

## Noncrystallographic Symmetry Constraints in Least-Squares Refinement

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A least-squares refinement procedure is presented whereby noncrystallographic symmetry constraints can be imposed on the positional parameters of any group of atoms in a crystal structure. This generalized form of the rigid group refinement technique of Scheringer allows specified distortions of the 'rigid' group to be refined along with the orientation parameters of the group. Thus, while the advantages of constrained refinement are retained, this generalization allows application of chemically reasonable constraints to systems whose configurations are not sufficiently well known to justify completely constrained (rigid group) refinement. This refinement technique can also be used to provide a direct assessment of the significance of an observed distortion from some idealized configuration. Several examples are presented including the refinement of a metal cluster complex wherein constraint of the refinement to the idealized  $C_{3v}$  symmetry lowers the number of independent positional parameters from 66 to 18.

### Introduction

The use of noncrystallographic constraints in least-squares refinement of X-ray structural data has been restricted primarily to the refinement of the orientation of rigid groups of atoms as described by Scheringer (1963). While this type of refinement has been very successfully applied to functional groups with well known bond distances and angles, it is too restrictive to be applied in cases where high local symmetry is known to exist but where accurate bond distances and angles are not available. A more general scheme will now be presented which allows specified distortions of the 'rigid' groups to be refined along with the group orientation parameters. In this way, noncrystallographic symmetry constraints can be imposed upon any group of atoms in the structure.

### Theory

The following refinement technique is based on a description of the molecular configuration in terms of a set of  $3N-6$  displacement coordinates of the type utilized in vibrational analysis (Wilson, Decius & Cross, 1955). The bases of the coordinates used in this technique, however, need not be orthogonal nor of course must they be eigenvectors of the vibrational secular equation. The distortions chosen are required only to be linearly independent and to serve as irreducible representations of the idealized point group for the particular set of atoms under consideration. In cases involving a noncrystallographic symmetry constraint, only those coordinates which span the space of all totally symmetric ( $A_1$ ) distortions must be described.

The bases of the distortional coordinates and the idealized configuration are most easily described in a Car-

tesian coordinate system wherein the coordinates are expressed in Ångström units. The crystallographic fractional coordinates of atom  $i$  are then the components of  $\mathbf{u}_i^c$  where

$$\mathbf{u}_i^c = \mathbf{u}_0 + \mathbf{P}\mathbf{u}_i^f .$$

The components of  $\mathbf{u}_0$  are the crystallographic fractional coordinates of the origin of the Cartesian coordinate system, and the components of  $\mathbf{u}_i^f$  are the coordinates of atom  $i$  in the Cartesian coordinate system. The  $\mathbf{P}$  matrix describes the orientation of the Cartesian coordinate system in the unit cell and can be expanded as

$$\mathbf{P} = \mathbf{T}\mathbf{R}_{\phi_y}\mathbf{R}_{\theta_x}\mathbf{R}_{\phi_z} .$$

In this expression  $\mathbf{R}_{\phi_z}$  represents a rotation about the  $z$  axis by an angle  $\phi$ , and  $\mathbf{T}$  is the transformation from a Cartesian coordinate system with the same origin. In a standard rigid group refinement the components of  $\mathbf{u}_0$  and the

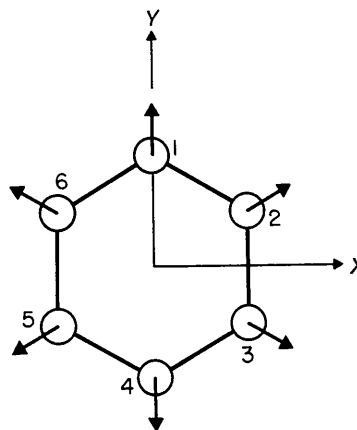


Fig. 1. The basis for a distortion coordinate corresponding to a change in interatomic distance under  $D_{6h}$  symmetry.

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orientation angles  $\Phi$ ,  $\theta$ , and  $\varrho$  are the parameters which are refined.

If specified distortions of the idealized configuration are to be allowed, the final configuration in the Cartesian coordinate system can be represented by

$$\mathbf{q}^G = \mathbf{q}^0 + \mathbf{A}\zeta$$

where  $\mathbf{q}^0$  represents the idealized configuration and the components of  $\zeta$  are the distortional coordinates to be refined. The  $\mathbf{A}$  matrix consists of the basis vectors of the corresponding distortions. In the following presentation the components of  $\mathbf{q}^G$  will be considered in the order  $x_1^G y_1^G z_1^G x_2^G y_2^G z_2^G \dots x_n^G y_n^G z_n^G$ .

