Anisotropic Temperature Factors and Screw Rotation Coefficients
from a Lattice Dynamical Viewpoint

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It is shown how the correct tensors for the description of the rigid-body motion of molecules in crystals can be obtained from a lattice dynamical calculation. This helps in understanding the tensor S introduced in the paper by Schomaker & Trueblood (*Acta Cryst.* (1968). B**24**, 63). An expression for the anisotropic temperature factors including the tensor S is obtained. The form of this expression is convenient for use in a least-squares structure refinement procedure.

Recent work on the lattice dynamics of naphthalene and anthracene has yielded calculated values for the mean-square translational and rotational tensors, **T** and ω (Pawley, 1967). It is easy to generalize the procedure for all crystals comprising rigid molecules to give the screw rotation matrix **S** introduced by Schomaker in 1964 (Schomaker & Trueblood, 1968). **S** is shown to be zero when the molecules are sited on symmetry centres, and this can be understood from lattice dynamics because the translational and rotational components of a lattice mode eigenvector must be $\pi/2$ out of phase (Cochran & Pawley, 1964).

When there is no centre of symmetry the dynamical matrix is Hermitian, giving complex eigenvectors. We may write a general eigenvector in an orthogonal coordinate system as

$$\sqrt{2}\;(u_1,u_2,u_3,iv_1,iv_2,iv_3,\theta_1,\theta_2,\theta_3,i\varphi_1,i\varphi_2,i\varphi_3)$$

or

$$\sqrt{2}\;(\mathbf{u},i\mathbf{v},\mathbf{\theta},i\mathbf{\varphi})\;. \tag{1}$$

The motion of an atom at **x** in a molecule in this mode is

$$\sqrt{2}(\mathbf{u}+\mathbf{\theta}\times\mathbf{x})\cos \omega t + \sqrt{2}(\mathbf{v}+\mathbf{\varphi}\times\mathbf{x})\sin \omega t$$

which should serve to explain the symbols, ω being the eigenfrequency. The mean square displacement of this atom is then

$$(\mathbf{u}+\mathbf{\theta}\times\mathbf{x})^2 + (\mathbf{v}+\mathbf{\varphi}\times\mathbf{x})^2\;. \tag{2}$$

As the two terms of this expression are similar, we will omit the second until equations (4).

It is customary to give the tensor $\mathbf{U}_x$ for the atom at **x**, which gives the mean square displacement in the direction of the unit vector **l** as $\sum_{ij} (U_x)_{ij}l_il_j$. It is well known that for a general vector **y**, the matrix **Y** with coefficients $Y_{ij}=y_iy_j$ behaves as a second order tensor, $\sum_{ij} Y_{ij}l_il_j$ being the square of the projection of **y** along **l**. Clearly then we can write

$$(U_x)_{ij}= \sum_{\text{modes}} (\mathbf{u}+\mathbf{\theta}\times\mathbf{x})_i(\mathbf{u}+\mathbf{\theta}\times\mathbf{x})_j$$

for $\mathbf{u}+\mathbf{\theta}\times\mathbf{x}$ is simply a displacement vector.

Expanding this for typical components we get

$$(U_x)_{11}= \sum_{\text{modes}} (u_1+\theta_2x_3-\theta_3x_2)^2$$
$$= T_{11}+\omega_{22}x_3^2+\omega_{33}x_2^2-2\omega_{23}x_2x_3+2S_{21}x_3$$
$$-2S_{31}x_2$$

$$(U_x)_{23}= \sum_{\text{modes}} (u_2+\theta_3x_1-\theta_1x_3)(u_3+\theta_1x_2-\theta_2x_1)$$
$$= T_{23}+\omega_{31}x_1x_2+\omega_{12}x_3x_1-\omega_{23}x_1^2-\omega_{11}x_3x_2$$
$$+ S_{33}x_1-S_{13}x_3+S_{12}x_2-S_{22}x_1\;, \tag{3}$$

where we have defined

$$T_{ij}= \sum_{\text{modes}} (u_iu_j+v_iv_j)$$
$$\omega_{ij}= \sum_{\text{modes}} (\theta_i\theta_j+\varphi_i\varphi_j) \tag{4}$$
$$S_{ij}= \sum_{\text{modes}} (\theta_iu_j+\varphi_iv_j)\;.$$

