of molecular-distortion analysis which is based on Cartesian symmetry coordinates. This model applies Eckart's formalism, which is well known in molecular-vibration theory, in order to resolve the spatial orientation of the reference structure. As examples, the procedure is applied to cases of distortion in tetrahedral  $ML_4(T_d)$  and octahedral  $ML_6(O_h)$  molecules.

### 2. Method

The first step, which is mandatory in the analysis of molecular distortion when the molecular geometry is to be described by Cartesian coordinates, is the determination of the relative positions of the molecular structure to be analyzed and a reference structure: generally speaking the relative disposition of the two molecular structures may correspond to a distortion which is to some extent reducible into rigid rotations or translations of the reference structure, and which are, in the absence of external fields, not significant from a chemical point of view.

Within the Cartesian coordinate description, for a molecule with  $N$  atoms, the molecular distortion, *i.e.* the nuclear displacement from a hypothetical reference configuration, is expressed by a vector,  $\mathbf{D}$ , which has  $3N$  components.  $\mathbf{D}$  represents the distance vector between the point defining, in nuclear configuration space, the structure to be analyzed and that of the reference structure. This distance is also a function of the relative displacements and rotations of the two structures. In the second step one of the structures, for example the reference one, must be moved and rotated in such a way that the vector  $\mathbf{D}$  does not contain any contribution from rigid translations or rotations.

The translation problem is easily resolved by making the centers of mass of the two structures coincide. The rotation problem is slightly more difficult to resolve.

Let  $\mathbf{r}_i$  ( $i = 1 \dots N$ ) be the nuclear position vector of the structure to be analyzed relative to any molecular coordinate system  $K(\mathbf{X}, \mathbf{Y}, \mathbf{Z})$ , a coordinate system with the origin located at the center of mass of the molecule and moving with it, *i.e.* the vector's position  $\mathbf{r}_i$  remains constant within  $K$ . In addition let  $r_i^\alpha$  ( $i = 1 \dots N$ ;  $\alpha = x, y, z$ ) indicate the components of the  $\mathbf{r}_i$ 's within  $K$ . We also introduce  $\mathbf{a}_i$  ( $i = 1, \dots, N$ ), the nuclear position vector of the reference structure relative to any molecular coordinate system  $K'(\mathbf{X}, \mathbf{Y}, \mathbf{Z})$ , a coordinate system with the origin located at the center of mass of the reference structure, and moving with it, and  $a_i^\alpha$  ( $i = 1, \dots, N$ ;  $\alpha = x, y, z$ ) indicates the components of the vector's position  $\mathbf{a}_i$  within  $K'$ .

Translation of the reference structure with respect to the structure to be analyzed is such that the

centers of mass are coincident, *i.e.* the two molecular coordinate systems  $K$  and  $K'$  have the same origin. Now, the problem is to determine the correct orientation between the two structures.

Let us consider the following three Eckart vectors:

$$\begin{aligned} \mathbf{F}_1 &= \sum_{j=1}^N m_j a_j^x \mathbf{r}_j \\ \mathbf{F}_2 &= \sum_{j=1}^N m_j a_j^y \mathbf{r}_j \\ \mathbf{F}_3 &= \sum_{j=1}^N m_j a_j^z \mathbf{r}_j \end{aligned} \quad (2.1)$$

where  $m_j$  is the mass of the  $j$ th atom.

The Eckart vectors have a well defined orientation within the  $K$  molecular frame with components:

$$\begin{aligned} F_1^\alpha &= \sum_{j=1}^N m_j a_j^x r_j^\alpha \\ F_2^\alpha &= \sum_{j=1}^N m_j a_j^y r_j^\alpha \\ F_3^\alpha &= \sum_{j=1}^N m_j a_j^z r_j^\alpha. \end{aligned} \quad (2.2)$$

By symmetrical orthonormalization of the Eckart vectors we obtain the unit vectors  $\mathbf{f}_1$ ,  $\mathbf{f}_2$ , and  $\mathbf{f}_3$ , which define the Eckart reference frame:

$$\mathbf{f}_i = \sum_{j=1}^3 \mathbf{F}_j e_{ji} \quad i = 1, 2, 3 \quad (2.3)$$

where  $e_{ji}$  is the  $j$ th element of the matrix  $E$  which is defined as:

$$E = \mathbf{F}^{-1/2}$$

and  $\mathbf{F}$  is the Gram-Schmidt matrix of the Eckart vectors with elements  $f_{ij}$ :

$$f_{ij} = \mathbf{F}_i \cdot \mathbf{F}_j$$

where the dot denotes the inner vector product, and:

$$\mathbf{F}^{-1/2} \mathbf{F}^{-1/2} = \mathbf{F}^{-1}$$

where  $\mathbf{F}^{-1}$  is the inverse of the  $\mathbf{F}$  matrix. Obviously,  $\mathbf{F}^{-1/2}$  ( $\mathbf{F}^{-1}$ ) only exists if  $\mathbf{F}$  is defined as positive, that is, the Eckart vectors are linearly independent.

The unit vectors  $\mathbf{f}_1$ ,  $\mathbf{f}_2$ ,  $\mathbf{f}_3$  provide the solution to the problem: we merely have to orientate the reference structure with respect to the structure to be analyzed so that its molecular coordinate system  $K'$  has the unit vectors  $\mathbf{X}'$ ,  $\mathbf{Y}'$  and  $\mathbf{Z}'$  collinear with  $\mathbf{f}_1$ ,  $\mathbf{f}_2$  and  $\mathbf{f}_3$ , respectively, see Fig. 1. Under this condition, the nuclear displacement vectors:

$$\mathbf{d}_i = \mathbf{r}_i - \mathbf{a}_i$$

satisfy the well known Eckart conditions (Eckart, 1935; Louck & Galbraith, 1976):

$$\sum_i^N m_i \mathbf{d}_i = 0 \quad (2.4a)$$

$$\sum_i^N m_i \mathbf{a}_i \wedge \mathbf{d}_i = 0 \quad (2.4b)$$

where  $\wedge$  denotes the external, or cross-vector product. From (2.4a,b) it can be seen that the molecular-distortion vector  $\mathbf{D}$  is free from rigid translations or rotations.