The refinement of  $\zeta_k$  in the non-linear least-squares procedure necessitates only the calculation of  $dF/d\zeta_k$ , which can be expanded as

$$\frac{dF}{d\zeta_k} = \sum_i \frac{\partial F}{\partial x_i^G} \cdot \frac{\partial x_i^G}{\partial \zeta_k} + \frac{\partial F}{\partial y_i^G} \cdot \frac{\partial y_i^G}{\partial \zeta_k} + \frac{\partial F}{\partial z_i^G} \cdot \frac{\partial z_i^G}{\partial \zeta_k},$$

where the sum is taken over all the atoms in the group.

The derivatives  $\frac{\partial x_i^G}{\partial \zeta_k}$  can be further expanded as

$$\begin{aligned} \frac{\partial x_i^G}{\partial \zeta_k} &= \frac{\partial}{\partial \zeta_k} (x_0 + [P_{11}x_i^G + P_{12}y_i^G + P_{13}z_i^G]) \\ &= [P_{11}A_{3i-2,k} + P_{12}A_{3i-1,k} + P_{13}A_{3i,k}]. \end{aligned}$$

Thus, only the introduction of the  $\mathbf{A}$  matrix is required to generalize the rigid-group procedure of Scheringer to include refinement of specified distortions and thereby to allow application of noncrystallographic symmetry constraints.

### Application

Consider the hypothetical refinement of a six-membered ring with idealized  $D_{6h}$  symmetry. The technique described above could be used to refine the interatomic distance in such a group subject to the  $D_{6h}$  constraint. The basis for the one distortional coordinate  $\zeta$  to be

refined is represented in Fig. 1. The  $\mathbf{A}$  matrix for this refinement consists of the column vector

$$\mathbf{A} = \left( 0, 1, 0, \frac{\sqrt{3}}{2}, \frac{1}{2}, 0, \frac{\sqrt{3}}{2}, -\frac{1}{2}, 0, 0, -1, 0, -\frac{\sqrt{3}}{2}, -\frac{1}{2}, 0, -\frac{\sqrt{3}}{2}, \frac{1}{2}, 0 \right).$$

The normalization of  $\mathbf{A}$  is arbitrary and in this case was chosen in such a way that the value of  $\zeta$  gives the change in interatomic distance directly in Ångström units.

Organometallic compounds of the general formula  $M_3(\text{CO})_9X$  (where  $M_3 = \text{Co}_3, \text{Co}_2\text{Fe}$ ;  $X = \text{S}, \text{Se}, \text{Te}$ ) have been investigated in this laboratory, and the constrained refinements of these compounds afford a more complicated illustration of the technique. These compounds crystallize in the triclinic space group  $P\bar{1}$  with either two or four molecules per cell. The vibrational symmetry species of the  $M_3(\text{CO})_9X$  molecule (see Fig. 2) in the idealized  $C_{3v}$  point group are  $12A_1 + 8A_2 + 20E$ , and therefore constraint of the refinement to  $C_{3v}$  molecular symmetry requires description of 12 totally symmetric distortional modes. The refinement thus involves 6 group orientation parameters and 12 distortional coordinates, as compared to a total of 66 positional parameters for the completely unconstrained atomic refinement. Three of the twelve chosen distortions are represented in Fig. 3; the transpose of the entire  $\mathbf{A}$  matrix is given in Table 1.

In the structural determination of  $\text{FeCo}_2(\text{CO})_9\text{Se}$ , an idealized  $C_{3v}$  model of the molecule was constructed from the known molecular parameters of  $\text{FeCo}_2(\text{CO})_9\text{S}$ . (In both of these compounds a statistical disorder of the iron and cobalt makes the metal atoms indistinguishable.) This model was refined subject to the  $C_{3v}$  constraint with 6 orientation parameters, 12 distortional coordinates and 22 individual isotropic temperature factors. Upon convergence of the  $C_{3v}$  refinement ( $R_1 = 0.069$ ,  $R_2 = 0.061$ ) the constraints were removed and the refinement continued with 66 positional par-

