

The Analysis of the Anisotropic Thermal Motion of Molecules in Crystals

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(Received 24 February 1956)

A method is given for determining the anisotropic rigid-body translational and rotational vibration tensors of molecules in crystals from the vibration tensors of individual atoms.

1. Introduction

The preceding paper (Cruickshank, 1956*a*) has described how the magnitudes of the harmonic anisotropic thermal motion of atoms in crystals may be determined. The present paper is chiefly concerned with crystals containing molecules, and its chief object is to show how the magnitudes of the atomic motions can be used to determine the rigid-body vibrations of the molecules.

We assume that symmetric tensors U^r have been found for each atom r such that

$$\overline{u^2} = \sum_{i=1}^3 \sum_{j=1}^3 U_{ij}^r l_i l_j \quad (1.1)$$

is the mean square amplitude of vibration of atom r in the direction specified by the unit vector $\mathbf{l} = (l_1, l_2, l_3)$. We also assume that the axes are orthogonal, and possibly defined by the molecule rather than by the crystal. This may necessitate transformations of the U_{ij}^r as obtained by the methods of the previous paper. Transformations from monoclinic crystal axes to orthogonal crystal axes have been given by Rollett & Davies (1955); any orthonormal transformations needed may be made by the ordinary rules for tensor transformations.

If there are N atoms in the asymmetric unit, our problem is to interpret the N sets of U_{ij}^r in terms of the rigid-body and internal vibrations of the molecule. In general the contributions from the rigid-body vibrations will be much larger than the contributions from the internal vibrations, so that it is natural first to attempt to interpret the U_{ij}^r solely in terms of rigid-body vibrations. The simplest hypothesis we can make about anisotropic rigid-body vibrations is to suppose that the motion of a molecule can be expressed in terms of two symmetric tensors, each with six independent components, one giving the translational vibrations of the mass centre and the other the angular oscillations (or librations) about the centre.

If \mathbf{T} is the tensor giving the mean-square amplitude of the translational vibrations, the translational contribution to the motion of any atom will be simply

$$\sum_{i=1}^3 \sum_{j=1}^3 T_{ij} l_i l_j \quad (1.2)$$

For the librations we may assume that

$$\sum_{i=1}^3 \sum_{j=1}^3 \omega_{ij} t_i t_j \quad (1.3)$$

is the mean-square amplitude of libration about an axis defined by a unit vector \mathbf{t} through the centre. The movement of an atom at $\mathbf{r} = (x, y, z)$ in a direction \mathbf{l} due to a libration is possible only when the molecule turns about an axis parallel to $\mathbf{l} \wedge \mathbf{r}$. Further, if the molecule turns through a small angle ε about this axis the component of the movement of the atom along \mathbf{l} is $|\mathbf{l} \wedge \mathbf{r}| \varepsilon$. Accordingly, by (1.3) the mean-square amplitude of vibration of the atom in the direction \mathbf{l} due to small librations is

$$\sum_{i=1}^3 \sum_{j=1}^3 \omega_{ij} (\mathbf{l} \wedge \mathbf{r})_i (\mathbf{l} \wedge \mathbf{r})_j \quad (1.4)$$

Thus for rigid-body vibrations we assume that each of atomic U_{ij}^r tensors can be expressed as

$$\sum_{i=1}^3 \sum_{j=1}^3 U_{ij}^r l_i l_j = \sum_{i=1}^3 \sum_{j=1}^3 (T_{ij} l_i l_j + \omega_{ij} (\mathbf{l} \wedge \mathbf{r})_i (\mathbf{l} \wedge \mathbf{r})_j) \quad (1.5)$$

The problem is now to find the \mathbf{T} and $\boldsymbol{\omega}$ tensors, given N U^r tensors.

2. Determination of T_{ij} and ω_{ij}

If we expand the right-hand-side of (1.5), using $T_{21} = T_{12}$, etc., we obtain

$$T_{11} l_1^2 + 2T_{12} l_1 l_2 + \dots + \omega_{11} (l_2 z - l_3 y)^2 + 2\omega_{12} (l_2 z - l_3 y)(l_3 x - l_1 z) + \dots \quad (2.1)$$

If we group the coefficients of $l_i l_j$, manipulation yields

$$l_1^2 (T_{11} + z^2 \omega_{22} + y^2 \omega_{33} - 2yz \omega_{23}) + 2l_1 l_2 (T_{12} - xy \omega_{33} - z^2 \omega_{12} + xz \omega_{23} + yz \omega_{13}) + \dots \quad (2.2)$$

Equating coefficients of $l_i l_j$ with those on the left-hand side of (1.5), we obtain the typical results

$$T_{11} = T_{11} + z^2 \omega_{22} + y^2 \omega_{33} - 2yz \omega_{23}, \quad (2.3a)$$

and

$$T_{12} = T_{12} - xy \omega_{33} - z^2 \omega_{12} + xz \omega_{23} + yz \omega_{13}. \quad (2.3b)$$