When the reference structure has a point symmetry  $G$  higher than the real structure, the distortion is conveniently analyzed if the vector  $\mathbf{D}$  is expressed in terms of symmetry coordinates related to the point group  $G$  (Murray-Rust, Bürgi & Dunitz, 1978a). A general Cartesian basis  $[\mathbf{x}(i), \mathbf{y}(i), \mathbf{z}(i), i = 1, \dots, N]$  for  $\mathbf{D}$  spans a representation,  $\Gamma$ , of the group  $G$  which is generally reducible:

$$\Gamma = \sum_{\alpha}^{\oplus} n_{\alpha} \Gamma_{\alpha} \quad (2.5)$$

where  $\sum_{\alpha}^{\oplus}$  denotes the direct sum, and  $\Gamma_{\alpha}$  is the  $\alpha$ th irreducible representation, IR,  $n_{\alpha}$  times contained in  $\Gamma$ .

Substituting  $U$ , the unitary matrix which operates on the Cartesian basis, in (2.5):

$$(\mathbf{s}_1, \mathbf{s}_2, \dots, \mathbf{s}_{3N}) = [\mathbf{x}(1), \mathbf{y}(1), \mathbf{z}(1), \dots, \mathbf{x}(N), \mathbf{y}(N), \mathbf{z}(N)] U \quad (2.6)$$

and the new components of the vector  $\mathbf{D}$ , the Cartesian symmetry coordinates, are given by:

$$\begin{pmatrix} s_1 \\ s_2 \\ s_3 \\ \vdots \\ s_{3N-2} \\ s_{3N-1} \\ s_{3N} \end{pmatrix} = U^{-1} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ \vdots \\ x_N \\ y_N \\ z_N \end{pmatrix}. \quad (2.7)$$

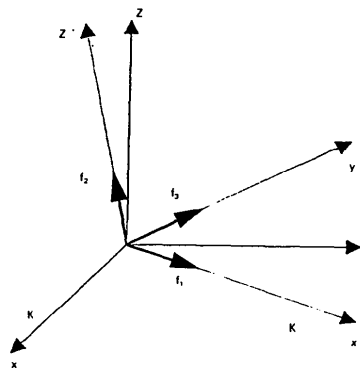


Fig. 1. Orientation of the structure to be analyzed with respect to the reference structure.  $K$  is the molecular coordinate system of the former and  $K'$  is that of the latter.  $\mathbf{f}_1$ ,  $\mathbf{f}_2$ ,  $\mathbf{f}_3$  are unit vectors of the Eckart frame (see text). When  $x'$ ,  $y'$ ,  $z'$  are collinear with  $\mathbf{f}_1$ ,  $\mathbf{f}_2$ ,  $\mathbf{f}_3$ , respectively, the two structures are not related by rigid translations or rotations.

$U$  is defined in such a way that three of the coordinates  $s_\gamma$  correspond to rigid translation, and another three (two for linear molecules) to rigid rotation. Therefore, the remaining  $3N - 6(5)$  symmetry coordinates  $s_\gamma$  represent real variations of the molecular geometry. In this way the problem of redundancy encountered with symmetry coordinates relative to internal parameters, is avoided.

Molecular distortions can be analyzed both by referring to the molecular static model, *i.e.* a set of nuclei labelled  $1, \dots, N$  with point masses  $m_1, \dots, m_N$  placed at positions specified by the vectors  $\mathbf{r}_i$  ( $i = 1, N$ ) (Louck & Galbraith, 1976), as well as by referring to the molecular geometrical model, *i.e.* the set of vectors  $\mathbf{r}_i$  relative to the nuclear positions; if we consider the former model, we have to use the mass-weighted Cartesian coordinates ( $x_i' = m_i^{1/2}x_i$ ) in (2.7) instead of the Cartesian coordinates (Mezey & Maruani, 1990); whereas if we consider the latter model we must put  $m_i = 1$ , ( $i = 1, N$ ), in (2.1). For the examples given in the numerical section we will refer to the molecular static model.

Within the symmetry-coordinate description, molecular distortions are conveniently analyzed by exploiting the expansion:

$$\mathbf{D} = \sum_{\alpha} \sum_{i=1}^{n_{\alpha}} \mathbf{D}_{\Gamma_{\alpha}} i \quad (2.8)$$

where  $\mathbf{D}_{\Gamma_{\alpha}} i$  is the projection of  $\mathbf{D}$  into the subspace  $Q_{\Gamma_{\alpha}} i$  defined by the components of the basis which spans the  $i$ th IR of  $\alpha$ -type. A fundamental characteristic of the right-handed terms of (2.8) is that they each represent a partial distortion which retains some of the determined symmetry element of the reference structure.

Generally, a symmetry distortion  $\mathbf{D}_{\Gamma_{\alpha}} i$  will maintain those symmetry elements for which

$$R(\Gamma_{\alpha}; g) \mathbf{D}_{\Gamma_{\alpha}} i = \mathbf{D}_{\Gamma_{\alpha}} i \quad (2.9)$$

holds, where  $R(\Gamma_{\alpha}; g)$  is the matrix relative to the  $g$ -element in the  $\Gamma_{\alpha}$  IR. It is immediately evident that in an arbitrary distortion  $\mathbf{D}_{\Gamma_{\alpha}} i$  only those elements represented in the IR  $\Gamma_{\alpha}$  by the unit matrix, whose character is equal to the dimension of IR  $\Gamma_{\alpha}$ , will be maintained. The symmetry subgroup formed by these symmetry elements is an invariant subgroup of  $G$ , known as the kernel of the IR.

However, in the case of a degenerate IR, higher symmetries than the kernel symmetry can be maintained. These symmetries are called co-kernel (epikernel) symmetries (Melvin, 1956), and correspond to special symmetry distortions, or special positions in the multidimensional subspace  $Q_{\Gamma_{\alpha}}$ . As examples, we report in Table 1 the kernel and co-kernel symmetries and the related special positions for some of the IR's of  $T_d$  and  $O_h$  point groups. As

Table 1. Symmetry kernels and co-kernels, with related special positions, SP, for some of the multidimensional irreducible representations,  $\Gamma_j$ , of the  $T_d$  and  $O_h$  point groups

Co-kernel apex refers to the spatial orientation of the relative principal symmetry element, axis or plane, according to the standard nomenclature (McWeeny, 1963). For example, in  $C_3^{xyx}$  the ternary axis is  $C_3^{xyz}$ , *etc.* The special positions are given in terms of vector components in the two- or three-dimensional spaces representing the  $\Gamma_j$ 's ( $a$  and  $b$  are real numbers).