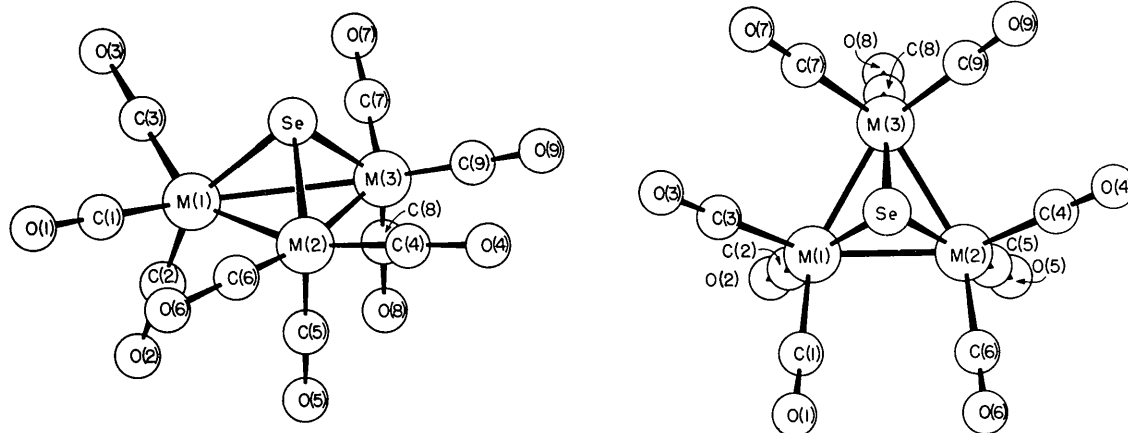


Fig. 2. Idealized molecular configuration of  $\text{Co}_3(\text{CO})_9\text{Se}$  and  $\text{FeCo}_2(\text{CO})_9\text{Se}$  corresponding to  $3m$  ( $C_{3v}$ ) symmetry.

ameters and 22 isotropic temperature factors. This unconstrained refinement converged to  $R_1=0.055$  and  $R_2=0.040$ . Application of Hamilton's (1965)  $R$  factor ratio test indicated a deviation from  $C_{3v}$  symmetry at the 0.005 significance level. The differences in the atomic coordinates obtained from these two refinements were then calculated; it was observed that the shift of the selenium atom position was 0.01 Å, the largest metal shift was 0.02 Å, the largest carbon shift was 0.10 Å, and the largest oxygen shift was 0.18 Å. It was also noted that while the final metal-metal distances varied by as much as  $4\sigma$  from the mean, the metal-metal distance obtained from the constrained  $C_{3v}$  refinement was within  $1\sigma$  of the mean. Further details of this refinement will be published elsewhere.

In addition to the application of symmetry constraints, this refinement technique can be used to determine the significance of an observed distortion from some idealized symmetry. An example of this application is afforded by the refinement of (2,5-dimethylthiophene)chromium tricarbonyl (Perry & Dahl, 1970). The dimethylthiophene portion of the structure was first refined subject to a  $C_{2v}$  constraint. Introduction of two additional coordinates corresponding to displacement of the sulfur atom and the methyl carbon atoms respectively from the plane of the four ring carbon atoms (thereby reducing the idealized symmetry from  $C_{2v}$  to  $C_s$ ) resulted in the least-squares evaluation of two  $\zeta$  parameters and their standard deviations. A comparison of these parameters with their standard deviations

gave a direct indication of the significance of the corresponding distortions.

### Discussion

The changes necessary to implement the above refinement technique have been incorporated into a local rigid body version of the Busing, Martin & Levy (1962) *ORFLS* least-squares refinement program. Input to the modified program (*ORFLSE*) includes an  $A$  matrix which contains the basis vectors for the distortional coordinates to be used in the refinement. This program allows refinement of either a group temperature factor or individual isotropic temperature factors. In the above treatment only the atomic positional parameters are considered, and in the modification of the program no provision was made to place constraints on individual atomic temperature factors. In practice it is often useful to vary the temperature factors of the group atoms independently, since a poorly positioned atom will usually exhibit a large temperature factor.