If the molecule is planar and the axes are chosen with the z axis parallel to the plane normal, we obtain the following relations:

$$\left. \begin{aligned} U_{11} &= T_{11} + y^2 \omega_{33}, \\ U_{22} &= T_{22} + x^2 \omega_{33}, \\ U_{33} &= T_{33} + y^2 \omega_{11} + x^2 \omega_{22} - 2xy \omega_{12}, \\ U_{12} &= T_{12} - xy \omega_{33}, \\ U_{23} &= T_{23} - x^2 \omega_{23} + xy \omega_{13}, \\ U_{13} &= T_{13} - y^2 \omega_{13} + xy \omega_{23}. \end{aligned} \right\} \quad (2.4)$$

We may notice that the forms for U_{11} and U_{22} , and U_{33} and U_{13} are similar. The libration (ω_{33}) about the z axis affects only the motions (U_{11} , U_{22} , U_{12}) of the atom in the plane of the molecule; while the motions perpendicular to the plane are caused by libration about any axis in the plane (ω_{11} , ω_{22} , ω_{12}) and by T_{33} .

Since in general the number of observed U_{ij}^r will be greater than the number (12) of independent T_{ij} and ω_{ij} , the direct inverses of (2.3) are not of much interest, and the T_{ij} and ω_{ij} are best determined by least-squares. Assuming for simplicity that the same weights are attached to each U_{ij}^r , and denoting the observed U_{ij}^r as $U_{ij}^{\text{obs.}}$, the U_{ij}^r calculated in terms of T_{ij} and ω_{ij} by (2.3) as $U_{ij}^{\text{calc.}}$, and the unknowns T_{ij} and ω_{ij} as A_q , the least-squares normal equations will be

$$\sum_q \left\{ \sum_n \left(\frac{\partial U_n^{\text{calc.}}}{\partial A_p} \right) \left(\frac{\partial U_n^{\text{calc.}}}{\partial A_q} \right) \right\} A_q = \sum_n U_n^{\text{obs.}} \left(\frac{\partial U_n^{\text{calc.}}}{\partial A_p} \right). \quad (2.5)$$

To evaluate these equations we need $\partial U_n^{\text{calc.}}/\partial A_p$ that is we must evaluate $\partial U_{ij}/\partial T_{kl}$ and $\partial U_{ij}/\partial \omega_{kl}$ from (2.3). The typical terms are:

$$\left. \begin{aligned} \text{(i)} \quad \partial U_{ij}/\partial T_{kl} &= 1 \text{ if } i = k \text{ and } j = l, \\ &= 0 \text{ otherwise.} \end{aligned} \right\} \quad (2.6)$$

$$\left. \begin{aligned} \text{(ii)} \quad \partial U_{11}/\partial \omega_{11} &= 0; \quad \partial U_{22}/\partial \omega_{11} = z^2; \\ &\quad \partial U_{33}/\partial \omega_{11} = y^2; \\ \partial U_{12}/\partial \omega_{11} &= 0; \quad \partial U_{23}/\partial \omega_{11} = -yz; \\ &\quad \partial U_{13}/\partial \omega_{11} = 0: \end{aligned} \right\} \quad (2.7)$$

and

$$\left. \begin{aligned} \partial U_{11}/\partial \omega_{12} &= 0; \quad \partial U_{22}/\partial \omega_{12} = 0; \\ &\quad \partial U_{33}/\partial \omega_{12} = -2xy; \\ \partial U_{12}/\partial \omega_{12} &= -z^2; \quad \partial U_{23}/\partial \omega_{12} = xz; \\ &\quad \partial U_{13}/\partial \omega_{12} = yz: \text{ etc.} \end{aligned} \right\} \quad (2.8)$$

The twelfth-order normal equations are shown in Fig. 1. Each matrix element on the left-hand side represents the contribution from the $6U_{ij}$ for each atom; the elements have thus to be summed over all atoms. The matrix is symmetric and the elements below the diagonal have been omitted for simplicity. Each element of the right-hand side vector must also be summed over all atoms.