$\Gamma_j$	Co-kernel (SP)
$E(T_d)$	$D_{3d}^2(1/2a, -3^{1/2}/2a); D_{2d}^2(1/2a, 3^{1/2}/2a); D_{2d}^2(a, 0)$ $D_2(a, b)$ (Kernel)
$T_2(T_d)$	$C_3^2(a, 0, 0); C_3^2(0, a, 0); C_3^2(0, 0, a)$ $C_3^{xyx}(a, a, a); C_3^{xyx}(a, \bar{a}, \bar{a}); C_3^{xyx}(\bar{a}, a, \bar{a}); C_3^{xyx}(\bar{a}, \bar{a}, a)$ $C_3^{yz}(a, b, b); C_3^{yz}(a, b, \bar{b}); C_3^{yz}(b, a, b); C_3^{yz}(b, a, \bar{b}); C_3^{yz}(b, b, a);$ $C_3^{yz}(b, \bar{b}, a)$
$E_2(O_h)$	$C_1(a, b, c)$ (Kernel)
$E_2(O_h)$	$D_{3h}^2(1/2a, -3^{1/2}/2a); D_{3h}^2(1/2a, 3^{1/2}/2a); D_{3h}^2(a, 0)$ $D_{2h}(a, b)$ (Kernel)
$T_{2g}(O_h)$	$D_{3h}^2(a, 0, 0); D_{3h}^2(0, a, 0); D_{3h}^2(0, 0, a)$ $D_{3h}^{xyx}(a, a, a); D_{3h}^{xyx}(a, \bar{a}, \bar{a}); D_{3h}^{xyx}(\bar{a}, a, \bar{a}); D_{3h}^{xyx}(\bar{a}, \bar{a}, a)$ $C_{2h}^2(a, b, b); C_{2h}^2(a, b, \bar{b}); C_{2h}^2(b, a, b); C_{2h}^2(b, a, \bar{b}); C_{2h}^2(b, b, a);$ $C_{2h}^2(b, \bar{b}, a)$
$T_{1u}(O_h)$	$C_1(a, b, c)$ (Kernel)
$T_{1u}(O_h)$	$C_4^2(a, 0, 0); C_4^2(0, a, 0); C_4^2(0, 0, a)$ $C_3^{xyx}(a, a, a); C_3^{xyx}(a, \bar{a}, \bar{a}); C_3^{xyx}(\bar{a}, a, \bar{a}); C_3^{xyx}(\bar{a}, \bar{a}, a)$ $C_2^2(0, a, a); C_2^2(0, a, \bar{a}); C_2^2(a, 0, a); C_2^2(a, 0, \bar{a}); C_2^2(a, a, 0);$ $C_2^2(a, \bar{a}, 0);$ $C_2^{yz}(a, b, b); C_2^{yz}(a, b, \bar{b}); C_2^{yz}(b, a, b); C_2^{yz}(b, a, \bar{b}); C_2^{yz}(b, b, a);$ $C_2^{yz}(b, \bar{b}, a)$ $C_2^2(0, a, b); C_2^2(a, 0, b); C_2^2(a, b, 0)$
$T_{2u}(O_h)$	$C_1(a, b, c)$ (Kernel)
$T_{2u}(O_h)$	$D_{3d}^2(a, 0, 0); D_{3d}^2(0, a, 0); D_{3d}^2(0, 0, a)$ $D_{3d}^{xyx}(a, a, a); D_{3d}^{xyx}(a, \bar{a}, \bar{a}); D_{3d}^{xyx}(\bar{a}, a, \bar{a}); D_{3d}^{xyx}(\bar{a}, \bar{a}, a)$ $C_2^2(0, a, a); C_2^2(0, a, \bar{a}); C_2^2(a, 0, a); C_2^2(a, 0, \bar{a}); C_2^2(a, a, 0);$ $C_2^2(a, \bar{a}, 0)$ $C_2^{yz}(a, b, b); C_2^{yz}(a, b, \bar{b}); C_2^{yz}(b, a, b); C_2^{yz}(b, a, \bar{b}); C_2^{yz}(b, b, a);$ $C_2^{yz}(b, \bar{b}, a)$ $C_2^2(0, a, b); C_2^2(a, 0, b); C_2^2(a, b, 0)$
	$C_1(a, b, c)$ (Kernel)

pointed out by Murray-Rust, Bürgi & Dunitz (1978a,b), the description of molecular distortions in terms of symmetry coordinates allows us to define quantitatively the concept of approximate symmetry, or pseudosymmetry, PS.

If we only consider a few terms in the double sum of (2.9), we can obtain a hypothetical structure with a symmetry greater than the one observed. We refer to this symmetry as the approximate symmetry of the real structure.

Generally, the distortion associated with each possible approximate symmetry, PSD, will be represented by a vector  $\mathbf{D}(\text{PS})$ , given by:

$$\mathbf{D}(\text{PS}) = \sum_{\alpha} \sum_{i=1}^{n_{\alpha}} \mathbf{D}_{\Gamma_{\alpha}} i(\text{PS}) \quad (2.10)$$

where  $\mathbf{D}_{\Gamma_{\alpha}} i(\text{PS})$  is the projection of the vector  $\mathbf{D}$ , the total distortion, along the special position associated with the epikernel symmetry of lower order containing PS as a subgroup. The ratio  $|\mathbf{D}(\text{PS})|/|\mathbf{D}|$  can be

considered to be a measure of the degree of approximation of the PS symmetry.\*

The molecular configurations associated with the hypothetical intermediate symmetries can be obtained directly in terms of the distortion with respect to the reference configuration, by expressing the related vectors  $\mathbf{D}(\text{PS})$  in the Cartesian basis, with a transformation inverse to (2.7).

Furthermore it can be useful to discuss the molecular distortions as a gradual loss of symmetry (Cammi, Oleari & Oleari, 1984; Ceulemans, Beyenes & Vanquickenborne, 1984; Boca, Breza & Pelikan, 1989). This hypothetical process of 'descent in symmetry' can be represented by a chain having as extremes the symmetry groups of the reference structure and the real one,  $S$ :

$$G \rightarrow \text{PS}^{(1)} \rightarrow \dots \rightarrow \text{PS}^{(N)} \rightarrow S \quad (2.11)$$

where  $\text{PS}^{(i)}$  ( $i = 1, \dots, N$ ) are the approximate symmetries in decreasing order. Often, it is possible to represent the molecular distortion by considering alternative descent pathways. Since each approximate symmetry can be classified by means of the above-defined degree of approximation, the trends of such degrees characterize the various pathways. Examples of 'descent in symmetry' will be shown in the numerical section.

