principle (or density rule) (Kitaigorodsky, 1973) this latter isomer is expected to be the more stable form. It should be pointed out, however, that the density rule holds, in principle, only for small hydrocarbon species. It seems that the only conclusion one can draw to explain the existence of both isomers is that the differences in molecular and packing energies for the two forms must cancel (*i.e.* be approximately equal and of opposite sign). This behaviour leads to the role played by the aforementioned 'crystal forces', which appear to be in competition with ligand-packing optimization around the metal frame. Slightly different crystallization conditions may suffice in altering the subtle energy balance between these two factors in determining the final stereogeometry.

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Interpretation of Atomic Displacement Parameters: Intramolecular Translational Oscillation and Rigid-Body Motion

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Abstract

An extension of the rigid-body model which includes intramolecular translational oscillations is presented. Some symmetry aspects are discussed, especially for cases where several symmetrically equivalent groups in a molecule perform coupled translational oscillations. The relationship between the general model and difference displacement parameters ΔU between pairs of atoms along their internuclear vector is elaborated. Some examples in the field of transition-metal complexes are given.

Introduction

Atomic displacement parameters, determined routinely with almost every crystal structure analysis, contain information on *atomic motion* and on *atomic disorder* in the crystal. A picture of *molecular motion* (and disorder) would, in many instances, be more informa-

tive than the long lists of atomic anisotropic displacement parameters (ADP's) usually provided (although often not published), just as a molecular diagram showing bond distances and angles is more revealing than the lists of coordinates from which it is derived. A distinction between atomic motion and disorder is usually not possible from diffraction measurements at a single temperature. However, many kinds of disorder attenuate Bragg intensities in proportion to the mean-square displacements of the atoms perpendicular to the Bragg plane as do atomic motions. Such disorder can therefore be modelled by ADP's (Dunitz, Schomaker & Trueblood, 1988). We carefully use the term ADP, while referring generally to atomic or molecular 'motions', whether or not the actual nature of the displacements has been established.

Interpretation of ADP's in terms of molecular motion is beset with a major difficulty: while ADP's for individual atoms can be determined from Bragg intensities, all correlations of motion between atoms remain unknown (Scheringer, 1987). To make up for this deficiency any interpretation of ADP's in terms of molecular and intramolecular motion has to borrow heavily from other experiments, from theory, and often from chemical common sense. Cruickshank (1956), for example, argued that in essence aromatic hydrocarbons may be considered as rigid bodies undergoing librational and translational oscillations in the crystal and showed how mean-square amplitudes for such motions can be determined from ADP's. Of course, the very concept of a rigid body introduces correlations between atomic motions. Schomaker & Trueblood (1968) showed that Cruickshank's model is valid only for molecules with inversion symmetry and generalized it to molecules with any symmetry. They introduced a coupling tensor $\mathbf{S}$ along with Cruickshank's translation and libration tensors $\mathbf{T}$ and $\mathbf{L}$ to express the correlation between translational and rotational oscillations. The TLS analysis showed that ADP's depend on differences $S_{ii} - S_{jj}$ of the diagonal elements of $\mathbf{S}$, implying, in turn, that the absolute values of the molecular-motion parameters S_{ii} cannot be determined from ADP's. Again, this difficulty arises from incomplete knowledge about the correlation of atomic motions.

The model of molecular rigid-body motion has been extended by Johnson (1970a) and by Schomaker & Trueblood (1984). They analysed the cases of rigid-body motion combined with one or more large-amplitude internal rotations. In their model, a rigid group (RG), attached to a rigid frame (MAIN), is assumed to rotate about a specified axis, usually the chemical bond connecting RG to MAIN. Correlation between atomic motions is introduced through the definitions of RG, MAIN and the axis of rotation. Once again, however, the assumed correlations are insufficient to determine all parameters of the motion. In general, the mean-square internal rotation amplitude $\langle \varphi^2 \rangle$ cannot be obtained, only its sum with the quadratic correlation $2\langle \varphi l^{\parallel} \rangle$ between overall and internal rotation in the direction of the internal rotation axis can.

These and other aspects of interpreting ADP's have been reviewed recently by Dunitz, Schomaker & Trueblood (1988). In their article the emphasis is on organic molecules, for which rigid-body motion and internal rotation are the most important contributions to large-amplitude motion. Our own involvement with inorganic crystal chemistry, e.g. Jahn–Teller deformations and spin equilibria, made it desirable to have a model combining rigid-body motion with internal translational motion. The molecule is divided as before into one or more RG's attached to MAIN. These groups perform translational oscillation along a specified direction, usually along the bond connecting RG to MAIN.

In this paper we first give an analysis of such motion and compare it with that for internal rotation. Next, we consider symmetry aspects, especially where several symmetrically equivalent RG's perform coupled translational oscillation. In the third section, approximations to the general model are discussed. The relationship between the general model and difference displacement parameters ΔU between pairs of atoms along their internuclear vector are treated in the fourth section. Some applications and examples are summarized in the concluding part.

Analysis of motion

The instantaneous displacement of an atom in the rigid frame of a molecule (MAIN) is

$$\mathbf{u} = (\mathbf{l} \times \mathbf{r}) + \mathbf{t}, \tag{1}$$

that of an atom in an attached rigid group (RG) is

$$\mathbf{u} = (\mathbf{l} \times \mathbf{r}) + \mathbf{t} + \sum \mu_i, \tag{2}$$

$\mathbf{t}$ is the translational, $(\mathbf{l} \times \mathbf{r})$ the rotational displacement; μ_i is the displacement along an internal coordinate i.

