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Internal Molecular Vibrations from Crystal Diffraction Data by Quasinormal Mode Analysis

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Abstract

The established procedure for analyzing molecular vibrations in terms of normal modes has been adapted so that experimental anisotropic thermal parameters can be used to study low-frequency internal vibrations of simple molecules in crystals. This involves quasinormal modes, which are linear combinations of selected low-frequency internal modes such as the torsional librations about individual bonds. Higher-frequency modes are neglected, since their contribution to the atomic mean-square displacements should be small. The force constants for selected low-frequency internal modes, together with the tensor components (**T**, **L**, **S**) that describe the overall molecular vibration, become the variables in an iterative least-squares refinement in which the observations are the atomic U_{ij} values. As a result, the concerted motion of the atoms for each quasinormal mode is defined and also its vibrational frequency. Corrections to bond lengths and angles due to internal vibrations can be calculated. In tests involving two different lipid crystal structures, the internal motions were introduced as torsions about two or three bonds occurring near the junction of an extended hydrocarbon chain with a relatively rigid massive atomic grouping. Compared with the simple rigid-body model, there were highly significant improvements in agreement between experimental and calculated U_{ij} values. Force constants for torsion about three C–S bonds were also in agreement [26 (5), 23 (6) and 22 (6) J mol^{-1} deg^{-2}]. In one of the crystal structures (determined at 123 K), the six C–C bonds of a paraffin chain have average lengths 1·526 (2) Å before correction, 1·527 (3) Å after correction for simple rigid-body libration and 1·536 (4) Å after corrections including the quasinormal vibrations. The latter agrees with the electron diffraction value 1·542 (4) Å for *n*-hexadecane.

Introduction

In the analysis of molecular vibrations in terms of atomic anisotropic thermal parameters, a model must be introduced in order to define how the individual atomic motions are correlated with each other. The most widely used is the rigid-body model (Cruickshank, 1956; Schomaker & Trueblood, 1968). When internal modes of vibration are appreciable, they may be taken into account by assuming that the molecule consists of rigid segments with the segments in relative motion (Johnson, 1970; Dunitz & White, 1973). Usually, they are assumed to ride on each other (Busing & Levy, 1964), but otherwise to move in an uncorrelated way.

There are certain kinds of molecules that are not well suited to analysis with these models. They include molecules with semi-rigid fused-ring systems, such as cholesterol and other steroids, and lipids in which a lengthy hydrocarbon chain is attached to a bulky more rigid segment, such as the fatty-acid esters of cholesterol. Thus, it would be desirable to treat the vibrations of atoms along the lipid chain as being correlated in various ways that can be readily defined and tested against the diffraction results. With this aim, we have developed a general procedure based on the normal coordinate analysis of molecular vibrations (Wilson, Decius & Cross, 1955). It is assumed that molecules in the crystal are vibrating independently of each other. The internal motion of each molecule is described in terms of quasinormal modes. A quasinormal mode is defined as some linear combination of a small number of internal modes of vibration. A particular internal mode would typically be the torsional motion of the molecule about a selected covalent bond. The major simplifying approximation is the neglect of high-frequency internal modes such as framework bond stretching and bond-angle bending. These modes have large force constants and thus make only a small contribution to the mean-square (m.s.) atomic displacements. As a result of such simplification, the internal motion of the molecule can

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be defined in terms of only a few variables, consisting of a force constant for each of the selected internal bond torsions. These force constants, together with the **TLS** tensor components (Schomaker & Trueblood, 1968), which describe the external modes, can be determined by an iterative least-squares procedure in which the observations are the atomic anisotropic thermal parameters obtained from X-ray or neutron diffraction.

1. Quasinormal modes for internal motions

For molecules in crystals, Higgs (1955) was able to separate the kinetic energy vibration into independent parts, one arising from internal distortion, and the other from the rigid motion of the molecule. The potential energy was separated in a similar way, neglecting the influence of intermolecular interaction on the internal modes and also the correlations between internal distortion and rigid motion (Coriolis terms). Only the internal contributions are described here, since the treatment of the rigid motion follows that of Schomaker & Trueblood (1968).

The internal kinetic and potential energy may be given as

$$2T_{\text{int}} = \dot{\mathbf{y}}'\mathbf{G}^{-1}\dot{\mathbf{y}}$$

$$2V_{\text{int}} = \mathbf{y}'\mathbf{F}\mathbf{y},$$

where the vector $\mathbf{y}$ has $3n-6$ components, one for each of the internal modes for a non-linear molecule of n atoms. Examples of internal modes are bond stretching, bond-angle bending, an out-of-plane bond bending or a bond torsion. The vector $\mathbf{y}$ is obtained from the vector $\mathbf{x}$ of atomic displacements in a Cartesian axial system by the transformation

$$\mathbf{y} = \mathbf{b}\mathbf{x},$$

where the matrix $\mathbf{b}$ of order $(3n-6)\times 3n$ depends only on the molecular geometry and can be derived by a standardized procedure (Wilson, Decius & Cross, 1955). Wilson's kinetic energy matrix is given by

$$\mathbf{G} = \mathbf{b}\mathbf{M}^{-1}\mathbf{b}',$$

where $\mathbf{M}$ is a diagonal matrix of atomic masses ($M_{ij} = m_j\delta_{ij}$, where δ_{ij} is the Kronecker delta and $m_{3i-2} = m_{3i-1} = m_{3i}$), and $\mathbf{F}$ is the symmetric force constant matrix.

If the force constants have been determined, the secular equation

$$|\mathbf{GF} - \lambda\mathbf{I}| = 0$$

can be solved to give the frequencies of the normal modes of vibration and the relative contributions of all the internal modes to each normal mode.