### 3. Application to $ML_4 (T_d)$ and $ML_6 (O_h)$ molecules

As examples of applications of molecular-distortion analysis using Cartesian symmetry coordinates, we have considered distortions in tetrahedral  $ML_4$  and octahedral  $ML_6$  molecules.

#### 3.1. Symmetry Cartesian coordinates for $ML_4 (T_d)$ and $ML_6 (O_h)$ molecules

The sets of mass-weighted Cartesian displacement coordinates in tetrahedral  $ML_4$  and octahedral  $ML_6$  molecules form the bases for the following reducible representations:

$$\Gamma_i(ML_4; T_d) = A_1 + E + T_1 + 3T_2 \quad (3.1a)$$

$$\Gamma_i(ML_6; O_h) = A_{1g} + E_g + 3T_{1u} + T_{1g} + T_{2g}. \quad (3.1b)$$

Assuming for the  $ML_4 (T_d)$  reference molecular structure the Cartesian coordinate system and the atomic labelling shown in Fig. 2 we have the following symmetry coordinates:

$$\begin{aligned} S_1(A_1) &= (m_L/12)^{1/2}(x_1 + y_1 + z_1 - x_2 - y_2 \\ &\quad + z_2 - x_3 + y_3 - z_3 + x_4 - y_4 - z_4) \\ S_{2a}(E; z^2) &= (m_L/24)^{1/2}(x_1 + y_1 - 2z_1 - x_2 - y_2 \\ &\quad - 2z_2 - x_3 + y_3 + 2z_3 + x_4 - y_4 \\ &\quad + 2z_4) \\ S_{2b}(E; x^2 - y^2) &= (m_L/8)^{1/2}(x_1 - y_1 - x_2 + y_2 - x_3 \\ &\quad - y_3 - x_4 + y_4) \\ S_{3a}(T_1; R_x) &= (m_L/4)^{1/2}(-y_1 + z_1 - y_2 - z_2 + y_3 \\ &\quad + z_3 + y_4 - z_4) \\ S_{3b}(T_1; R_y) &= (m_L/4)^{1/2}(x_1 - z_1 + x_2 + z_2 - x_3 \\ &\quad + z_3 - x_4 + z_4) \\ S_{3c}(T_1; R_z) &= (m_L/4)^{1/2}(-x_1 + y_1 + x_2 - y_2 - x_3 \\ &\quad - y_3 + x_4 + y_4) \\ S_{4a}(T_2; x) &= (m_M + 4m_L)^{-1/2}[m_L(x_1 + x_2 + x_3 \\ &\quad + x_4) + m_M x_M] \\ S_{4b}(T_2; y) &= (m_M + 4m_L)^{-1/2}[m_L(y_1 + y_2 + y_3 \\ &\quad + y_4) + m_M y_M] \\ S_{4c}(T_2; z) &= (m_M + 4m_L)^{-1/2}[m_L(z_1 + z_2 + z_3 \\ &\quad + z_4) + m_M z_M] \\ S_{5a}(T_2; x) &= (m_M + 4m_L)^{-1/2}(m_M m_L)^{-1/2}[(x_1 \\ &\quad + x_2 + x_3 + x_4)/2 - 2x_M] \\ S_{5b}(T_2; y) &= (m_M + 4m_L)^{-1/2}(m_M m_L)^{-1/2}[(y_1 \\ &\quad + y_2 + y_3 + y_4)/2 - 2y_M] \\ S_{5c}(T_2; z) &= (m_M + 4m_L)^{-1/2}(m_M m_L)^{-1/2}[(z_1 \\ &\quad + z_2 + z_3 + z_4)/2 - 2z_M] \\ S_{6a}(T_2; x) &= (m_L/8)^{1/2}(y_1 + z_1 + y_2 - z_2 - y_3 \\ &\quad + z_3 - y_4 - z_4) \\ S_{6b}(T_2; y) &= (m_L/8)^{1/2}(x_1 + z_1 + x_2 - z_2 - x_3 \\ &\quad - z_3 - x_4 + z_4) \\ S_{6c}(T_2; z) &= (m_L/8)^{1/2}(x_1 + y_1 - x_2 - y_2 + x_3 \\ &\quad - y_3 - x_4 + z_4). \end{aligned} \quad (3.2)$$

One can easily note that the symmetry coordinates  $S_3$  and  $S_4$  correspond to rigid rotation and translation, respectively.

Assuming for the  $ML_6 (O_h)$  reference molecular structure the Cartesian reference system and the atomic labelling as shown in Fig. 3 we have the following symmetry coordinates:

\* As suggested by a referee, in the case of the Cartesian displacement coordinates it is easy to include the e.s.d.'s of the symmetry coordinates and therefore also give a quantitative assessment of symmetric configurations within experimental e.s.d.'s.