The mean-square displacement amplitudes are (for one internal motion)

$$\overline{\mathbf{uu}} = -(\mathbf{r} \times \overline{\mathbf{ll}} \times \mathbf{r}) - (\mathbf{r} \times \overline{\mathbf{lt}}) + (\overline{\mathbf{tl}} \times \mathbf{r}) + \overline{\mathbf{tt}}$$
$$- (\mathbf{r} \times \overline{\mathbf{l\mu}}) + (\overline{\mu\mathbf{l}} \times \mathbf{r}) + \overline{\mathbf{t}\mu} + \overline{\mu\mathbf{t}} + \overline{\mu\mu}, \tag{3}$$

where symbols of the type $\overline{\mathbf{xx}}$ represent expectation values of a dyadic product, i.e. $\langle \mathbf{x}\tilde{\mathbf{x}} \rangle$.

In the conventional $\mathbf{U}, \mathbf{T}, \mathbf{L}, \mathbf{S}$ notation of Schomaker & Trueblood (1968) supplemented by symbols for terms involving μ, the above expression abbreviates to

$$\mathbf{U} \doteq -(\mathbf{r} \times \mathbf{L} \times \mathbf{r}) - (\mathbf{r} \times \mathbf{S}) + (\tilde{\mathbf{S}} \times \mathbf{r}) + \mathbf{T}$$
$$- (\mathbf{r} \times \mathbf{M}_l) + (\tilde{\mathbf{M}}_l \times \mathbf{r}) + \mathbf{M}_t + \tilde{\mathbf{M}}_t + \mathbf{M} \tag{4}$$

($\tilde{S}$ is the transpose of S). For an internal translational oscillation the contribution to the instantaneous displacement is simply

$$\mu = \tau \qquad (5)$$

and

$$M_l(\tau) = l\tau$$
$$M_t(\tau) = t\tau$$
$$M(\tau) = \tau\tau. \qquad (6)$$

Certain aspects of these equations become more transparent in an orthogonal coordinate system with one axis parallel to τ, the other two perpendicular to τ. If the components of l, t and τ are taken as

$$l = (l_1{}^\perp, l_2{}^\perp, l^\parallel)$$
$$t = (t_1{}^\perp, t_2{}^\perp, t^\parallel)$$
$$\tau = (0,0,\tau), \qquad (7)$$

then the M-type matrices are

$$M_l(\tau) = \begin{bmatrix} 0 & 0 & \langle l_1{}^\perp\tau\rangle \\ 0 & 0 & \langle l_2{}^\perp\tau\rangle \\ 0 & 0 & \langle l^\parallel\tau\rangle \end{bmatrix}$$

$$M_t(\tau) = \begin{bmatrix} 0 & 0 & \langle t_1{}^\perp\tau\rangle \\ 0 & 0 & \langle t_2{}^\perp\tau\rangle \\ 0 & 0 & \langle t^\parallel\tau\rangle \end{bmatrix}$$

$$M(\tau) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \langle\tau^2\rangle \end{bmatrix} \qquad (8)$$

The matrix $M_l(\tau) = l\tau$ expresses the coupling between overall rotation and internal translation, the matrix $M_t(\tau) = t\tau$ the coupling between overall and internal translation. For an RG consisting of a single atom, the origin of the coordinate system may be chosen to coincide with this atom. In this case, M_l is indeterminate because $r = 0$ and only the sum $M_t + \tilde{M}_t + M$ can be obtained, i.e. the quantities $\langle t_1{}^\perp\tau\rangle$, $\langle t_2{}^\perp\tau\rangle$ and $2\langle t^\parallel\tau\rangle + \langle\tau^2\rangle$. For a sufficiently general RG the elements of M_l can also be determined, but $M_t + \tilde{M}_t + M$, i.e. $2\langle t^\parallel\tau\rangle + \langle\tau^2\rangle$, can still not be separated. This kind of indeterminacy is analogous to that involving the diagonal elements of S, as mentioned in the *Introduction*.

These results for internal translation show a one-to-one correspondance with those for internal rotation with instantaneous displacement

$$\mu = (\varphi \times r), \qquad (9)$$

where φ is the axis of internal rotation and r is the position vector of an atom in the RG relative to an arbitrary origin on φ. With definitions of axes and

components of l, t and φ analogous to those of l, t and τ above [(7)], the mean-square displacement matrices involving φ are

$$M_l(\varphi) = \begin{bmatrix} 0 & 0 & \langle l_1{}^\perp\varphi\rangle \\ 0 & 0 & \langle l_2{}^\perp\varphi\rangle \\ 0 & 0 & \langle l^\parallel\varphi\rangle \end{bmatrix}$$

$$M_t(\varphi) = \begin{bmatrix} 0 & 0 & \langle t_1{}^\perp\varphi\rangle \\ 0 & 0 & \langle t_2{}^\perp\varphi\rangle \\ 0 & 0 & \langle t^\parallel\varphi\rangle \end{bmatrix}$$

$$M(\varphi) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \langle\varphi^2\rangle \end{bmatrix} \qquad (10)$$

The contribution to U from internal rotation is $[M_t(\varphi) \times r] - [r \times \tilde{M}_t(\varphi)] - r \times [M_l(\varphi) + \tilde{M}_l(\varphi) + M(\varphi)] \times r$ and even for a general RG the quantities $2\langle l^\parallel\varphi\rangle + \langle\varphi^2\rangle$ cannot be obtained separately (Dunitz, Schomaker & Trueblood, 1988), the indeterminacy being analogous to that in $2\langle t^\parallel\tau\rangle + \langle\tau^2\rangle$.