The quasinormal modes of vibration are introduced as approximations by selecting a certain number k of the internal modes, which are presumed to be of low frequency, and then freezing the remainder. The vector $\mathbf{y}$ is arranged so that the k components for the selected modes occur at the end and the initial $(3n-6-k)$ components are constrained to be zero. Components of the matrices $\mathbf{b}$, $\mathbf{F}$ and $\mathbf{G}$ are arranged in a corresponding way. Thus the column vector $\mathbf{y}$ is written

$$\mathbf{y} = \begin{bmatrix} \mathbf{0} \\ \cdots \\ \mathbf{s} \end{bmatrix}$$

and the transformation matrix is partitioned to give

$$\mathbf{b} = \begin{bmatrix} \mathbf{b}_1 \\ \cdots \\ \mathbf{b}_2 \end{bmatrix}$$

where $\mathbf{0} = \mathbf{b}_1\mathbf{x}$ and $\mathbf{s} = \mathbf{b}_2\mathbf{x}$. The energy relationships for the quasinormal modes become

$$2T_{\text{int}} = \dot{\mathbf{s}}'\mathbf{G}_0^{-1}\dot{\mathbf{s}}$$

$$2V_{\text{int}} = \mathbf{s}'\mathbf{F}_0\mathbf{s},$$

where the matrices $\mathbf{F}_0$ and $\mathbf{G}_0^{-1}$ are of order $k\times k$. The matrix $\mathbf{F}_0$ is simply derived from $\mathbf{F}$ by deleting all but the last k rows and columns. Since $\mathbf{F}_0$ is symmetric it consists of $k(k+1)/2$ independent components f_{lm}. The matrix $\mathbf{G}_0^{-1}$ is obtained from $\mathbf{G}$ as described by Wilson, Decius & Cross (1955; see their Appendix IX).

Thus if the matrices $\mathbf{G}$ and $\mathbf{G}^{-1}$ are partitioned to obtain

$$\mathbf{G} = \begin{bmatrix} \mathbf{G}_{11} & \vdots & \mathbf{G}_{12} \\ \cdots & & \cdots \\ \mathbf{G}_{21} & \vdots & \mathbf{G}_{22} \end{bmatrix} \quad \text{and} \quad \mathbf{G}^{-1} = \begin{bmatrix} (\mathbf{G}^{-1})_{11} & \vdots & (\mathbf{G}^{-1})_{12} \\ \cdots & & \cdots \\ (\mathbf{G}^{-1})_{21} & \vdots & (\mathbf{G}^{-1})_{22} \end{bmatrix},$$

where $\mathbf{G}_{22}$ and $(\mathbf{G}^{-1})_{22}$ are of order $k\times k$, then $\mathbf{G}_0^{-1} = (\mathbf{G}^{-1})_{22}$ and $\mathbf{G}_0 = [(\mathbf{G}^{-1})_{22}]^{-1} = \mathbf{G}_{22} - \mathbf{G}_{21}(\mathbf{G}^{-1})_{11}\mathbf{G}_{12}$. The quasinormal modes are then described by the solutions of the modified secular equation

$$|\mathbf{G}_0\mathbf{F}_0 - \lambda\mathbf{I}| = 0.$$

These give the frequencies ω_i from the eigenvalues $\lambda_i = 4\pi^2c^2\omega_i^2$ and define the relative magnitudes of the vectors of internal ($\mathbf{s}$) and quasinormal ($\mathbf{Q}$) coordinates through the relationship $\mathbf{s} = \mathbf{LQ}$, where $\mathbf{L}$ is the matrix of the eigenvectors.

2. The mean-square amplitudes of the quasinormal modes

The time-averaged mean-square (m.s.) amplitudes of the quasinormal modes can be expressed as the diagonal matrix $\boldsymbol{\Sigma}^Q = \langle\mathbf{QQ}'\rangle$. In the harmonic approximation, the diagonal components are given by the quantum-mechanical relationship

$$\langle Q_iQ_i\rangle = \frac{h}{8\pi^2c\omega_i}\coth\left(\frac{hc\omega_i}{2kT}\right).$$

According to Cyvin (1968), the corresponding matrix for m.s. amplitudes in terms of the internal coordinates is

$$\begin{aligned}\boldsymbol{\Sigma}^{s} &= \langle \mathbf{ss}' \rangle = \mathbf{L}\langle \mathbf{QQ}' \rangle \mathbf{L}' \\ &= P_1\mathbf{F}_0^{-1} + P_2\mathbf{G}_0 + P_3\mathbf{G}_0\mathbf{F}_0\mathbf{G}_0 + P_4\mathbf{G}_0\mathbf{F}_0\mathbf{G}_0\mathbf{F}_0\mathbf{G}_0 + \ldots,\end{aligned} \tag{1}$$

where a power-series expansion has been introduced for the hyperbolic cotangent function (see also Appendix *A*). The factors P_1, P_2 *etc.* are found to be simply proportional to various powers of kT. Thus a system of equations is developed relating the m.s. amplitudes of selected internal modes with their corresponding force constants. However, the form of the power-series expansion for $\coth(x)/x$ must be carefully chosen in order to achieve an adequate approximation at the temperature and in the frequency range of interest. The approximation $\coth(x)/x = (1/x^2) + 1/4$ (Morino, Kuchitsu, Takahashi & Maeda, 1953) gives errors of less than 15% for $0{\cdot}05 < x < 2{\cdot}5$ corresponding to $T = 300$ K and $20 < \omega < 1050\ \text{cm}^{-1}$. We have chosen a four-term expansion with coefficients fitted by least squares having similar accuracy over a wider range $0{\cdot}05 < x < 10{\cdot}0$, corresponding to $T = 300$ K and $20 < \omega < 4200\ \text{cm}^{-1}$ or $T = 100$ K and $\omega < 1400\ \text{cm}^{-1}$ (He, 1984). The expression for $\boldsymbol{\Sigma}^s$ then consists of the first four terms in the expansion (1) with $P_1 = 1{\cdot}00021kT$, $P_2 = 2{\cdot}61124\,kT \times (h/4\pi kT)^2 \times 10^{-1}$, $P_3 = -2{\cdot}80087kT(h/4\pi kT)^4 \times 10^{-3}$ and $P_4 = 9{\cdot}42058kT(h/4\pi kT)^6 \times 10^{-6}$.