$$\begin{aligned}
S_{1a}(A_{1g}) &= (m_L/6)^{1/2}(x_1 + y_2 - x_3 - y_4 \\
&\quad - z_5 + z_6) \\
S_{2a}(E_g; z^2) &= (m_L/12)^{1/2}(-x_1 - y_2 + x_3 + y_4 \\
&\quad - 2z_5 + 2z_6) \\
S_{2b}(E_g; x^2 - y^2) &= (m_L/4)^{1/2}(x_1 - y_2 - x_3 + y_4) \\
S_{3a}(T_{1u}; x) &= (m_M + 6m_L)^{-1/2}[m_L^{1/2}(x_1 + x_2 \\
&\quad + x_3 + x_4 + x_5 + x_6) + m_M^{1/2}x_M] \\
S_{3b}(T_{1u}; y) &= (m_M + 6m_L)^{-1/2}[m_L^{1/2}(y_1 + y_2 \\
&\quad + y_3 + y_4 + y_5 + y_6) + m_M^{1/2}x_M] \\
S_{3c}(T_{1u}; z) &= (m_M + 6m_L)^{-1/2}[m_L^{1/2}(z_1 + z_2 \\
&\quad + z_3 + z_4 + z_5 + z_6) + m_M^{1/2}x_M] \\
S_{4a}(T_{1u}; x) &= (m_M + 6m_L)^{-1/2}\{[4m_L/(m_M^2 \\
&\quad + 2m_L)]^{1/2}(x_1 + x_3) - [(m_M \\
&\quad + 2m_L)/4]^{1/2}(x_2 + x_4 + x_5 + x_6) \\
&\quad + [4m_M m_L/(m_M + 2m_L)]^{1/2}x_M\} \\
S_{4b}(T_{1u}; y) &= (m_M + 6m_L)^{-1/2}\{[4m_L/(m_M^2 \\
&\quad + 2m_L)]^{1/2}(y_1 + y_3) - [(m_M \\
&\quad + 2m_L)/4]^{1/2}(y_2 + y_4 + y_5 + y_6) \\
&\quad + [4m_M m_L/(m_M + 2m_L)]^{1/2}x_M\} \\
S_{4c}(T_{1u}; z) &= (m_M + 6m_L)^{-1/2}\{[4m_L/(m_M^2 \\
&\quad + 2m_L)]^{1/2}(z_1 + z_3) - [(m_M \\
&\quad + 2m_L)/4]^{1/2}(z_2 + z_4 + z_5 + z_6) \\
&\quad + [4m_M m_L/(m_M + 2m_L)]^{1/2}x_M\} \\
S_{5a}(T_{1u}; x) &= (m_M + 2m_L)^{-1/2}[-(m_M/2)^{1/2} \\
&\quad \times (x_1 + x_3) + (2m_L)^{1/2}x_M] \\
S_{5b}(T_{1u}; y) &= (m_M + 2m_L)^{-1/2}[-(m_M/2)^{1/2} \\
&\quad \times (y_1 + y_3) + (2m_L)^{1/2}y_M] \\
S_{5c}(T_{1u}; z) &= (m_M + 2m_L)^{-1/2}[-(m_M/2)^{1/2} \\
&\quad \times (z_1 + z_3) + (2m_L)^{1/2}z_M] \\
S_{6a}(T_{1g}; R_x) &= (m_L/4)^{1/2}(-z_2 + z_4 - y_5 + y_6) \\
S_{6b}(T_{1g}; R_y) &= (m_L/4)^{1/2}(z_1 - z_3 + x_5 - x_6) \\
S_{6c}(T_{1g}; R_z) &= (m_L/4)^{1/2}(-y_1 + x_2 + y_3 - x_4) \\
S_{7a}(T_{2g}; xy) &= (m_L/4)^{1/2}(y_1 + x_2 - y_3 - x_4) \\
S_{7b}(T_{2g}; xz) &= (m_L/4)^{1/2}(z_1 - z_3 - x_5 + x_6) \\
S_{7c}(T_{2g}; yz) &= (m_L/4)^{1/2}(z_2 - z_4 - y_5 + y_6) \\
S_{8a}[T_{2u}; x(y^2 - z^2)] &= (m_L/4)^{1/2}(x_2 + x_4 - x_5 - x_6) \\
S_{8b}[T_{2u}; y(z^2 - x^2)] &= (m_L/4)^{1/2}(-y_1 - y_3 + y_5 + y_6) \\
S_{8c}[T_{2u}; z(x^2 - y^2)] &= (m_L/4)^{1/2}(z_1 - z_2 + z_3 - z_4).
\end{aligned}$$

(3.3)

In this case one immediately recognizes the symmetry coordinates  $S_3$  and  $S_5$  as the rigid rotation and translation, respectively.

### 3.2. Numerical results

We have considered the distorted tetrahedral  $PO_4$  and the octahedral  $MO_6$  ( $M = Cd, Li, Mn$ ) structural unit in  $LiMnPO_4$  and  $Cd_2P_2O_7$ .  $LiMnPO_4$  (Geller & Durand, 1960) belongs to the orthorhombic system, with space group  $Pnmb$  ( $D_{2h}^{16}$ ) and four stoichiometric units per unit cell. The distorted tetrahedron  $PO_4$  maintains a symmetry plane, coincident with the (010) crystallographic plane, the distorted octahe-

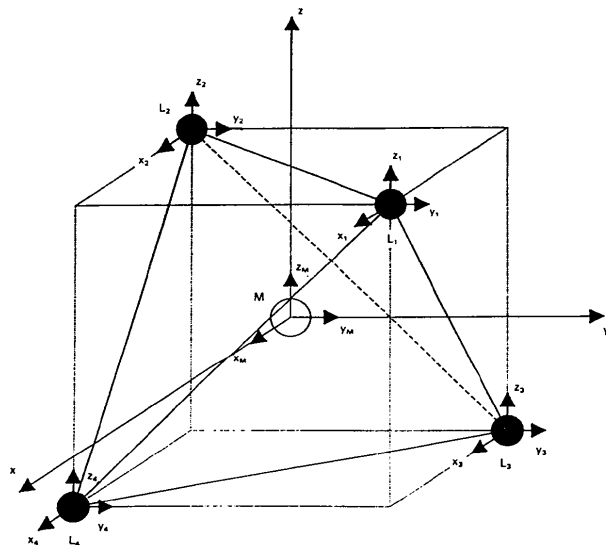


Fig. 2.  $ML_4$  tetrahedral molecule. Principal-axis system and displacement-axis system.

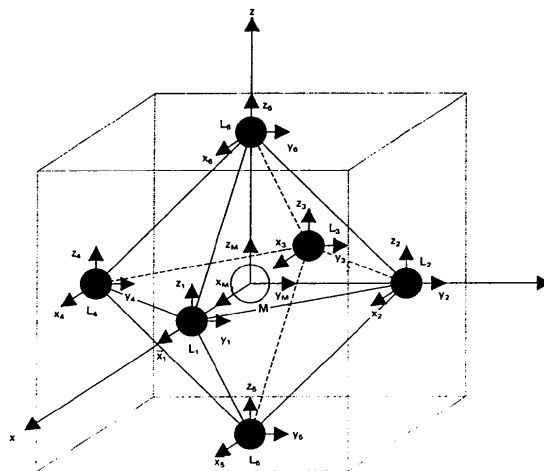


Fig. 3.  $ML_6$  octahedral molecule. Principal-axis system and displacement-axis system.

dron  $\text{LiO}_6$  maintains only the inversion center, and finally  $\text{MnO}_6$  conserves a symmetry plane, parallel to (010).

$\text{Cd}_2\text{P}_2\text{O}_7$  (Calvo & Au, 1969) belongs to the triclinic system, space group  $P\bar{1}$ , with two molecular units in the unit cell. The two tetrahedral clusters, which form the pyrophosphate unit, and the  $\text{CdO}_6$  octahedron are so strongly distorted that they do not have any symmetry element, and belong to the trivial symmetry group,  $C1$ .

In all cases the molecular coordinate system  $K$  of the distorted structures has been assumed to have the origin located at the center of mass and to have unit vectors  $X$ ,  $Y$ ,  $Z$  collinear with the crystallographic axes  $a$ ,  $b$  and  $c$ , respectively (properly orthogonalized if necessary). The labelling assumed for the atoms in the distorted structures is shown in Fig. 4. The molecular coordinate system  $K'$  and the atom labelling for the reference structures  $\text{MO}_4 (T_d)$  and  $\text{MO}_6 (O_h)$  is shown in Figs. 2 and 3 respectively.