One particular advantage of a refinement of the type described above is the reduction in the number of parameters to be refined. In addition to decreasing the calculation time, this reduction in the number of parameters is desirable in cases where the amount of data is limited. In such cases this procedure should also help to avoid false minima in the refinement. Further advantages are an increase in the rate of convergence which results from the application of chemically reasonable constraints and (as in the case of standard rigid-group

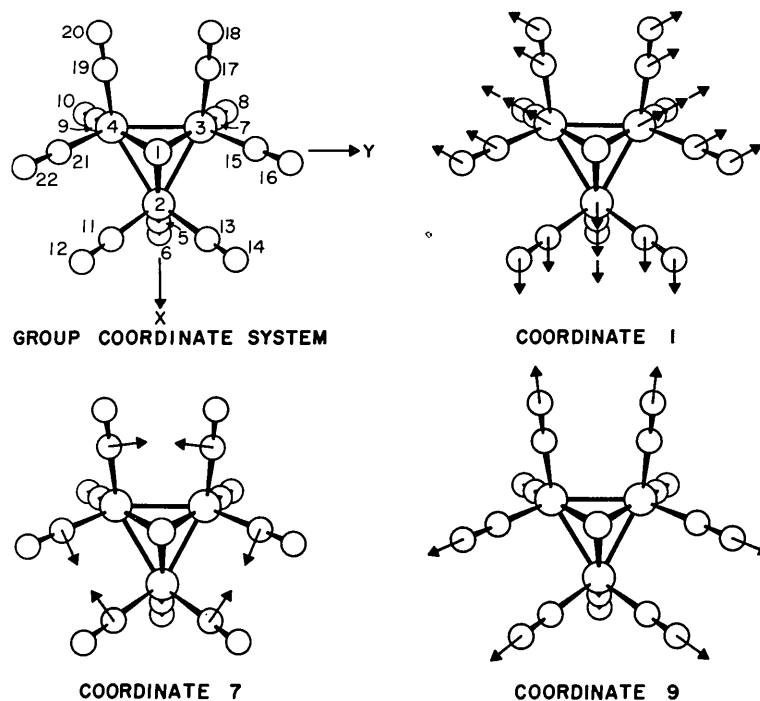


Fig. 3. The group coordinate system and representations of three of the distortions used in the refinement of  $M_3(CO)_9X$ .

refinement) an increase in the range of initial parameters from which the refinement will converge.

In the refinement of biologically important structures (such as many of the antibiotics) the introduction of constraints should prove particularly valuable. In disordered structures where refinement of individual atoms is impossible, the application of reasonable constraints to the system could allow satisfactory refinement without the limitations imposed by a completely constrained (rigid-group) refinement (Bailey & Dahl, 1965).

Fortran 4 and Fortran 63 versions of *ORFLSE* are available through Dr L. F. Dahl, Department of Chemistry, University of Wisconsin, Madison, Wisconsin, 53706.

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## Determination of the Normal Vibrational Displacements in Several Perovskites by Inelastic Neutron Scattering\*

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Relative displacements of the atoms corresponding to the lowest frequency long wavelength transverse optic phonon of several materials with the perovskite structure were determined directly by a least-squares refinement of the integrated intensity of inelastic neutron scattering. The modes of  $\text{KTaO}_3$  and  $\text{SrTiO}_3$  were identified as being of the Slater type, in which oxygen atoms vibrate against Ta and Ti atoms. In the case of  $\text{RbMnF}_3$ , however, an entirely different vibrational motion was obtained, in which Rb ions vibrate out of phase with the rigid  $\text{MnF}_3$  group.

### Introduction

The lattice dynamical theory of ferroelectric phase transitions in perovskite structures predicts that there exists a close relationship between the vibrational displacement associated with soft optic phonons at the Brillouin zone center (wave-vector  $\mathbf{q}=0$ ), and the static structure of the ferroelectric phase (Cochran, 1960). It is of great interest to see what kind of atomic vibrational displacements exist for soft optic modes in such substances and, where possible, to compare with static spontaneous displacements.

In connection with this idea, approximate mode assignments of the three infrared active modes for  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$  and other related substances have been made by several authors, with results which are in wide

disagreement. Last (1957) originally suggested a vibration of the cation out of phase with a rigid  $\text{TiO}_3$  group vibration as the possible mode of the lowest frequency  $q=0$  transverse optic (TO) phonon for  $\text{BaTiO}_3$ . This suggestion was later supported by Perry & Khanna (1964) and Perry, McCarthy & Rupprecht (1965), who showed as evidence that the mode frequencies for several titanium perovskites depended systematically upon the cation mass. Spitzer, Miller, Kleinman & Howarth (1962), however, deduced a stretching type motion in which Ti atom vibrates against the  $\text{O}_6$  octahedron, from the fact that the infrared resonance strengths for the soft mode are the same order of magnitude for the three substances,  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$  and  $\text{TiO}_2$ . (Hereafter, we shall call this type of vibration a 'Slater mode', since it was originally pointed out by Slater (1950) that the structure resulting from such a distortion is energetically favorable because of strong local field effects.) This argument recently has been extended by Axe

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