3. Refinement of force-constant parameters by least squares

The matrix $\boldsymbol{\Sigma}^x_{\text{int}}$ of m.s. amplitudes for the internal vibrations of the atoms in a Cartesian crystal axial system can be derived from the internal coordinates by the transformation

$$\boldsymbol{\Sigma}^x_{\text{int}} = \langle \mathbf{xx}' \rangle = \mathbf{a}\langle \mathbf{yy}' \rangle \mathbf{a}' = \mathbf{a}_2\langle \mathbf{ss}' \rangle \mathbf{a}_2', \tag{2}$$

where the matrix $\mathbf{a}$ is obtained by the unique transformation (Higgs, 1955)

$$\mathbf{a} = \mathbf{M}^{-1}\mathbf{b}'\mathbf{G}^{-1}. \tag{3}$$

The matrix $\mathbf{a}$ can then be partitioned so that the last k columns form the submatrix $\mathbf{a}_2$. It should be noted that since all except the last k components of the vector $\mathbf{y}$ have been constrained to zero value, some atoms may not be explicitly involved in the components of the vector $\mathbf{s}$. Nevertheless, information concerning the complete molecular structure is retained in $\mathbf{a}_2$, which is of order $3n \times k$. As a result of the transformation (2), the matrix $\boldsymbol{\Sigma}^x_{\text{int}}$ is symmetric of order $3n \times 3n$, which is consistent with the participation of all n atoms of the molecule in the internal vibrations.

When the additivity of m.s. amplitudes from internal and external modes of vibration is assumed (Higgs, 1955), the resultant m.s. amplitude matrix becomes

$$\boldsymbol{\Sigma}^x = \boldsymbol{\Sigma}^x_{\text{int}} + \boldsymbol{\Sigma}^x_{\text{ext}},$$

where $\boldsymbol{\Sigma}^x_{\text{ext}}$ is expressed in terms of the **T**, **L**, **S** tensors for rigid-body motion (Schomaker & Trueblood, 1968) and $\boldsymbol{\Sigma}^x_{\text{int}}$ is obtained from (2) with substitution of $\langle \mathbf{ss}' \rangle$ from (1). The anisotropic thermal parameters U_{ij} from a crystal structure determination lead to estimates of $6n$ independent components of the symmtric matrix $\boldsymbol{\Sigma}^x$. They belong in the 3×3 blocks along the diagonal. From these estimates and the corresponding components of $\boldsymbol{\Sigma}^x$, $6n$ observational equations can be derived in which the variables will in general consist of the 20 independent **TLS** components and the $k(k+1)/2$ independent components f_{lm} of the force-constant matrix, $\mathbf{F}_0$. The number of variables can be further reduced by the approximation wherein a simple form is assumed for the matrix $\mathbf{F}_0$. For a stable molecule, $\mathbf{F}_0$ should be positive definite. The off-diagonal terms express interactions between the internal deformations and are usually small compared with diagonal terms. By considering only nearest-neighbor interactions, the number of independent force constants becomes $(2k-1)$, and by neglecting all interactions, as we have done so far, the number becomes k. Thus, relatively few additional variables may be required in order to describe the internal molecular vibrations in terms of quasinormal modes. These variables can be determined by an extension of the least-squares procedure already formulated for the simple rigid-body model. The necessary derivatives of $\boldsymbol{\Sigma}^x_{\text{ext}}$ with respect to **T**, **L**, **S** components have been given by Schomaker & Trueblood (1968). Only the derivatives of $\boldsymbol{\Sigma}^x_{\text{int}}$ with respect to f_{lm} components are considered here.

If we write $\mathbf{F}_0 = [\mathbf{f}_{ij}]$, then

$$\partial \mathbf{F}_0 / \partial f_{lm} = [\partial \mathbf{f}_{ij} / \partial f_{lm}] = \mathbf{F}_{lm},$$

where

$$\begin{aligned}\partial f_{ij}/\partial f_{lm} &= \delta_{ij,lm} + \delta_{ji,ln} &&\text{for } l \neq m\\ &\ \delta_{ij,lm} &&\text{for } l = m.\end{aligned}$$

With relationships from Appendix *B*,*

$$\begin{aligned}\partial \boldsymbol{\Sigma}^s / \partial f_{lm} = {}& -P_1\mathbf{F}_0^{-1}\mathbf{F}_{lm}\mathbf{F}_0^{-1} + P_3\mathbf{G}_0\mathbf{F}_{lm}\mathbf{G}_0 \\ &+ P_4\{[\mathbf{G}_0\mathbf{F}_{lm}\mathbf{G}_0\mathbf{F}_0\mathbf{G}_0] + [\mathbf{G}_0\mathbf{F}_{lm}\mathbf{G}_0\mathbf{F}_0\mathbf{G}_0]'\}.\end{aligned} \tag{4}$$

Hence, in the Cartesian axial system,

$$\partial \boldsymbol{\Sigma}^x_{\text{int}} / \partial f_{lm} = \mathbf{a}_2[\partial \boldsymbol{\Sigma}^s / \partial f_{lm}]\mathbf{a}_2'.$$

Because the observational equations are non-linear with respect to f_{lm}, an iterative least-squares refinement is necessary. Reasonable starting values for f_{lm} must be assigned.