As we have seen, for one-atom RG's not all six independent parameters of internal motion can be determined. This applies also for certain other RG's with symmetry in the bond distances. These indeterminacies are tied to geometric relationships among the position vectors and are analogous to the problems of rigid-body analysis for molecules in which the atomic positions define a conic section (Cruickshank, 1956; Schomaker & Trueblood, 1968; Johnson, 1970b, 1980). We have been unable to find a general procedure allowing a systematic identification of such pathological RG's. Instead, we had to analyse each new type of RG individually. For this purpose, it is convenient to use coordinate systems that reflect as well as possible the (approximate) symmetry in the distances and angles of the RG. (As an exercise the interested reader may try to show that for a two-atom RG in which φ intersects the midpoint of the interatomic vector at a right angle, only five independent internal-motion parameters may be determined).

For simplicity, the discussion so far has been based on a very special coordinate system. Note, however, that the transformation properties of M tensors with respect to coordinate rotation and shift of origin are the same as for T, L and S tensors (Schomaker & Trueblood, 1968). A shift of origin changes T and S but leaves U and L unaltered. If T_{old} and S_{old} refer to r_{old}, then a shift s of origin such that $r_{old} = r_{new} + s$ leads to

$$L_{new} = L_{old}$$
$$S_{new} = S_{old} - (L_{old} \times s)$$
$$T_{new} = T_{old} - (s \times S_{old}) + (\tilde{S}_{old} \times s)$$
$$\qquad - (s \times L_{old} \times s). \qquad (11)$$

Usually an **s** is chosen which minimizes the trace of T_{new} [$tr(T_{new})$] and symmetrizes S_{new}. It is

$$s = [tr(L_{old})1 - L_{old}]^{-1} \langle 1 \times t \rangle_{old}, \qquad (12)$$

where **1** is a unit matrix. For an RG undergoing internal translational oscillation, an analogous condition minimizes the trace of all translational motions [$tr(T + M_t(\tau) + \tilde{M}_t(\tau) + M(\tau)_{old}$],

$$s = [tr(L_{old})1 - L_{old}]^{-1} (\langle 1 \times t \rangle_{old} + \langle 1 \times \tau \rangle_{old}). \qquad (13)$$

Sometimes it is convenient to refer $M_l(\tau)$, $M_t(\tau)$ and $M(\tau)$ to an arbitrarily oriented orthogonal coordinate system. They then take the following form

$$M_l(\tau) = l\tau = \begin{bmatrix} \langle l_1\tau \rangle\alpha & \langle l_1\tau \rangle\beta & \langle l_1\tau \rangle\gamma \\ \langle l_2\tau \rangle\alpha & \langle l_2\tau \rangle\beta & \langle l_2\tau \rangle\gamma \\ \langle l_3\tau \rangle\alpha & \langle l_3\tau \rangle\beta & \langle l_3\tau \rangle\gamma \end{bmatrix}$$

$$M_t(\tau) + \tilde{M}_t(\tau) + M(\tau) = t\tau + \tau t + \tau\tau$$

$$= \begin{bmatrix} 2\langle t_1\tau \rangle\alpha & \langle t_1\tau \rangle\beta & \langle t_1\tau \rangle\gamma \\ +\langle t_2\tau \rangle\alpha & +\langle t_3\tau \rangle\alpha \\ +\langle \tau^2 \rangle\alpha^2 & +\langle \tau^2 \rangle\alpha\beta & +\langle \tau^2 \rangle\alpha\gamma \\ \langle t_2\tau \rangle\alpha & 2\langle t_2\tau \rangle\beta & \langle t_2\tau \rangle\gamma \\ +\langle t_1\tau \rangle\beta & & +\langle t_3\tau \rangle\beta \\ +\langle \tau^2 \rangle\alpha\beta & +\langle \tau^2 \rangle\beta^2 & +\langle \tau^2 \rangle\beta\gamma \\ \langle t_3\tau \rangle\alpha & \langle t_3\tau \rangle\beta & 2\langle t_3\tau \rangle\gamma \\ +\langle t_1\tau \rangle\gamma & +\langle t_2\tau \rangle\gamma \\ +\langle \tau^2 \rangle\alpha\gamma & +\langle \tau^2 \rangle\beta\gamma & +\langle \tau^2 \rangle\gamma^2 \end{bmatrix} \quad (14)$$

α, β, γ are the direction cosines of the internal translation direction τ with respect to the orthogonal but otherwise arbitrarily oriented axes. The six independent quantities corresponding to $\langle l_1^\perp\tau \rangle$, $\langle l_2^\perp\tau \rangle$, $\langle l^{\parallel}\tau \rangle$, $\langle t_1^\perp\tau \rangle$, $\langle t_2^\perp\tau \rangle$, $\langle t^{\parallel}\tau \rangle$ above are now $\langle l_1\tau \rangle$, $\langle l_2\tau \rangle$, $\langle l_3\tau \rangle$, $\langle t_1\tau \rangle + \alpha\langle \tau^2 \rangle/2$, $\langle t_2\tau \rangle + \beta\langle \tau^2 \rangle/2$, $\langle t_3\tau \rangle + \gamma\langle \tau^2 \rangle/2$.

