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On the Contributions of the Internal Modes of Molecules to the Debye–Waller Factors. II. Theoretical Considerations

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Abstract

It is shown that the expressions for the contributions of the internal modes of molecules to the Debye–Waller factors as derived, on the one hand, by means of lattice dynamics and, on the other hand, by means of the **FG** method common in spectroscopy, are identical after some approximations have been made in the lattice dynamical formulation. It is pointed out that for those methods of establishing the force constant matrix of the internal modes, where the eigenvalues of the **FG** matrix are constrained to be the squares of the observed frequencies, only standard eigenvector routines need be applied in determining the mean-square-amplitude matrix. Hence, in this case, series expansions which were suggested to circumvent the determination of eigenvalues are superfluous.

1. Introduction

The calculation of the contributions of the internal modes of molecules to the Debye–Waller factors should follow a theory of the crystal (lattice dynamics), but, as a rule, crystallographers adopt the **FG** method which was established in spectroscopy and refers to isolated molecules. If one starts from the equations of lattice dynamics and eliminates the typical (intermolecular) crystal effects, the equations of lattice dynamics should become equivalent with those of the **FG** matrix formalism. This equivalence, which is not obvious, will be proved in this paper.

In a further part of the paper, we show how the formalism of the **FG** method can be simplified by introducing standard eigenvector routines. The mean-square-amplitude matrix of the internal modes of the molecules then can often be obtained in a simple fashion, and the series expansions proposed (Cyvin, 1968; Øystein, 1972) are superfluous.

2. The lattice dynamical approach

Here we make use of the description which was developed in earlier work (Scheringer, 1972*a*,*b*). The $3n \times 3n$ mean-square-amplitude matrix $\mathbf{U}$ of the n atoms in the unit cell is given by

$$\mathbf{U} = N^{-1}\,\mathbf{Q} \sum_{\mathbf{q}} (\mathbf{R}\boldsymbol{\Lambda}^{-1}\boldsymbol{\Gamma}\tilde{\mathbf{R}})_{\mathbf{q}}\,\mathbf{Q}^{T}. \qquad (1)$$

The superscript T denotes the transposed matrix, -1 the inverse, and $\sim$ the conjugate complex transposed matrix. N is the number of cells in the crystal, $\mathbf{Q}$ a $3n \times 3n$ diagonal matrix, with the 3 elements $m_r^{-1/2}$ for the rth atom (m_r = mass). $\boldsymbol{\Lambda}(\mathbf{q})$ is a $3n \times 3n$ diagonal matrix containing, as elements, the squares of the frequencies $\omega_j(\mathbf{q})$. $\mathbf{q}$ denotes a wave vector of the

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crystal. $\mathbf{R}(\mathbf{q})$ are unitary matrices containing the eigenvectors of the mass-normalized dynamical matrices $\mathbf{M}(\mathbf{q})$, *i.e.*

$$\mathbf{M} = \mathbf{R}\mathbf{\Lambda}\tilde{\mathbf{R}}, \tag{2}$$

for all $\mathbf{q}$. $\mathbf{\Gamma}(\mathbf{q})$ in (1) is a $3n \times 3n$ diagonal matrix, and its elements are the mean thermal energies of the normal modes. We define the diagonal matrix $\mathbf{\Delta} = \mathbf{\Lambda}^{-1}\,\mathbf{\Gamma}$ with the elements

$$\Delta_j(\mathbf{q}) = \frac{\hbar}{2\omega_j(\mathbf{q})}\coth\left(\frac{\hbar\omega_j(\mathbf{q})}{2k_B T}\right), \tag{3}$$

where T is the temperature, and k_B Boltzmann's constant. To obtain the mean-square amplitudes of the internal modes from (1), we make the following assumptions: (1) the internal and external modes of the molecules are uncoupled, (2) the dispersion of the internal-mode branches in the crystal can be neglected, (3) the hybridization of the internal modes of the isolated molecules, which occurs in the crystal branches, does not alter the mean-square amplitudes of the atoms (Scheringer, 1972*b*; Venkataraman, Feldkamp & Sahni, 1975, p. 92). None of the assumptions holds rigorously. For high frequencies (1) and (2) are reasonably valid, but for frequencies ≤ 200 cm^{-1}, coupling between internal and external modes is likely to occur. Similarly, for the low-frequency branches, neglect of dispersion cannot be assumed, see the calculations presented by Decius & Hexter (1977, Fig. 6-8). Hybridization of the internal modes of the isolated molecules always occurs to some extent when a crystal is formed. However, since the atomic displacements are obtained by summing over the contributions from all branches, the change in the mean-square amplitudes of the atoms due to hybridization is probably small. Making use of these three assumptions, we can replace the average over all wave vectors $\mathbf{q}$ by $\mathbf{q} = \mathbf{0}$, and restrict our consideration to one molecule in the unit cell. It may consist of n atoms. Then we obtain from (1) for the internal modes of the molecule

$$\mathbf{U}_{\text{int}} = \mathbf{Q}\mathbf{R}\mathbf{\Delta}\mathbf{R}^T\mathbf{Q}^T. \tag{4a}$$