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* Note the prime in (4) indicating that the last term is transposed.

Our strategy has been to define a diagonal force constant matrix on the basis of physical intuition and then to optimize the force constants by stepwise regression. If a force constant is found to be insignificantly different from zero in terms of its e.s.d., it is deleteted from the assumed model.* Experience has shown this procedure to be robust. In both test cases described below, convergence was reached in less than ten cycles, assuming the initial values for all force constants to be $f_{ll} = 25\ \mathrm{J\,mol^{-1}\,deg^{-2}}$.

A full-matrix least-squares procedure is used to minimize the residual $\Sigma_k w_k \Delta_k^2$, where $\Delta_k = [(U_{ij})_o - (U_{ij})_c]_k$, in which $(U_{ij})_o$ is the value for an anisotropic thermal parameter for the kth atom derived from the crystal structure refinement and $(U_{ij})_c$ is the corresponding value calculated for the assumed molecular motion. These thermal parameters are referred to a Cartesian crystal axial system. The weights w_k are obtained from the mean variances in $(U_{ij})_o$ for the kth atom.

It is expected that a quasinormal mode analysis will be feasible for molecules with fifty atoms or more, but with increasing computational limitations. Although the $\mathbf{G}_0$ matrix may be small, it must be derived from other matrices of order approximately $3n \times 3n$, where n is the number of atoms.

4. Correction of bond lengths and angles for internal vibrations

The bond length and angle corrections due to the external and internal motions are additive. The external-motion corrections are treated in the same way as for simple rigid-body motion (Johnson & Levy, 1974) and will not be described here.

For the internal-motion corrections, it is important to note that all components in the m.s. amplitude matrix $\mathbf{\Sigma}^{x}_{\mathrm{int}}$ can be calculated in terms of the quasinormal vibrational model using (2) and (3). Thus, while values of the force constants may have been determined only from observations corresponding to the 3×3 block-diagonal components of $\mathbf{\Sigma}^{x}_{\mathrm{int}}$, the model allows the calculation of the remaining components, which describe the correlated internal motion of all pairs of atoms in the molecule.

Following Busing & Levy (1964) and Johnson (1970), the corrected bond length $\langle d_{ij} \rangle$ between atoms i and j is given by

$$\langle d_{ij} \rangle = d_{ij}^0 + \Delta / 2 d_{ij}^0,$$

where d_{ij}^0 is the uncorrected value and Δ is the m.s. relative displacement of atoms i and j in the plane normal to the bond. If x_ix_i, y_iy_i, z_iz_i are the diagonal components of $\mathbf{\Sigma}^{x}_{\mathrm{int}}$ corresponding to the ith atom and x_ix_j, y_iy_j and z_iz_j *etc.* are off-diagonal terms which couple the ith and jth atoms, then

$$\begin{aligned}\Delta = {} & \sin^2 \gamma_x (x_ix_i + x_jx_j - 2x_ix_j) \\ & + 2 \cos \gamma_x \cos \gamma_y (x_iy_j + x_jy_i - x_iy_i - x_jy_j) \\ & + \sin^2 \gamma_y (y_iy_i + y_jy_j - 2y_iy_j) \\ & + 2 \cos \gamma_y \cos \gamma_z (y_iz_j + y_jz_i - y_iz_i - y_jz_j) \\ & + \sin^2 \gamma_z (z_iz_i + z_jz_j - 2z_iz_j) \\ & + 2 \cos \gamma_z \cos \gamma_x (z_ix_j + z_jx_i - z_ix_i - z_jx_j),\end{aligned}$$

where $(\cos \gamma_x, \cos \gamma_y, \cos \gamma_z)$ are the direction cosines of the bond with respect to the Cartesian crystal axial system.

The corrections to bond angles due to the internal vibrations are also obtained from $\mathbf{\Sigma}^{x}_{\mathrm{int}}$, as described by Scheringer (1978). The lengthy equations are not reproduced here.

5. Applications

Quasinormal mode analyses have been carried out for two lipid crystal structures that involve molecules with an extended paraffin chain joined to a residue with relatively greater rigidity and inertia (Figs. 1, 2). Since the structures were determined by X-ray diffraction, the H-atom temperature factors are relatively inaccurate. Thus, the effect of the H atoms on the molecular vibrations has been neglected. Anisotropic thermal parameters for the other atoms indicate that

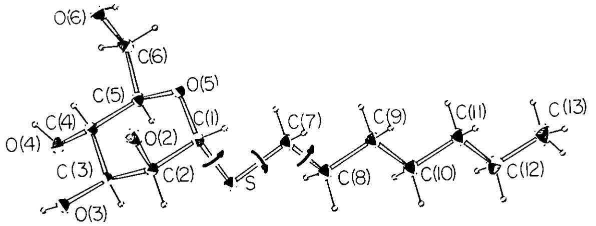

Fig. 1. Molecular structure of heptyl 1-thio-α-D-mannopyranoside (HTM) at 123 K (Carter, Ruble & Jeffrey, 1982). Thermal ellipsoids are at the 50% probability level. Arrows indicate the bonds where there are significant internal torsional librations.

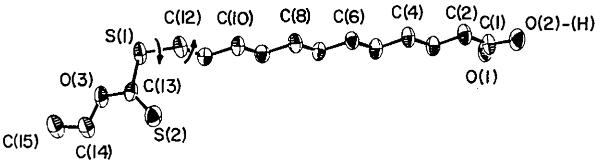

Fig. 2. Molecular structure of *O*-ethyl *S*-(11-carboxyundecyl)-dithiocarbonate (ECT) at room temperature (Abrahamsson & Pearson, 1976). Thermal ellipsoids are at the 50% probability level. The H atoms (except in the carboxylic acid group) were found in difference Fourier maps, but they are not shown here. Arrows indicate bonds involved in internal torsional librations.