Symmetry

The tensors M_t, M_l and M are subject to symmetry restrictions that are analogous to those for U, T, S and L themselves. For an RG with a given symmetry, $l\tau$ and φt obey the same restrictions as an S tensor of a molecule with the same symmetry. For $t\tau$, $\tau\tau$, $l\varphi$ and $\varphi\varphi$, the restrictions are those for U, T or L tensors. Details have been listed by Schomaker & Trueblood (1968).

For a molecule with site-symmetry group $G = \{g_1, g_2, g_i, g_n\}$, there may be several symmetrically related RG's. Let RG_i be related to RG_1 through the symmetry operation g_i. The internal motions of the RG's can be classified according to the irreducible representations Γ_j of G. Each Γ_j determines a specific pattern of correlations among the internal motions of individual

RG's. If the instantaneous displacement of RG_1 in a symmetry displacement coordinate transforming as Γ_j is μ_1, then that of RG_i is $\mu_i = h_{ij}\,\mu_1$, where h_{ij} is proportional to the element of the projection operator $p_i(\Gamma_j)$ corresponding to g_i. (The proportionality factor is n/l_j, where n is the order of G and l_j is the degeneracy of Γ_j.) The contribution of internal motion to the U's of the two RG's are

$$U^1(int.) = - (r_1 \times l\tau) + (\tau l \times r_1) + t\tau + \tau t + \tau\tau \quad (15)$$

and, respectively,

$$U^i(int.) = -[(g_i r_1) \times l\tau\tilde{h}_{ij}) + (h_{ij}\tau l \times (g_i r_1)]$$
$$+ (t\tau\tilde{h}_{ij}) + (h_{ij}\tau t) + (h_{ij}\tau\tau\tilde{h}_{ij}). \quad (16)$$

Back transformation of $U^i(int.)$ yields the identity

$$U^1(int.) = g_i^{-1} U^i(int.)(\tilde{g_i^{-1}}). \quad (17)$$

Comparison of individual terms on the left and right of (17) can provide information on some of the coupling terms in $l\tau$ and $t\tau$.

Consider the molecule $RG_1-MAIN-RG_2$ with $G = \{1, \bar{1}\}$ as an example. For an internal asymmetric stretching motion, h_{ij} is the identity matrix **1** and for a symmetric stretching motion it is the inversion matrix $\bar{1}$. For the asymmetric stretch, we find

$$l\tau = -l\tau\,1 = 0$$
$$t\tau = t\tau\,1 = t\tau$$
$$\tau\tau = 1\,\tau\tau\,1 = \tau\tau. \quad (18)$$

The couplings $l\tau$ are zero by symmetry, the couplings $t\tau$ are not. For the symmetric stretch,

$$l\tau = -l\tau\,\bar{1} = l\tau$$
$$t\tau = t\tau\,\bar{1} = 0$$
$$\tau\tau = \bar{1}\,\tau\tau\,\bar{1} = \tau\tau. \quad (19)$$

Couplings $l\tau$ are generally different from 0, couplings $t\tau$ are zero.

These results could have been found more easily. The overall libration **l** is *gerade* with respect to $\bar{1}$, the overall translation **t** is *ungerade*, and the internal translation τ is *ungerade* and *gerade*, respectively. This leads directly to the above zero or nonzero expectation values (as well as to **S** = 0). Analogous results for other symmetries are obtained most easily by using the explicit forms of $l\tau$, $t\tau$ and $\tau\tau$ given above [(8) or (14)]. The same general procedure can be applied to internal rotation, *i.e.* $M_l(\varphi)$ and $M_t(\varphi)$ and, indeed, to any combination of internal displacement coordinates, *i.e.* $\langle \mu_i \mu_j \rangle$.

Approximate models

In cases where a chemically symmetric molecule occupies a general position in the crystal (with site symmetry 1) it is often a good approximation to assume that the symmetry of the internal motion (h_{ij}) is

preserved, if the symmetry of the geometrical structure is at least approximately preserved (g_i). In such cases the symmetry relationship between U^1(int.) and U^i(int.) [(17)] no longer holds. This is because the overall motion (T, L, S) and the couplings to internal motion (tτ, lτ) do not, in general, show the approximate symmetry.

Nevertheless, the information on couplings is still available. With the approximate relationships

$$r_i \simeq g_i r_1$$

$$\tau(\text{group } i) \simeq h_{ij}\, \tau(\text{group 1}), \qquad (20)$$

we obtain

$$U^1(\text{int.}) \pm U^i(\text{int.}) = -(r_1 \times l\tau) \mp [(g_i r_1) \times l\tau \tilde{h}_{ij}]$$
$$+ (\tau l \times r_1) \pm [h_{ij}\tau l \times (g_i r_1)]$$
$$+ t\tau \pm (t\tau \tilde{h}_{ij}) + \tau t \pm (h_{ij}\tau t)$$
$$+ \tau\tau \pm (h_{ij}\tau\tau \tilde{h}_{ij}). \qquad (21)$$