The orientation of the reference structures was determined by the procedure described in the pre-

ceeding section, assuming an arbitrary initial bonding distance of  $M\text{—O}$ . The orientation of the reference structures  $\text{MO}_4 (T_d)$  and  $\text{MO}_6 (O_h)$  does not depend on this structural parameter.

The Cartesian displacement coordinates were then calculated with respect to the molecular coordinate system  $K'$ , and the corresponding symmetry coordinate was obtained *via* (3.2) and (3.3), for  $\text{MO}_4 (T_d)$  and  $\text{MO}_6 (O_h)$  respectively.

The definitive bonding distance  $M\text{—O}$  of the reference structures  $\text{MO}_4 (T_d)$  and  $\text{MO}_6 (O_h)$  was determined by setting the totally symmetric distortion coordinate  $S_1 = 0$ ; this choice is merely equivalent to minimizing the distortion between the reference structure and the structure to be analyzed. The calculations were executed by a FORTRAN program which is available upon request from the authors (Cammi & Cavalli, 1990).

3.2.1. *Tetrahedral  $\text{PO}_4$  fragments.* The main features of the reference tetrahedra, *i.e.* bonding distances and spatial orientations, are reported in Table 2. The corresponding values of the symmetry coordinates

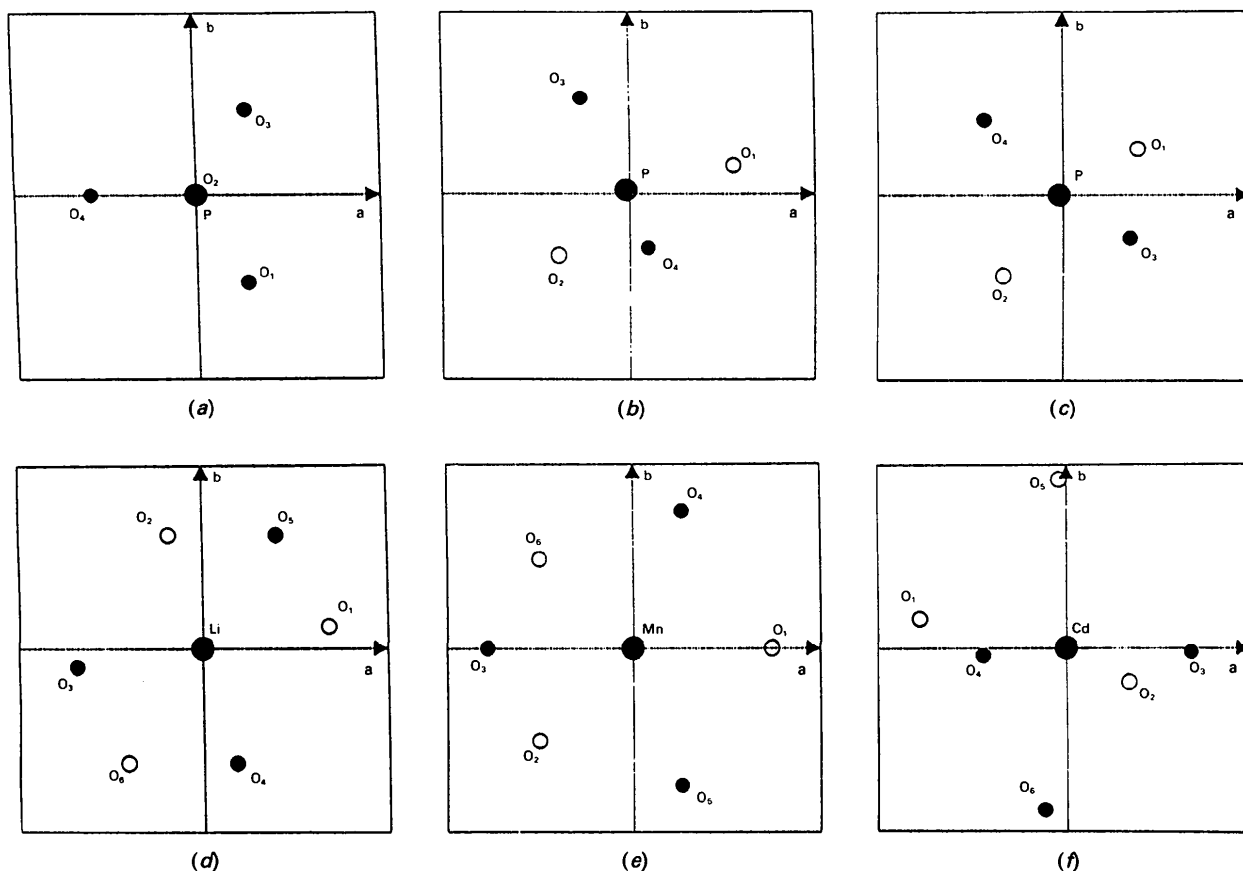


Fig. 4. Atomic labelling in the  $\text{PO}_4$  and  $\text{MO}_6$  structural units of  $\text{LiMnPO}_4$  ( $M = \text{Li}, \text{Mn}$ ) and  $\text{Cd}_2\text{P}_2\text{O}_7$  crystals. (a)  $\text{PO}_4$  ( $\text{LiMnPO}_4$ ), (b)  $\text{PO}_4(1)$  ( $\text{Cd}_2\text{P}_2\text{O}_7$ ), (c)  $\text{PO}_4(2)$  ( $\text{Cd}_2\text{P}_2\text{O}_7$ ), (d)  $\text{LiO}_6$  ( $\text{LiMnPO}_4$ ), (e)  $\text{MnO}_6$  ( $\text{LiMnPO}_4$ ), (f)  $\text{CdO}_6$  ( $\text{CdP}_2\text{O}_7$ ). Atoms are shown by their projection on the  $ab$  plane; white circles refer to a positive  $c$  coordinate value and black circles to a negative value.

Table 2. P—O distance (Å) and orientation of the PO<sub>4</sub> reference tetrahedron in Cd<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and LiMnPO<sub>4</sub>

The orientation is given in terms of direction cosines between the molecular coordinate system *K'* (see Fig. 2) and the crystallographic axes *a*, *b*, *c*.