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* Initial calculations have been carried out with the minimum necessary modification of a computer program (Craven & He, 1983) for thermal-motion analysis by the method of Dunitz & White (1973). Improvement might come from using the statistical technique of regression on principal components (Massy, 1965; Kendall & Stuart, 1966; Scheringer, 1968).

Table 1. *Molecular thermal motion parameters*

(*a*) *External vibrations*

Components and principal values of the translational (T) and librational (L) tensors are in units Å$^2 \times 10^4$ and deg^2. The cross tensor (S) is in units deg Å $\times 10^3$. Tensor components are with respect to the Cartesian crystal axes **a**, **c*** × **a**, **c***. Results for the three models are (i) simple rigid body, (ii) uncorrelated internal motions (Dunitz & White, 1973), (iii) internal motion from quasinormal modes.

	HTM (123 K)			ECT (294 K)		
	(i)	(ii)	(iii)	(i)	(ii)	(iii)
T_{11}	125 (7)	118 (6)	116 (6)	503 (21)	566 (24)	445 (21)
T_{22}	198 (8)	224 (7)	101 (14)	554 (39)	574 (37)	526 (37)
T_{33}	140 (6)	139 (5)	143 (5)	584 (30)	859 (72)	491 (33)
T_{12}	−15 (7)	−3 (6)	−3 (6)	146 (24)	206 (26)	123 (23)
T_{13}	18 (6)	12 (5)	9 (5)	−100 (23)	−262 (48)	−50 (23)
T_{23}	−12 (6)	−2 (6)	−26 (6)	−130 (31)	−314 (54)	−77 (29)
T_1	112	112	90	381	359	356
T_2	145	144	114	474	415	442
T_3	205	224	157	806	1226	664
L_{11}	2·3 (5)	3·0 (5)	0·2 (5)	18·3 (39)	27·0 (42)	11·0 (37)
L_{22}	0·9 (1)	0·9 (1)	0·8 (1)	1·1 (4)	6·6 (15)	0·5 (4)
L_{33}	0·4 (6)	1·8 (6)	1·7 (5)	9·9 (19)	10·2 (18)	7·2 (17)
L_{12}	0·1 (4)	0·2 (3)	0·3 (3)	−4·4 (11)	−11·8 (21)	−1·5 (12)
L_{13}	1·1 (4)	−0·7 (5)	−0·2 (4)	12·3 (26)	13·7 (25)	7·9 (24)
L_{23}	0·1 (4)	−0·2 (3)	0·3 (3)	−3·3 (8)	−5·0 (9)	−1·4 (8)
L_1	−0·1	0·9	0·9	−0·2	0·8	0·2
L_2	0·9	1·6	1·0	1·1	3·5	1·0
L_3	2·7	3·3	1·7	30·1	39·6	17·4
S_1	−2 (30)	−21 (26)	−5 (24)	13 (83)	−377 (136)	101 (77)
S_{12}	−93 (14)	−140 (15)	37 (20)	−13 (73)	−373 (113)	86 (67)
S_{13}	−6 (14)	−19 (12)	−23 (11)	222 (58)	629 (111)	193 (52)
S_{21}	8 (7)	11 (6)	14 (6)	−1 (21)	232 (64)	−37 (20)
S_{22}	−11 (21)	−18 (18)	11 (17)	64 (50)	218 (69)	−114 (44)
S_{23}	−1 (7)	−1 (6)	2 (5)	−124 (19)	−500 (97)	−101 (17)
S_{31}	27 (19)	18 (16)	20 (15)	−57 (44)	−203 (52)	14 (41)
S_{32}	−59 (17)	55 (26)	8 (17)	−72 (49)	−182 (53)	−3 (46)
S_{33}	14	38	7	51	159	13

(*b*) *Internal molecular librations*

Values are (ii) m.s. amplitudes of libration (deg^2) (Dunitz & White, 1973) and (iii) force constants for bond torsion (J mol^{-1} deg^2). For model (ii), internal librations are with respect to the rigid pyranoside group for HTM and the ethyldithiocarbonate group for ECT.

HTM (123 K)			ECT (294 K)		
	(ii)	(iii)		(ii)	(iii)
C(2)-C(1)-S-C(7)	−9·3 (17)	26 (5)	C(13)-S(1)-C(12)-C(11)	−16 (4)	22 (6)
C(1)-S-C(7)-C(8)	−3·5 (17)	23 (6)	S(1)-C(12)-C(11)-C(10)	−42 (30)	10 (3)
S-C(7)-C(8)-C(9)	+11·6 (27)	9 (2)			

both molecular frameworks are vibrating non-rigidly. Thus there are several significantly non-zero values for $\Delta_{AB} = \langle u_A^2 \rangle - \langle u_B^2 \rangle$, where m.s. displacements are calculated for atoms A and B along the direction of the intramolecular vector $A \cdots B$ (Hirshfeld, 1976).