In terms of the above example the result is, for $h_{ij}= 1$, $g_i = \bar{1}$,

$$U^1(\text{int.}) - U^2(\text{int.}) = -2(r_1 \times l\tau) + 2(\tau l \times r_1)$$

$$U^1(\text{int.}) + U^2(\text{int.}) = 2t\tau + 2\tau t + 2\tau\tau \qquad (22)$$

and, for $h_{ij} = \bar{1}, g_i = \bar{1}$,

$$U^1(\text{int.}) - U^2(\text{int.}) = 2t\tau + 2\tau t$$

$$U^1(\text{int.}) + U^2(\text{int.}) = -2(r_1 \times l\tau) + 2(\tau l \times r_1)$$
$$+ 2\tau\tau. \qquad (23)$$

The correlations between overall and internal motion are often small and can be neglected. The internal motion is then described by a single parameter, e.g. $\tau\tau = \langle \tau^2 \rangle$ for internal translation and $\varphi\varphi = \langle \varphi^2 \rangle$ for internal rotation. For internal rotation this simplified model is known as the Dunitz–White model (Dunitz & White, 1973). Both approximations are simplified variants of Johnson's (1970a) more general segmented-body model. They specifically exclude correlations between overall rigid-body motion and internal rigid-group motion as does the segmented-body model.

As mentioned by Dunitz, Schomaker & Trueblood (1988), $\langle \varphi^2 \rangle$ derived from experimental U's within the framework of the simplified model is meaningful only if $\langle \varphi^2 \rangle$ is large compared with $\langle (l^{\parallel})^2 \rangle$. The same applies to $\langle \tau^2 \rangle$ in relation to $\langle (t^{\parallel})^2 \rangle$, as may be seen from the following considerations. After rewriting

$$\langle t^{\parallel}\tau \rangle = c\,[\langle \tau^2 \rangle \langle (t^{\parallel})^2 \rangle]^{1/2}, \qquad (24)$$

where c is the correlation coefficient between internal and overall translation, it may be shown that if A is the determinable sum $\langle \tau^2 \rangle + 2\langle t^{\parallel}\tau \rangle$ then the following relationship holds:

$$+ [\langle \tau^2 \rangle / \langle (t^{\parallel})^2 \rangle]^{1/2} = -c + [c^2 + A/\langle (t^{\parallel})^2 \rangle]^{1/2}. \qquad (25)$$

For a physically meaningful model, the right-hand side of (25) must be real, i.e. $A/\langle (t^{\parallel})^2 \rangle \geq -1$ must hold. If $A = -\langle (t^{\parallel})^2 \rangle$ then $c = -1$ and $\langle \tau^2 \rangle = \langle (t^{\parallel})^2 \rangle$; if $A \gg$

$\langle (t^{\parallel})^2 \rangle$ then $c \simeq 0$ and $\langle \tau^2 \rangle \simeq A$. Finally, if $A \simeq 0$ then $\langle \tau^2 \rangle \simeq 4c^2\langle (t^{\parallel})^2 \rangle$, i.e. $\langle \tau^2 \rangle$ may be anything between 0 and $4\langle (t^{\parallel})^2 \rangle$.

The ratio $A/\langle (t^{\parallel})^2 \rangle$ depends on the choice of origin for the coordinate system [(11)–(13)]. An upper limit for $A/\langle (t^{\parallel})^2 \rangle$ may be obtained by choosing an origin that maximizes $\text{tr}[\tau\tau + t\tau + \tau t - (s \times l\tau) + (\tau l \times s)]/\text{tr}[T - (s \times S) + (S \times s) - (s \times L \times s)]$. For $l\tau = 0$, $A/\langle (t^{\parallel})^2 \rangle$ has a maximum if tr(T) is minimal [(12)]. If the components of $l\tau$ are much smaller than those of S, the value of $A/\langle (t^{\parallel})^2 \rangle$ obtained with minimal tr(T) is still an acceptable approximation to the upper limit of $A/\langle (t^{\parallel})^2 \rangle$.

ΔU values

ΔU values evaluated along internuclear vectors have been used to test for the non-rigidity of molecules in crystals (Rosenfield, Trueblood & Dunitz, 1978; Hirshfeld, 1976). In particular, for molecules with internal translations, ΔU values along bonds or averages of ΔU values for chemically equivalent bonds have been used to determine the mean-square amplitude of internal translation (Chandrasekhar & Bürgi, 1984; Ammeter, Bürgi, Gamp, Meyer-Sandrin & Jensen, 1979; Stebler & Bürgi, 1987). Such analyses may now be interpreted in terms of the above discussion.

Consider an atom undergoing internal translation along the bond attaching it to the main rigid body. Its positional coordinates can be expressed as $r_1 = (x_1, y_1, z_1)$ in the coordinate system with z parallel to this bond and x and y perpendicular to it. The atom to which it is bonded is located at $r_0 = (x_1, y_1, z_0)$. Corresponding U's are

$$U^1 = T - (r_1 \times S) + (\tilde{S} \times r_1) - (r_1 \times L \times r_1)$$
$$- (r_1 \times l\tau) + (\tau l \times r_1) - t\tau + \tau t + \tau\tau$$

$$U^0 = T - (r_0 \times S) + (\tilde{S} \times r_0) - (r_0 \times L \times r_0). \qquad (26)$$

The difference between the two is

ΔU (atom 1 − atom 0)

$$= -(r \times S) + (\tilde{S} \times \Delta r) - (\Delta r \times L \times \Delta r)$$
$$- (r_1 \times l\tau) + (\tau l \times r_1) + t\tau + \tau t + \tau\tau. \qquad (27)$$