Some simplification of Fig. 1 occurs if the molecule has planes of symmetry, and the axes are referred to these. In particular, there is considerable reduction if the molecule is planar. If we choose the molecular

U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}	T_{11}	T_{22}	T_{33}	T_{12}	T_{23}	T_{13}	ω_{11}	ω_{22}	ω_{33}	ω_{12}	ω_{23}	ω_{13}
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$	$-2yz^3 - x^2yz$	$-2xy^3 - xy^2z$	$-xz^3 - x^3z$	$-xy^3 - xy^3$	$-yz^3 - y^3z$
$z^2 U_{22}$	$x^2 U_{33}$	$y^2 U_{11}$	$-yz U_{23}$	$-xz U_{13}$	$-xy U_{12}$	0	$-2yz$	0	yz	xz	xy	$-2xz^3 - xy^2z$					

plane to be $z = 0$, the twelfth-order equation of Fig. 1 reduces to the following three fourth-order equations:

$$\begin{pmatrix} 1 & 0 & 0 & y^2 \\ 1 & 0 & x^2 & \\ 1 & -xy & & \\ & x^4 + y^4 + x^2y^2 & & \end{pmatrix} \begin{pmatrix} T_{11} \\ T_{22} \\ T_{12} \\ \omega_{33} \end{pmatrix} = \begin{pmatrix} U_{11} \\ U_{22} \\ U_{12} \\ y^2U_{11} + x^2U_{22} - xyU_{12} \end{pmatrix}, \quad (2.9)$$

$$\begin{pmatrix} 1 & y^2 & x^2 & -2xy \\ y^4 & x^2y^2 & -2xy^3 & \\ x^4 & -2x^3y & & \\ & 4x^2y^2 & & \end{pmatrix} \begin{pmatrix} T_{33} \\ \omega_{11} \\ \omega_{22} \\ \omega_{12} \end{pmatrix} = \begin{pmatrix} U_{33} \\ y^2U_{33} \\ x^2U_{33} \\ -2xyU_{33} \end{pmatrix}, \quad (2.10)$$

$$\begin{pmatrix} 1 & 0 & -x^2 & xy \\ 1 & xy & -y^2 & \\ x^4 + x^2y^2 & -xy^3 - x^3y & & \\ y^4 + x^2y^2 & & & \end{pmatrix} \begin{pmatrix} T_{23} \\ T_{13} \\ \omega_{23} \\ \omega_{13} \end{pmatrix} = \begin{pmatrix} U_{23} \\ U_{13} \\ -x^2U_{23} + xyU_{13} \\ xyU_{23} - y^2U_{13} \end{pmatrix}, \quad (2.11)$$

where again the matrix and right-hand side vector elements have to be summed over all atoms.

If further the molecule is symmetrical about the x and y axes (e.g. benzene or anthracene), these equations reduce still further to two third-order equations for $(T_{11}, T_{22}, \omega_{33})$ and $(T_{33}, \omega_{11}, \omega_{22})$, two second-order equations for (T_{23}, ω_{23}) and (T_{13}, ω_{13}) and two first-order equations for T_{12} and ω_{12} .

The accuracy of the determination of the T_{ij} and ω_{ij} may be estimated using the standard least-squares formula, namely

$$\sigma^2(A_p) = C_{pp}^{-1} \sigma^2(U), \quad (2.12)$$

where $\sigma^2(A_p)$ is the variance of one of the T_{ij} or ω_{ij} , C_{pp}^{-1} is the appropriate diagonal element of the matrix inverse to that on the left-hand side of the above equations, and $\sigma^2(U)$ is estimated as

$$\sigma^2(U) = \sum_n (U_n^{\text{obs.}} - U_n^{\text{calc.}})^2 / t,$$

where t is the difference between the total number of $U_{ij}^{\text{obs.}}$ and the number of parameters determined.

3. Discussion

Equations (2.9), (2.10) and (2.11) have been applied successfully in analyses of the molecular motions of

benzene (Cox, Cruickshank & Smith, 1956) and anthracene (Cruickshank, 1956b). Benzene, however, illustrates a possible difficulty. If there are only a few atoms in a molecule it may not be possible to determine all the T_{ij} and ω_{ij} uniquely. For instance, (2.10) shows that for a planar molecule four parameters are determined from the observed set of U_{33}^r . Accordingly at least four atoms are needed to determine these parameters; further, the atoms must not be equidistant from the centre. In general the minimum number of atoms for a complete solution is three, the atoms not being equidistant from the centre and their common plane not passing through it.

If the motions of a molecule can be successfully interpreted in terms of the \mathbf{T} and $\boldsymbol{\omega}$ tensors, it is often of great interest to find the magnitudes and directions of the principal axes of these tensors, as the molecular motions may then be interpreted in relation to the inertia tensor and to the intermolecular packing. Less interest then attaches to finding the principal axes of the vibrations of the individual atoms.

It is not possible to extend this kind of analysis to determine the internal vibrations of non-rigid molecules as the effects of the internal and rigid-body vibrations cannot be separated. For example, with a diatomic molecule it is impossible to determine how much of the motion of an atom along the interatomic line is due to rigid-body vibration and how much to the internal vibration. However, in special cases it may be possible to derive rough estimates of the vibration amplitudes of a small number of internal coordinates, e.g. if part of the molecule can be assumed rigid. On the other hand, if the magnitudes of the internal vibrations are known theoretically (Higgs, 1953), these may be subtracted from the total observed amplitudes to give the amplitudes of the rigid-body motions.

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