(*a*) *Heptyl* 1-*thio-α-*D*-mannopyranoside* (*HTM*) *at* 123 K

The crystal structure (space group $P2_12_12_1$) was determined from diffractometer data collected with $\theta/2\theta$ scans using graphite-monochromated Mo $K\alpha$ radiation and was refined to give $R = 0{\cdot}03$ (Carter, Ruble & Jeffrey, 1982). Analysis of the molecular vibrations assuming simple rigid-body motion gave $R_w = [\Sigma w_k \Delta_k^2 / \Sigma w_k (U_{ij})_o^2]^{1/2} = 0{\cdot}155$ and $s = [\Sigma w_k \Delta_k^2/(n-m)]^{1/2} = 4{\cdot}00$, where $n = 114$, the number of observations, and $m = 20$, the number of variables. Non-rigid behavior was indicated by highly significant values of Δ_{AB} for atoms at the opposite ends of the extended chains, such as 0·0164 Å^2 (14σ) for S···C(13), 0·0153 Å^2 (12σ) for C(4)···C(13). The model for the molecular motion was then extended to include quasinormal vibrations. Initially, eight force constants were introduced for torsional vibrations about the bond C(5)-C(6) in the carbohydrate residue, and for all the bonds C(1)-S through C(11)-C(12) in the extended chain (Fig. 1). The matrix $\mathbf{F}_0$ was assumed to have diagonal form. After least-squares refinement, only the force constants for torsions about the three bonds in the region of the ring-to-chain junction, C(1)-S, S-C(7), C(7)-C(8), were found to be significantly different from zero in terms of the corresponding e.s.d.'s. With the internal motion described in terms of these three force constants, the least-squares refinement converged giving

Table 2. *Bond lengths* (Å) *and angles* (°) *with thermal-motion corrections.*

Corrected values below are from the model with quasinormal modes.

(*a*) *HTM at* 123 K

Values for the pyranoside moiety are not given since corrections are small (<0·001 Å, 0·1°) for all three models used to describe the molecular thermal motion.

	Uncorrected	Corrected		Uncorrected	Corrected
C(1)-S	1·824 (2)	1·826 (2)	C(1)-S-C(7)	98·0 (1)	97·9 (1)
S-C(7)	1·818 (2)	1·825 (2)	S-C(7)-C(8)	110·2 (1)	109·9 (1)
C(7)-C(8)	1·526 (3)	1·533 (3)	C(7)-C(8)-C(9)	111·1 (1)	110·3 (1)
C(8)-C(9)	1·528 (3)	1·541 (3)	C(8)-C(9)-C(10)	113·0 (2)	111·8 (2)
C(9)-C(10)	1·530 (3)	1·540 (3)	C(9)-C(10)-C(11)	112·8 (2)	111·7 (2)
C(10)-C(11)	1·524 (3)	1·535 (3)	C(10)-C(11)-C(12)	112·9 (2)	111·6 (2)
C(11)-C(12)	1·524 (3)	1·536 (3)	C(11)-C(12)-C(13)	113·1 (2)	112·0 (2)
C(12)-C(13)	1·525 (3)	1·532 (3)			

(*b*) *ECT at* 294 K

E.s.d.'s in corrected values are the same as for the corresponding uncorrected values.

	Uncorrected	Corrected		Uncorrected	Corrected
C(1)-O(2)	1·296 (8)	1·308	O(1)=C(1)-O(2)	123·6 (4)	124·1
C(1)=O(1)	1·215 (8)	1·226	C(2)-C(1)=O(1)	123·3 (5)	123·6
C(1)-C(2)	1·494 (8)	1·502	C(2)-C(1)-O(2)	113·0 (5)	111·8
C(2)-C(3)	1·495 (10)	1·506	C(1)-C(2)-C(3)	116·4 (6)	115·2
C(3)-C(4)	1·517 (10)	1·527	C(2)-C(3)-C(4)	112·8 (6)	111·6
C(4)-C(5)	1·510 (10)	1·521	C(3)-C(4)-C(5)	115·6 (6)	114·4
C(5)-C(6)	1·505 (10)	1·515	C(4)-C(5)-C(6)	113·7 (6)	112·6
C(6)-C(7)	1·513 (10)	1·523	C(5)-C(6)-C(7)	115·6 (6)	114·4
C(7)-C(8)	1·504 (10)	1·514	C(6)-C(7)-C(8)	114·7 (6)	113·6
C(8)-C(9)	1·514 (10)	1·526	C(7)-C(8)-C(9)	114·8 (6)	113·6
C(9)-C(10)	1·503 (10)	1·512	C(8)-C(9)-C(10)	114·9 (6)	113·8
C(10)-C(11)	1·510 (10)	1·525	C(9)-(C(10)-C(11)	113·8 (6)	112·6
C(11)-C(12)	1·507 (10)	1·513	C(10)-C(11)-C(12)	113·2 (6)	112·4
C(12)-S(1)	1·805 (6)	1·808	C(11)-C(12)-S(1)	114·6 (6)	114·3
S(1)-C(13)	1·736 (6)	1·745	C(12)-S(1)-C(13)	104·6 (3)	104·5
C(13)-O(3)	1·331 (8)	1·334	S(1)-C(13)-O(3)	105·7 (4)	105·6
C(13)=S(2)	1·626 (6)	1·632	S(1)-C(13)=S(2)	127·8 (3)	127·6
O(3)-C(14)	1·466 (8)	1·471	O(3)-C(13)=S(2)	126·5 (4)	126·4
C(14)-C(15)	1·492 (10)	1·496	C(13)-O(3)-C(14)	119·1 (5)	118·9
			O(3)-C(14)-C(15)	105·1 (5)	105·0

$R_w = 0{\cdot}122$ and $s = 3{\cdot}19$. A statistical F test indicates an improvement over the simple rigid-body model, which can be accepted at a confidence level greater than 99%. A model of the type proposed by Dunitz & White (1973) was also tested. The internal motion was described as torsional librations about the same three bonds. However, in this model, the vibrations of the rigid segments of the molecule are assumed to be uncorrelated. Values for the agreement indices $R_w = 0{\cdot}128$ and $s = 3{\cdot}36$ are intermediate between those of the other models. Molecular parameters for all three models are in Table 1.