P—O	Cd <sub>2</sub> P <sub>2</sub> O <sub>7</sub>			LiMnPO <sub>4</sub>					
	PO <sub>4</sub> (1)	PO <sub>4</sub> (2)		PO <sub>4</sub>					
	1.537	1.541		1.540					
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>			
X	0.922	-0.261	-0.359	-0.054	0.930	0.271	-0.423	-0.707	-0.567
Y	0.332	0.856	0.244	0.926	0.051	-0.060	0.801	0.000	-0.699
Z	-0.199	-0.447	0.901	-0.373	-0.364	-0.961	0.423	-0.707	0.567

Table 3. Distortion symmetry coordinates (Å × a.u.<sup>1/2</sup>) for PO<sub>4</sub> fragments in Cd<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and LiMnPO<sub>4</sub>

	Cd <sub>2</sub> P <sub>2</sub> O <sub>7</sub>		LiMnPO <sub>4</sub>
	PO <sub>4</sub> (1)	PO <sub>4</sub> (2)	PO <sub>4</sub>
S <sub>2d</sub> (E; z <sup>2</sup> )	-0.172	-0.261	-0.039
S <sub>2d</sub> (E; x <sup>2</sup> - y <sup>2</sup> )	0.099	-0.353	-0.068
S <sub>3d</sub> (T <sub>2</sub> ; x)	0.415	0.115	0.125
S <sub>3d</sub> (T <sub>2</sub> ; y)	-0.230	0.163	0.215
S <sub>3d</sub> (T <sub>2</sub> ; z)	-0.409	0.147	-0.125
S <sub>6d</sub> (T <sub>2</sub> ; x)	0.077	0.104	-0.206
S <sub>6d</sub> (T <sub>2</sub> ; y)	0.218	0.123	-0.213
S <sub>6d</sub> (T <sub>2</sub> ; z)	0.107	-0.140	0.206

Table 4. Approximation values of the intermediate symmetries in the fragments PO<sub>4</sub>(1) and PO<sub>4</sub>(2) of Cd<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and PO<sub>4</sub> of LiMnPO<sub>4</sub>

	Cd <sub>2</sub> P <sub>2</sub> O <sub>7</sub>		LiMnPO <sub>4</sub>
	PO <sub>4</sub> (1)	PO <sub>4</sub> (2)	PO <sub>4</sub>
C <sub>2</sub> <sup>xy</sup>	0.926	0.494	0.539
C <sub>2</sub> <sup>yz</sup>	0.736	0.674	0.976
C <sub>2</sub> <sup>zx</sup>	0.941	0.935	1.000
C <sub>3</sub> <sup>xyz</sup>	0.485	0.944	0.654
C <sub>3</sub> <sup>yz</sup>	0.679	0.650	0.976
C <sub>3</sub> <sup>yz</sup>	0.967	0.684	0.539
C <sub>3</sub> <sup>yz</sup>	0.646	0.554	0.521
C <sub>2</sub> <sup>v</sup>	0.450	0.880	0.654
C <sub>2</sub> <sup>v</sup>	0.649	0.490	0.521
C <sub>3</sub> <sup>xyz</sup>	0.377	0.457	0.378
C <sub>3</sub> <sup>xyz</sup>	0.887	0.242	0.252
C <sub>3</sub> <sup>xyz</sup>	0.195	0.197	0.378
C <sub>3</sub> <sup>xyz</sup>	0.511	0.411	0.973
D <sub>2d</sub> <sup>xy</sup>	0.244	0.476	0.170
D <sub>2d</sub> <sup>yz</sup>	0.006	0.797	0.085
D <sub>2d</sub> <sup>yz</sup>	0.244	0.320	0.085
D <sub>2</sub>	0.282	0.804	0.170

for the distorted tetrahedra are shown in Table 3. The degrees of approximation for the possible intermediate symmetries, |D(PS)|/|D|, are reported in Table 4.

In the PO<sub>4</sub>(1) tetrahedra of Cd<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and the PO<sub>4</sub> tetrahedra of LiMnPO<sub>4</sub>, the distortion is clearly trigonal. In the former, where the real symmetry is C<sub>1</sub>, the distortion occurs along the ternary axis C<sub>3</sub><sup>xyz</sup>: the associated symmetry, C<sub>3</sub><sup>xyz</sup>, shows a good degree of approximation (0.88) and the three symmetry planes associated with it, C<sub>s</sub><sup>xy</sup>, C<sub>s</sub><sup>yz</sup> and C<sub>s</sub><sup>yz</sup> have

Table 5. M—O distance (Å) and orientation of the MO<sub>4</sub> reference tetrahedron in Cd<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and LiMnPO<sub>4</sub>

The orientation is given in terms of direction cosines between the molecular coordinate system *K'* (see Fig. 2) and the crystallographic axes *a*, *b*, *c*.

M—O	Cd <sub>2</sub> P <sub>2</sub> O <sub>7</sub>			LiMnPO <sub>4</sub>					
	PO <sub>4</sub> (1)	PO <sub>4</sub> (2)		PO <sub>4</sub>					
	1.540	1.537		1.541					
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>			
X	-0.987	-0.008	0.507	0.824	0.000	0.566	0.832	-0.019	0.555
Y	0.072	-0.091	0.860	-0.400	-0.707	0.583	-0.367	0.731	0.575
Z	-0.142	-0.982	-0.068	-0.400	0.707	0.583	-0.416	-0.682	0.601

approximation values of 0.93, 0.94 and 0.97, respectively.

In accordance with this, the distortion in this case can be represented by three 'descent in symmetry' pathways:

$$T_d \rightarrow C_{3v}^{xyz} \rightarrow C_s^{xy} \rightarrow C_1$$

$$T_d \rightarrow C_{3v}^{xyz} \rightarrow C_s^{zx} \rightarrow C_1$$

$$T_d \rightarrow C_{3v}^{xyz} \rightarrow C_s^{yz} \rightarrow C_1.$$

In the PO<sub>4</sub> unit of LiMnPO<sub>4</sub>, with C<sub>s</sub> as the real symmetry, the distortion occurs along the C<sub>3</sub><sup>xyz</sup> axis, and the relative point group C<sub>3v</sub><sup>xyz</sup> has a higher approximation value (0.97) than the above case. Also, one of the symmetry planes (σ<sup>zx</sup>) is maintained in the final structure. The best symmetry descent path is obviously the following:

$$T_d \rightarrow C_{3v}^{xyz} \rightarrow C_s^{zx}.$$

For the PO<sub>4</sub>(2) unit of Cd<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, with C<sub>1</sub> as the real symmetry, the distortion occurs along the binary axis C<sub>2</sub><sup>y</sup>. Here, we have the groups D<sub>2d</sub><sup>y</sup>, C<sub>2v</sub><sup>y</sup>, C<sub>s</sub><sup>zx</sup> and C<sub>s</sub><sup>zx</sup> with approximation values of 0.80, 0.88, 0.94 and 0.94, respectively. Consequently, the following two symmetry descent pathways are almost equivalent:

$$T_d \rightarrow D_{2d}^y \rightarrow C_{2v}^y \rightarrow C_s^{zx} \rightarrow C_1$$

$$T_d \rightarrow D_{2d}^y \rightarrow C_{2v}^y \rightarrow C_s^{zx} \rightarrow C_1.$$