Now $\mathbf{R}$ is real, *i.e.* $\mathbf{R} = \mathbf{R}^T = \mathbf{R}^{-1}$. In (4*a*), $\mathbf{\Delta}$ contains $3n-6$ diagonal elements Δ_j of (2) (for $\mathbf{q} = \mathbf{0}$) for the $3n-6$ internal modes. The contributions of the external modes which are always present in the crystal (for $|\mathbf{q}| > 0$) must be excluded in (4*a*). Formally, we achieve this by setting the remaining six elements Δ_j equal to zero for all wave vectors $\mathbf{q}$. Thus $\mathbf{U}_{\text{int}}$ is singular, and of rank $3n-6$. In the same way we exclude the eigenvectors of the external modes, and achieve this by reducing $\mathbf{R}$ to a $3n \times (3n-6)$ rectangular matrix $\mathbf{R}_{\text{int}}$. If we also reduce $\mathbf{\Delta}$ to a $3n-6$ diagonal matrix $\mathbf{\Delta}_{\text{int}}$, we obtain from (4*a*)

$$\mathbf{U}_{\text{int}} = \mathbf{Q}\mathbf{R}_{\text{int}}\,\mathbf{\Delta}_{\text{int}}\,\mathbf{R}_{\text{int}}^T\,\mathbf{Q}^T. \tag{4b}$$

Finally, with the exclusion of the external modes, we can also write for the mass-normalized dynamical matrix (for $\mathbf{q} = \mathbf{0}$)

$$\mathbf{M}_{\text{int}} = \mathbf{R}\mathbf{\Lambda}\mathbf{R}^T = \mathbf{R}_{\text{int}}\,\mathbf{\Lambda}_{\text{int}}\,\mathbf{R}_{\text{int}}^T, \tag{5}$$

where $\mathbf{M}_{\text{int}}$ is also singular and of rank $3n-6$.

3. The spectroscopic approach

Here we follow the formulations given by Cyvin (1959, 1968) and sum up the FG method as follows. Let $\mathbf{u}$ be the $3n$ vibrational coordinates of the n atoms in a molecule expressed in a Cartesian reference system and $\mathbf{S}$ the $3n-6$ symmetry coordinates of the internal modes, then the matrices $\mathbf{B}$ and $\mathbf{A}$ are defined by

$$\mathbf{S} = \mathbf{B}\mathbf{u}, \quad \mathbf{u} = \mathbf{A}\mathbf{S}, \tag{6}$$

where

$$\mathbf{A} = \mathbf{Q}\mathbf{Q}^T\,\mathbf{B}^T\,\mathbf{G}^{-1}, \tag{7}$$

and

$$\mathbf{G} = \mathbf{B}\mathbf{Q}(\mathbf{B}\mathbf{Q})^T, \tag{8}$$

see also Decius & Hexter (1977, p. 36). $\mathbf{G}^{-1}$ is the kinetic energy matrix referred to the $3n-6$ symmetry coordinates $\mathbf{S}$. In practice, first $\mathbf{B}$ is set up and then $\mathbf{G}$ and $\mathbf{A}$ are calculated from $\mathbf{B}$. Let $\mathbf{F}$ be the force constant matrix of the internal modes referred to the symmetry coordinates $\mathbf{S}$ and $\mathbf{E}$ the unit matrix, then the secular equation is given by

$$\det(\mathbf{F} - \Lambda_{j,\text{int}}\,\mathbf{G}^{-1}) = 0, \quad j = 1, \ldots 3n-6. \tag{9}$$

The eigenvalues $\mathbf{\Lambda}_{\text{int}}$ can be obtained by means of the $(3n-6) \times (3n-6)$ matrix $\mathbf{L}$ which formally diagonalizes $\mathbf{FG}$, *i.e.*

$$\mathbf{L}^T\,\mathbf{F}\mathbf{G}\mathbf{L}^{T-1} = \mathbf{\Lambda}_{\text{int}}. \tag{10}$$