(*b*) *O-Ethyl S-*(11*-carboxyundecyl*) *dithiocarbonate* (*ECT*)

This crystal structure (space group $P\bar{1}$) was determined from ten-point $\theta/2\theta$ step-scan diffractometer data collected at room temperature using graphite-monochromated Cu $K\alpha$ radiation (Abrahamsson & Pearson, 1976). Structure refinement gave $R = 0{\cdot}065$. The molecule (Fig. 2) is extended except for a twist (torsion angle 89°) at the C(12)-S(1) bond, which joins the paraffin chain and the dithiocarbonate group. Non-rigid vibrations of the molecular framework are indicated by significant Δ_{AB} values such as 0·024 Å^2 (8σ) for O(1)···S(2), 0·030 Å^2 (10σ) for O(2)···S(1) and 0·029 Å^2 (7σ) for C(1)···S(2).

A simple rigid-body model for the molecular vibrations gave $R_w = 0{\cdot}144$ and $s = 2{\cdot}98$. Inclusion of quasinormal modes involving torsion about the bonds S(1)-C(12) and C(12)-C(11) gave $R_w = 0{\cdot}126$ and $s = 2{\cdot}34$, this improvement being significant at a confidence level greater than 99%. The Dunitz & White model with torsional librations about the same two bonds gave $R_w = 0{\cdot}132$ and $s = 2{\cdot}76$. In this case, only the torsion about the S(1)-C(12) bond has a significant m.s. amplitude. Molecular parameters for all three models are in Table 1.

Discussion

The internal vibrations of both HTM and ECT have been analyzed in terms of highly simplified sets of quasinormal modes. In each structure, the molecule is treated as two rigid segements joined by a flexible region with motion involving correlated torsions about two (ECT) or three (HTM) bonds. If there are appreciable contributions to the atomic vibrational amplitudes due to the many other internal modes, their expression is collective. To some extent, these other modes are likely to be accounted for in the molecular **T**, **L** and **S** parameters.

In Table 1, results from this model (iii) are also compared with those assuming (i) simple rigid-body motion, and (ii) a segmented body model in which the segments ride on each other but otherwise vibrate in an uncorrelated way (Dunitz & White, 1973). It can be seen that many **T**, **L** and **S** components are significantly different in the three models. Compared with the values for the simple rigid-body model, magnitudes of the **T**, **L** and **S** components tend to be larger for model (ii) and smaller for model (iii). The effect can also be seen in the magnitudes of the principal values for **T** and **L**. For model (ii) the m.s. amplitudes for the internal librations are negative except for the torsion about one bond (Table 1*b*). In physical terms, it appears that the introduction of internal motion according to the Dunitz & White model leads to a slight enhancement of the overall rigid-body vibrations, which is largely offset by dampening due to the internal motion. In model (iii), the introduction of quasinormal modes has the opposite effect. Contributions to the atomic m.s. displacements from rigid-body motion are reduced when a part of the motion is interpreted as being internal. In HTM, model (iii) gives rise to a highly significant reduction in T_{22}, which is translational motion in a direction almost normal to the plane of the zigzag paraffin chain (Fig. 3; Carter *et al.*, 1982). This result seems reasonable since the atomic displacements due to internal torsional motion in the chain should be greatest in this direction.

Bond lengths and angles before and after corrections due to molecular libration and quasinormal vibrations are in Table 2. Corrections assuming models (i) and (ii) are not given since they are all small. Thus for the six C–C bonds in the HTM paraffin chain, uncorrected distances range from 1·524 to 1·530 Å with average value 1·526 (2) Å. After corrections according to models (i) and (ii), the average in both cases increases to 1·527 (3) Å. Similar small increases are obtained for ECT. The corrections for the quasinormal vibrations are considerably greater, giving an average C–C distance of 1·536 (4) Å for the HTM chain, in good agreement with the value 1·542 (4) Å obtained by electron diffraction from gaseous *n*-hexadecane (Fitzwater & Bartell, 1976). For ECT, the ten C–C bond lengths for atoms C(2) through C(12) have an average value 1·508 (6) Å before correction and 1·518 (7) Å after corrections including the effects of quasinormal vibrations. Although these corrections are appreciable, they appear to be underestimated, indicating that the model may have greater limitations in the case of ECT. However, because the ECT X-ray data were collected at room temperature, atomic m.s. displacements are much larger than for HTM and were not as accurately determined. It should be noted that the two uncorrected C–S bond lengths in HTM may be slightly different (2·6σ). The difference is not affected by corrections assuming models (i) and (ii), but with model (iii) these bond lengths become effectively the same (1·826, 1·825 Å).

For HTM and ECT, there is good agreement among the force constants determined for the torsion about the three S–C bonds (average value 24 J mol^{-1} deg^{-2}) and also the adjacent C–C bonds (10 J mol^{-1} deg^{-2}). Using diffraction data from more than 125 crystal structures, Trueblood & Dunitz (1983) have estimated force constants for torsions of small librating groups about various kinds of bonds. The force constants obtained for HTM and ECT are small but they fall within the range of values reported by Trueblood & Dunitz.

An important aspect of the quasinormal vibration model is that it leads to a description of the concerted motions of molecular subunits and also to estimates of the frequencies for these modes. For HTM, these frequencies are 51, 82 and 117 cm^{-1}. Although each quasinormal mode is a combination of three internal torsional modes, the principal component in the lowest-frequency vibration (51 cm^{-1}) is a torsion about S–C(1). The next (82 cm^{-1}) consists mainly of torsion about S–C(7), while the third (117 cm^{-1}) has important contributions from torsions about both S–C bonds and also from torsion about C(7)–C(8). For ECT, the model involves only two quasinormal modes, which have frequencies 49 and 59 cm^{-1}. The lower-frequency mode is mainly a torsion about the S(1)–C(12) bond.