3.2.2. Octahedral MO<sub>6</sub> (M = Cd, Li, Mn) fragments. The bonding distance M—O and the spatial orientation of the reference octahedra are reported in Table 5. The values of the Cartesian symmetry coordinates for the three cases are shown in Table 6, and the approximation values of the intermediate symmetries are shown in Table 7.

In the CdO<sub>6</sub> group, which has only trivial C<sub>1</sub> symmetry, a predominant pseudosymmetry is not observed; however, several pseudosymmetries of immediately higher order than C<sub>1</sub> have rather close approximation values, in any case larger than 0.80: C<sub>s</sub><sup>y</sup> (0.85), C<sub>2</sub><sup>yz</sup> (0.86), C<sub>2</sub><sup>zx</sup> (0.86), C<sub>s</sub><sup>zx</sup> (0.84), C<sub>s</sub><sup>yz</sup> (0.83). Clearly the related pathways for the descent in

Table 6. Distortion symmetry coordinates ( $\text{\AA} \times \text{a.u.}^{1/2}$ ) for  $MO_6$  octahedral fragments in  $Cd_2P_2O_7$  and  $LiMnPO_4$

	$Cd_2P_2O_7$	$LiMnPO_4$	
	$CdO_6$	$LiO_6$	$MnO_6$
$S_{2a}(E_g; z^2)$	-0.171	0.542	-0.098
$S_{2b}(E_g; x^2 - y^2)$	-0.184	0.177	0.100
$S_{7a}(T_{2g}; xy)$	1.749	2.880	-0.777
$S_{7b}(T_{2g}; zx)$	-1.086	-0.900	-0.777
$S_{7c}(T_{2g}; yz)$	-0.263	-0.121	-0.112
$S_{4a}(T_{1u}; x)$	-0.625	0.000	0.634
$S_{4b}(T_{1u}; y)$	2.000	0.000	-1.404
$S_{4c}(T_{1u}; z)$	-0.455	0.000	-1.404
$S_{5a}(T_{1u}; x)$	0.043	0.000	0.221
$S_{5b}(T_{1u}; y)$	0.032	0.000	-0.341
$S_{5c}(T_{1u}; z)$	0.127	0.000	-0.341
$S_{8a}(T_{2u}; x(y^2 - z^2))$	0.346	0.000	0.000
$S_{8b}(T_{2u}; y(z^2 - x^2))$	0.150	0.000	1.930
$S_{8c}(T_{2u}; z(x^2 - y^2))$	-1.741	0.000	-1.930

Table 7. Intermediate symmetries with approximation values (in parentheses) greater than  $1/\sqrt{2}$  in  $CdO_6$ ,  $Cd_2P_2O_7$  and  $LiO_6$ ,  $MnO_6$  in  $LiMnPO_4$

$LiMnPO_4$		
$CdO_6$	$LiO_6$	$MnO_6$
$C_{2v}^{zx}$ (0.753)	$D_{3d}^{xy}$ (0.733)	$C_{2v}^{yz}$ (0.922)
$C_2^{yz}$ (0.784)	$D_{2h}^{xy}$ (0.954)	
$C_{2v}^{xy}$ (0.841)	$C_{2v}^{xy}$ (0.970)	
$C_2^{xy}$ (0.825)	$C_{2h}^{xy}$ (0.982)	
$C_2^{yz}$ (0.753)	$C_{2h}^{xy}$ (0.762)	
$C_2^{xy}$ (0.767)	$C_{2h}^{xy}$ (0.712)	
$C_2^{yz}$ (0.768)	$C_{2h}^{xy}$ (0.871)	
$C_2^{yz}$ (0.858)		
$C_2^{xy}$ (0.864)		
$C_2^z$ (0.778)		
$C_2^y$ (0.848)		

symmetry are almost equivalent. As an example, we report only three of the most significant ones:

$$O_h \rightarrow C_{2v}^{zx} \rightarrow C_2^{zx} \rightarrow C_1$$

$$O_h \rightarrow C_{2v}^{zx} \rightarrow C_2^y \rightarrow C_1$$

$$O_h \rightarrow C_{2v}^{zx} \rightarrow C_2^{xy} \rightarrow C_1.$$

In the  $LiO_6$  unit, with  $C_i$  as the real symmetry, the predominant distortion is along the  $z$  axis: the  $D_{2h}^{xy}$  pseudosymmetry and its subgroups  $C_{2v}^{xy}$  and  $C_{2h}^{xy}$  have considerable approximation values, 0.95, 0.97 and 0.98, respectively. Thus, the best symmetry descents are:

$$O_h \rightarrow D_{2h}^{xy} \rightarrow C_{2h}^{xy} \rightarrow C_i$$

$$O_h \rightarrow D_{2h}^{xy} \rightarrow C_2^{xy} \rightarrow C_i.$$

Finally, in  $MnO_6$ , where the real symmetry is  $C_s$ , the distortion develops along the binary axis defining

the  $C_{2v}^{yz}$  pseudosymmetry, with an approximation value of 0.92. Therefore we have:

$$O_h \rightarrow C_{2v}^{yz} \rightarrow C_s^{yz}.$$

#### 4. Concluding remarks

We have proposed a general procedure for molecular-distortion analysis using Cartesian symmetry coordinates. Characteristics of the method are:

(i) The explicit definition of the spatial disposition of the reference structure with respect to the structure to be analyzed in terms of the Eckart frame.

(ii) The direct use of the  $3N - 6(5)$  Cartesian symmetry coordinates to describe the real variation of the molecular structure, avoiding the redundancy problem one can encounter by using symmetry coordinates related to the internal geometrical parameters, *i.e.* bond distances and angles. The method has been applied to the cases of  $ML_4$  ( $T_d$ ) and  $ML_6$  ( $O_h$ ) type molecules.

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