It may be obvious that these are tensors, but this can be shown as follows. Consider

$$\mathbf{U}_x=\mathbf{T}+\mathbf{V}_x\omega\tilde{\mathbf{V}}_x-\mathbf{V}_x\mathbf{S}-\tilde{\mathbf{S}}\tilde{\mathbf{V}}_x\;, \tag{5}$$

where

$$\mathbf{V}_x=\begin{pmatrix} 0 & -x_3 & x_2 \\ x_3 & 0 & -x_1 \\ -x_2 & x_1 & 0 \end{pmatrix}$$

is a second order antisymmetric tensor. Writing this out in full gives exactly equation (3). Now as U_x must transform as a second order tensor so must the right side of equation (4), and this is clearly consistent with **T**, ω and **S** transforming as second order tensors. Scrutiny of the terms in equation (3) shows that **S** is defined in agreement with Schomaker & Trueblood, and these authors show that the trace of **S** is indeterminate. This can be seen by factorizing two elements of the second equation, giving $(S_{33}-S_{22})x_1$. The diagonal elements of **S** always appear in this combined form and therefore individual estimates by X-ray methods are not possible.

It has been shown that the inclusion of **T** and ω in the least-squares structures refinement using X-ray data vastly decreases computer time and has always resulted in a closer fit with experiment than the usual

least-squares process (Pawley, 1966). The method has been described by Pawley (1964) whose equation (1) uses the term $T+V_x\omega\tilde{V}_x$ in the anisotropic temperature factor exponential. To generalize to include S one needs to replace this by the present equation (5), and the extra partial differentials needed are straightforward. In searching for the effects of S this method is clearly superior to the analysis of individual atomic anisotropic temperature factors obtained by the usual process.

To calculate T, ω and S from a lattice dynamical model requires the description of the atoms of a molecule in a suitable coordinate system. The inertia axes are the obvious choice, and it is hoped that published results of T, ω and S will be in this coordinate system. Schomaker & Trueblood suggest transformation to coordinates where the average motion corresponds to six independent simple motions, but in view of the multitude of vibrational modes present this transformation cannot be regarded as physically meaningful or useful.

Finally let us investigate the symmetry properties of S. In discussing the transformation properties of equation (5) it was tacitly assumed that we were dealing with proper rotations. The symmetry restrictions imposed on T, ω and S by proper rotations are identical and well known. Schomaker & Trueblood give all the restrictions imposed also by improper rotations, so one example here will suffice. Consider a crystal whose molecules lie on a plane of symmetry perpendicular to z. Then if (1) is an eigenvector, then so is

$$\sqrt{2}\,(u_1, u_2, -u_3, iv_1, iv_2, -iv_3,$$
$$-\theta_1, -\theta_2, \theta_3, -i\varphi_1, -i\varphi_2, i\varphi_3)\,.$$

Here the infinitesimal rotations θ and φ transform as the small displacements u and v except for a sign change. Equation (4) then shows that of S only S_{13}, S_{23}, S_{31}, S_{32} are non-zero, exactly those components which are zero in T and ω. Thus for any symmetry we can obtain the restrictions on T, ω and S simply by writing down the components of symmetry related eigenvectors and performing the summations of equation (4). The rules soon become obvious and the results agree with the tabulation of Schomaker & Trueblood.

References

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Caractères Structuraux des Diacides Aliphatiques Saturés à Nombre Impair de Carbones, COOH[CH₂]₂ₙ₊₁COOH

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The structure of the α form of brassylic acid, COOH[CH₂]₁₁COOH, has been determined. Comparison between structures of four dicarboxylic acids (α forms) with odd numbers of carbon atoms shows the constancy of molecular configuration, in particular of the carboxylic groups and hydrogen bonds, and the characteristic form of the molecular assemblage.

Introduction

Les diacides impairs, à partir de l'acide glutarique sont connus sous deux formes: α ($P2_1/c$) et β ($C2/c$). La forme α est stable à basse température (Dupré La Tour, 1932).

L'acide brassylique α (C_{13}) est le dernier corps de la série des dioïques à nombre impair de carbones dont nous avons pu obtenir des cristaux et déterminer la structure.

Nous avons déjà montré pour les acides pimélique (C_7), azélaïque (C_9) et undécanedioïque (C_{11}) que la molécule est allongée suivant l'axe Oz et que la valeur du paramètre c de la maille monoclinique est directement liée à la longueur de la chaine carbonée. En étendant ces remarques à l'acide brassylique et par analyse directe des projections de la fonction de Patterson nous avons pu déterminer cette structure. Nous nous bornerons dans une première partie à donner les résultats cristallographiques, après l'affinement ($R=0,088$).