The component along the bond is

ΔU (atom 1 − atom 0)

$$= -2\langle l_2^{\perp}\tau \rangle x_1 + 2\langle l_1^{\perp}\tau \rangle y_1 + 2\langle t^{\parallel}\tau \rangle + \langle \tau^2 \rangle. \qquad (28)$$

If more than one rigid group is attached to the main rigid body, the symmetry consideration and approximations discussed above apply. For the centrosymmetric fragment RG_1–MAIN–RG_2 undergoing symmetric stretching motion in a non-centrosymmetric environment, the two ΔU's are ($i = 1,2$)

$$\Delta U_i \simeq \mp 2\langle l_2^{\perp}\tau \rangle x_1 \pm 2\langle l_1^{\perp}\tau \rangle y_1 \pm 2\langle t^{\parallel}\tau \rangle + \langle \tau^2 \rangle \quad (29)$$

and their average is

$$\overline{\Delta U} \simeq \langle \tau^2 \rangle. \tag{30}$$

It is straightforward but somewhat tedious to show that this relationship also holds for the symmetric stretch deformations of MX_3 fragments with (approximate) D_{3h} symmetry and MX_4 fragments with (approximate) T_d symmetry.

Applications and examples

The essential results of the above treatment have been used in the analysis of several problems. These include Jahn–Teller deformations in Cu^{II} (Ammeter, Bürgi, Gamp, Meyer-Sandrin & Jensen, 1979; Stebler & Bürgi, 1987) and Mn^{III} complexes (Vedani, 1981), spin equilibria in Fe^{III} complexes (Chandrasekhar & Bürgi, 1984) and Si/Al disorder in alkali feldspars (Armbruster, Bürgi, Kunz, Gnos, Brönnimann & Lienert, 1989; Kunz & Armbruster, 1989). These investigations all follow the same scheme. From the given atomic coordinates and ADP's, bond distances and ΔU's were calculated and averaged with respect to all bonds in the polyhedra (d_l: long distance, d_s: short distance). In some structures the bond distances show patterns such as in (I) or (II) or (III) (for Cu and Mn), (IV) or (V) for the Fe^{III} complex, (VI) or (VII) for the

(I)   (II)   (III)

(IV)   (V)   (VI)   (VII)
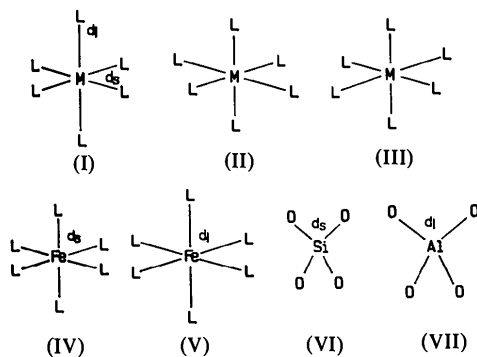
alumosilicate and the ΔU's are small, *i.e.* these structures are more or less ordered. In other structures the observed bond distances correspond to averages, *e.g.* [(I) + (II) + (III)]/3, [(IV) + (V)]/2 and [(VI) + (VII)]/2, respectively and the ΔU's are large. In some of these examples, oscillation between the limiting structures is fast compared with the time it takes to measure a Bragg intensity, in others there is static disorder. From the previous discussion we know that $\overline{\Delta U} \simeq \langle \tau^2 \rangle$ where τ is related to the displacement of a ligand atom necessary to go from (I) to (II) to (III), from (IV) to (V) or from (VI) to (VII). In the first example the ligands are displaced on average from their mean position by $2\langle d_l - d_s \rangle/3$ with probability $1/3$ and by $-(d_l - d_s)/3$ with probability $2/3$. The contribution to U(ligand)

Table 1. *Observed difference displacement parameters ΔU for various kinds of disorder, calculated ΔU's from ordered structures*

	ΔU(obs.)(Å^2)	ΔU(calc.)(Å^2)	References
$K_2Pb[Cu(NO_2)_6]$	0·0156 (20)	—	(a)
	0·0207 (8)		(a)
$Tl_2Pb[Cu(NO_2)_6]$	0·0159	—	(a)
$K_2Sn[Cu(NO_2)_6]$	—	0·0169	(a), (e)
$K_2Ba[Cu(NO_2)_6]$	—	0·0159	(a), (e)
$[Co(NH_3)_6][MnF_6]$	0·0144 (10)	—	(b)
$[Cr(NH_3)_6][MnF_6]$	0·0161 (10)	—	(b)
K_2NaMnF_6	—	0·0088	(b), (e)
MnF_3	—	0·0151	(b), (e)
$[Fe(S_2CNR_2)_3]$	0·0071	0·0056	(c), (f)
$(Si_{0.5}Al_{0.5})O_4$	0·0056	0·0042	(d), (g)

References: (a) Ammeter, Bürgi, Gamp, Meyer-Sandrin & Jensen (1979); (b) Vedani (1981); (c) Chandrasekhar & Bürgi (1984); (d) Kunz & Armbruster (1989); (e) calculated from 33% (I), 33% (II), 33% (III); (f) calculated from 50% low-spin (IV), 50% high-spin (V); (g) calculated from 50% (VI), 50% (VII).

along τ and therefore to ΔU is then $2\langle d_l - d_s \rangle^2/9$. Similarly, for the other two examples the corresponding quantities are $(d_l - d_s)^2/4$. Since estimates of d_l and d_s are available from ordered structures, $\langle \tau^2 \rangle$ can be estimated independently and compared to experimental values of ΔU (Table 1). In general the agreement is good. The differences between observed and calculated values are partly due to neglect of the usual intramolecular stretching vibrations in our estimate of $\langle \tau^2 \rangle$. These vibrations have been calculated from force-constant information to have mean-square amplitudes of about 20–30×10^{-4} Å^2 for the transition-metal complexes (Chandrasekhar & Bürgi, 1984). For SiO_4 and AlO_4 tetrahedra they have been determined experimentally as $\sim 5 \times 10^{-4}$ Å^2 (Armbruster, Bürgi, Kunz, Gnos, Brönnimann & Lienert, 1989). The remaining differences contain experimental error and inadequacies in the model fitted to the diffraction data. They may also reflect the fact that observed and calculated quantities are not obtained from the same but only from chemically similar compounds.