In principle, such frequencies that have been derived from Bragg diffraction data may be compared with values derived from infrared or Raman spectra or from neutron inelastic scattering. Unfortunately, such data are not available for HTM or ECT.

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APPENDIX *A*

The derivation of m.s. amplitude matrices

The mean-square amplitude matrix in a normal coordinate system is a diagonal matrix $\boldsymbol{\Sigma}^{\mathbf{Q}}$,

$$\boldsymbol{\Sigma}^{\mathbf{Q}} = \langle \mathbf{Q}\mathbf{Q}' \rangle$$

with

$$\langle Q_i Q_i \rangle = \frac{h}{8\pi^2 c\omega_i} \coth \frac{hc\omega_i}{2kT}.$$

We assume the approximation

$$\coth(x)/x \simeq p_1 x^{-2} + p_2 + p_3 x^2 + p_4 x^4$$

with coefficients $p_1 = 1{\cdot}00021$, $p_2 = 2{\cdot}61124 \times 10^{-1}$, $p_3 = -2{\cdot}80087 \times 10^{-3}$ and $p_4 = 9{\cdot}42058 \times 10^{-6}$ determined by least-squares fitting in the range $0{\cdot}05 < x < 10{\cdot}0$ (He, 1984). Then with $\lambda_i = 4\pi^2 c^2 \omega_i^2$, we have

$$\langle Q_i Q_i \rangle = kT\left\{p_1 \lambda_i^{-1} + p_2\left(\frac{h}{4\pi kT}\right)^2 + p_3\left(\frac{h}{4\pi kT}\right)^4 \lambda_i + p_4\left(\frac{h}{4\pi kT}\right)^6 \lambda_i^2\right\}$$

or, in matrix form,

$$\begin{aligned}\boldsymbol{\Sigma}^{\mathbf{Q}} &= \langle \mathbf{QQ}' \rangle \\ &= kT\left\{p_1 \boldsymbol{\Lambda}^{-1} + p_2\left(\frac{h}{4\pi kT}\right)^2 \mathbf{I} + p_3\left(\frac{h}{4\pi kT}\right)^4 \boldsymbol{\Lambda} + p_4\left(\frac{h}{4\pi kT}\right)^6 \boldsymbol{\Lambda}^2\right\}. \qquad (A.1)\end{aligned}$$

Transformation back to internal coordinates gives

$$\begin{aligned}\boldsymbol{\Sigma}^{s} &= \mathbf{L}\boldsymbol{\Sigma}^{\mathbf{Q}}\mathbf{L}' \\ &= kT\left\{p_1 \mathbf{L}\boldsymbol{\Lambda}^{-1}\mathbf{L}' + p_2\left(\frac{h}{4\pi kT}\right)^2 \mathbf{LIL}' + p_3\left(\frac{h}{4\pi kT}\right)^4 \mathbf{L}\boldsymbol{\Lambda}\mathbf{L}' + p_4\left(\frac{h}{4\pi kT}\right)^6 \mathbf{L}\boldsymbol{\Lambda}^2\mathbf{L}'\right\}. \qquad (A.2)\end{aligned}$$

By recognizing that

$$\begin{gathered}\mathbf{L}\boldsymbol{\Lambda}^{-1}\mathbf{L}' = \mathbf{F}_0^{-1} \\ \mathbf{LIL}' = \mathbf{LL}' = \mathbf{G}_0 \\ \mathbf{L}\boldsymbol{\Lambda}^n\mathbf{L}' = (\mathbf{G}_0\mathbf{F}_0)^n\mathbf{G}_0,\end{gathered}$$

we find that (A.2) reduces to

$$\begin{aligned}\boldsymbol{\Sigma}^{s} = kT\Bigg\{&p_1 \mathbf{F}_0^{-1} + p_2\left(\frac{h}{4\pi kT}\right)^2 \mathbf{G}_0 \\ &+ p_3\left(\frac{h}{4\pi kT}\right)^4 \mathbf{G}_0\mathbf{F}_0\mathbf{G}_0 \\ &+ p_4\left(\frac{h}{4\pi kT}\right)^6 \mathbf{G}_0\mathbf{F}_0\mathbf{G}_0\mathbf{F}_0\mathbf{G}_0\Bigg\}. \qquad (A.3)\end{aligned}$$

With $P_1 = kTp_1$, $P_2 = kT(h/4\pi kT)^2 p_2$ *etc.*, this immediately leads to (1).

APPENDIX *B*

Matrix differentiation

The following rules for matrix differentiation are frequently used:

$$\begin{gathered}\frac{\partial}{\partial v_{ij}}[\mathbf{AX}] = \mathbf{A}\left[\frac{\partial}{\partial v_{ij}}\mathbf{X}\right] \\ \frac{\partial}{\partial v_{ij}}[\mathbf{XY}] = \left[\frac{\partial}{\partial v_{ij}}\mathbf{X}\right]\mathbf{Y} + \mathbf{X}\left[\frac{\partial}{\partial v_{ij}}\mathbf{Y}\right] \\ \frac{\partial}{\partial v_{ij}}\mathbf{X}^{-1} = \mathbf{X}^{-1}\left[\frac{\partial}{\partial v_{ij}}\mathbf{X}\right]\mathbf{X}^{-1},\end{gathered}$$

where $\mathbf{A}$ is a matrix with constant elements, $\mathbf{X}$ and $\mathbf{Y}$ are matrices with variable elements, v_{ij}.

Since $\mathbf{G}_0$ is a constant matrix and $\mathbf{F}_0$ is a variable matrix it is trivial to derive (4).

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