The model may be generalized for any degree of disorder. Here we consider two limiting structures with occupations p and $(1-p)$, respectively. The average of the mean distances is $d = pd_l + (1-p)d_s$, the mean contribution to $\langle \tau^2 \rangle$ is $p(d_l-d)^2 + (1-p)(d-d_s)^2 = (d_l-d)(d-d_s)$. Fig. 1 shows for the case of $(Si/Al)O_4$ tetrahedra that this model accounts well for the experimental $\overline{\Delta U}$'s.

The importance of working with averaged $\overline{\Delta U}$ and d values is shown by comparison of Fig. 1 with Fig. 2. The unaveraged values (Fig. 2) show much more scatter and hardly reveal a discernible trend. The improvement in Fig. 1 comes from the disappearance of coupling terms on averaging [(29) and (30)].

Hirshfeld (1976) has argued that $\overline{\Delta U}$'s along bonds between first-row atoms should be less than about 10×10^{-4} Å^2 and has used this criterion to test the

quality of the corresponding U's as determined from diffraction experiments. Later, it was found that this criterion had to be relaxed to $20–30 \times 10^{-4}$ Å for bonds to octahedrally coordinated transition metals (Chandrasekhar & Bürgi, 1984). Our present analysis allows a more detailed interpretation of this rule of thumb. Consider an octahedral complex ML_6 undergoing normal stretching vibrations, i.e. a_{1g}, e_g and t_{2u} modes. From the arguments given above, the gerade modes contribute to $\langle \tau^2 \rangle$ but not to $\langle t^{\parallel}\tau \rangle$ whereas the ungerade modes contribute to both $\langle \tau^2 \rangle$ and $\langle t^{\parallel}\tau \rangle$. Thus,

$$\overline{\Delta U} = \langle \tau^2 \rangle_{a_{1g}} + \langle \tau^2 \rangle_{e_g} + \langle \tau^2 \rangle_{t_{2u}} + 2\langle t^{\parallel}\tau \rangle_{t_{2u}}$$

if M is placed at the origin. The last term may well be different for the same complex in different crystalline environments leading to different values of $\overline{\Delta U}$. An example is $[\mathrm{Ru(H_2O)_6}]^{2+}$ (Table 2), where $\overline{\Delta U}$ for the

Table 2. ΔU from diffraction and spectroscopic experiments for $[\mathrm{Ru(H_2O)_6}]^{2+}$

	$\Delta U(\text{Å}^2)$	$T(\text{K})$	Method	References
$\mathrm{Rb_2[Ru(H_2O)_6](SO_4)_2}$	0.0019	160	IR, Raman	(a)
	0.0023	296		
$\mathrm{K_2[Ru(H_2O)_6](SO_4)_2}$	0.0036 (2)	160	X-ray	(b)
	0.0037 (4)	296		
$\mathrm{[Ru(H_2O)_6](CH_3C_6H_4SO_3)_2}$	0.0020 (7)	RT	X-ray	(c)

References: (a) calculated from force constants given by Bernhard & Ludi (1984); (b) Raselli & Bürgi (1988); (c) Bernhard, Bürgi, Hauser, Lehmann & Ludi (1982).

tosylate salt agrees well with the value calculated from spectroscopic data, whereas $\overline{\Delta U}$ for the sulfate salt (measured at 160 and 296 K and determined by high-order refinements) is clearly larger. If we accept the value from normal-coordinate analysis as an estimate of $\langle \tau^2 \rangle$, then for the sulfate salt $\langle t^{\parallel}\tau \rangle_{t_{2u}} = 7 \times 10^{-4}$ Å^2. Given the calculated contributions $\langle \tau^2 \rangle_{t_{2u}}$ of 10×10^{-4} Å^2 and an approximately isotropic T tensor with $\langle t^2 \rangle \simeq 125 \times 10^{-4}$ Å^2, the correlation between overall translation and t_{2u}-stretching motion is $c = \langle t^{\parallel}\tau \rangle / (\langle t^2 \rangle \langle \tau^2 \rangle_{t_{2u}})^{1/2} \simeq 0.2$. The corresponding correlation in the tosylate salt is much smaller. This difference may be related to different hydrogen-bonding interactions in the two crystal lattices. Systematic investigations could possibly shed light on such questions. In any case, this example shows how a combination of spectroscopic and diffraction data can provide additional information on the correlation between internal and overall molecular motion in a crystal.

The above analysis of octahedral complexes depends on the fact that the ligand atoms are lighter than those of the metal and that therefore their mean-square displacement amplitudes are larger than those of the metal. A similar situation occurs with bonds to hydrogen. The formalism described here could serve as a basis for improved rigid-body/internal-motion refinements of neutron diffraction data for hydrocarbon molecules.

Given the wealth of diffraction and spectroscopic data on atomic motion in molecules and crystals, the models described here and elsewhere may be useful in the transformation of almost meaningless lists of ADP's to chemically significant descriptions of molecular motion in crystals.
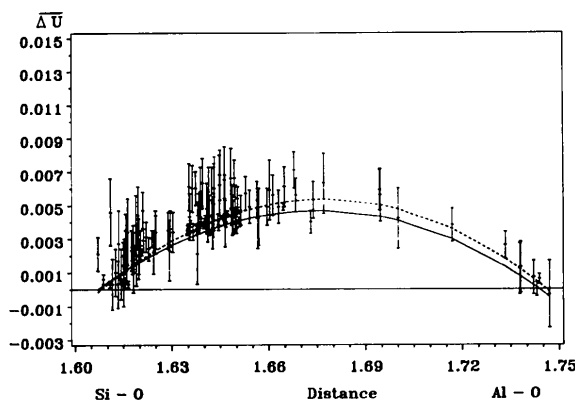

Fig. 1. Average values $\overline{\Delta U}$ (Å^2) in 138 (Si/Al)O$_4$ tetrahedra as a function of (Si/Al)–O distance (Å). Error bars $\pm$ $[\sigma^2(\Delta U)]^{1/2}$. [Outliers in the data set not included, see Kunz & Armbruster (1989).] Dotted line: $\overline{\Delta U} = 1.124$ [1.746 $-$ d(Si,Al–O)] $\times$ [d(Si,Al–O) $-$ 1.608] (Å^2) (quadratic least-squares curve excluding outliers); solid line: $\overline{\Delta U} = [1.744 - d(\mathrm{Si,Al-O})] \times [d(\mathrm{Si,Al-O}) - 1.607]$ (Å^2) (model).
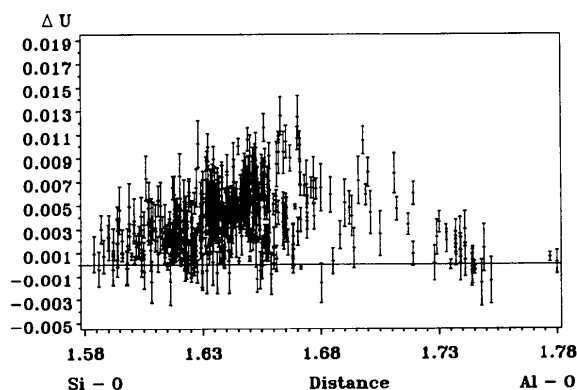
The author thanks Dr Th. Armbruster and Mr M. Kunz for permission to reproduce Figs. 1 and 2 (Kunz & Armbruster, 1989) and Professor J. D. Dunitz and K. N. Trueblood for their comments on the manuscript.

Fig. 2. ΔU values (Å^2) for individual (Si/Al)–O bonds as a function of (Si/Al)–O distance (Å).

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Hydrogen-Bond Distances and Angles in the Structures of Amino Acids and Peptides

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Abstract

Intermolecular hydrogen-bond parameters for amino acids and the corresponding peptides in the solid state are presented. Crystallographic data were retrieved from the Cambridge Structural Database. The interactions investigated include hydrogen bonds between the main chains as well as hydrogen-bonding side chains. The tendency for peptides to line up 'head to tail' in crystal structures is demonstrated. The mean hydrogen-bond angles in $C^\alpha\text{--}COO^-\cdots {}^+H_3N\text{--}C^\alpha$ and $\text{>}C\text{=}O\cdots H\text{--}N\text{<}$ interactions are not significantly different, but there are higher relative frequencies of bonds with angles in the intervals 180–170° and 150–110° for the former. The amino-acid histidine shows an exceptional ability to form short hydrogen bonds. In the protonated state, it is donor of two types of bonds with significantly different mean $N\cdots O$ distances [2·644 (17) and 2·730 (17) Å]. A side-chain aspartyl– or glutamyl–COO^- group on average accepts 4·00 H atoms. These groups are better acceptors than main-chain carboxylate groups.

Introduction

Most researchers in the field of crystallography will have a fairly good idea which hydrogen-bond lengths to expect for different interactions. However, despite the rapidly increasing number of published structures and also papers on hydrogen bonds, a peptide chemist may well have difficulties telling whether an $N\cdots O$ distance

of 2·80 Å should be classified as long or short in a specific amino-acid or peptide structure. The present paper deals with this group of compounds and supplies acceptor$\cdots$donor [$r(Acc\cdots Don)$] and H$\cdots$acceptor [$r(H\cdots Acc)$] distances and donor–H$\cdots$acceptor angles [$\alpha(Don\text{--}H\cdots Acc)$] for most interactions likely to be encountered in crystals.

Methodology

The Cambridge Structural Database (CSD) presently (May 1988 release; Allen *et al.*, 1979) contains information on more than 67 000 organic compounds. A subfile of crystallographic data for 749 amino-acid and peptide structures (chemical class 48) was generated from the database.* Only entries with diffractometer-measured intensity data, R factors < 0·075 and experimentally determined H-atom positions were accepted. The subfile was then searched for interactions between hydrogen-bond donors and acceptors of the main chain. Finally, amino-acid residues with a donor and/or acceptor group in the side chain (all unsubstituted) were treated one by one in order to obtain parameters for different types of hydrogen

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* A list of references for the 749 structures that contain the interactions described in this article has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51751 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.