Since $\mathbf{FG}$ is not symmetric, $\mathbf{L}$ is not orthogonal. With (9) and (10) we further obtain

$$\mathbf{L}^T\,\mathbf{G}^{-1}\,\mathbf{L} = \mathbf{E}, \quad \mathbf{L}^T\,\mathbf{F}\mathbf{L} = \mathbf{\Lambda}_{\text{int}}, \tag{11}$$

i.e. also $\mathbf{G} = \mathbf{L}\mathbf{L}^T$. With $\mathbf{L}$, the mean-square-amplitude matrix referred to the symmetry coordinates $\mathbf{S}$ is given by

$$\mathbf{\Sigma} = \langle \mathbf{S}\mathbf{S}^T \rangle = \mathbf{L}\mathbf{\Delta}_{\text{int}}\,\mathbf{L}^T \tag{12}$$

(Cyvin, 1959, equation 12). The $3n \times 3n$ mean-square-amplitude matrix referred to the Cartesian coordinates $\mathbf{u}$ is then obtained by transformation, *i.e.*

$$\begin{aligned}\mathbf{U}_{\text{int}} &= \langle \mathbf{u}\mathbf{u}^T \rangle = \mathbf{A}\mathbf{\Sigma}\mathbf{A}^T \\ &= \mathbf{Q}(\mathbf{G}^{-1}\,\mathbf{B}\mathbf{Q})^T\,\mathbf{L}\mathbf{\Delta}_{\text{int}}\,\mathbf{L}^T(\mathbf{G}^{-1}\,\mathbf{B}\mathbf{Q})\,\mathbf{Q}^T. \end{aligned} \tag{13}$$

4. Proof of equivalence

The equivalence of (4) and (13) is not obvious. In the lattice dynamical treatment, first the dynamical matrix

M is set up, second, the eigen-values and -vectors are calculated and, third, the external-mode contributions to **U** are excluded by $\Lambda_j = 0$. In the spectroscopic treatment, first the $(3n-6) \times (3n-6)$ matrices **F** and **G** are set up, second, the eigenfrequencies and **L** are calculated and, third, the system is extended to the $3n \times 3n$ matrix $\mathbf{U}_{\text{int}}$.

To prove the equivalence of (4) and (13), we first eliminate the **G** matrix in (13) by using $\mathbf{G}^{-1} = \mathbf{L}^{T-1}\mathbf{L}^{-1}$. We obtain

$$\mathbf{U}_{\text{int}} = \mathbf{Q}(\mathbf{L}^{-1}\mathbf{BQ})^T \boldsymbol{\Delta}_{\text{int}} \mathbf{L}^{-1}\mathbf{BQQ}^T. \qquad (14)$$

To show that (4) and (14) are equivalent, we first have to show that $\boldsymbol{\Delta}_{\text{int}}$ in (4) and (14) is identical and, second, that $\mathbf{R}_{\text{int}} = (\mathbf{L}^{-1}\mathbf{BQ})^T$. Since $\boldsymbol{\Delta}_{\text{int}}$ is fully determined by the frequencies ω_j and a few constants, the first part of our proof is to show that the eigenvalues $\Lambda_{j,\text{int}}$, which are contained in (4) and (14), are identical. Here we have to assume, of course, that we use the same physical model for the force constants in both cases, so that (4) and (14) only appear to be different descriptions of the same physical situation. Since the force constants of the internal modes can be expressed naturally in the system of the $3n-6$ symmetry coordinates, we use this system to begin with; thus our force constants are defined by the matrix **F**. Now we have to transform **F** to the Cartesian reference system in which $\mathbf{M}_{\text{int}}$ of (5) is defined, and then show that the eigenvalues of (5) and (14) are identical. With (6) we obtain for the transformation

$$\mathbf{M}_{\text{cart}} = \mathbf{B}^T\mathbf{FB}. \qquad (15)$$

To obtain $\mathbf{M}_{\text{int}}$, the mass normalization has to be performed; this yields

$$\mathbf{M}_{\text{int}} = (\mathbf{BQ})^T\mathbf{FBQ}. \qquad (16)$$

Equation (16) represents the lattice dynamical description of our force constant model of the internal modes, and thus contains the eigenvalues of (4) and (5).

The eigenvalues of (14) are contained in (9)–(11), and in order to obtain them in a more useful form, we first rewrite the secular equation (9). Here we transform $\mathbf{G}^{-1}$ to **E** in a different way to that in (9)–(11) (there we had $\mathbf{G}^{-1}\mathbf{G} = \mathbf{E}$) and start from

$$\mathbf{B}^T\mathbf{G}^{-1}\mathbf{B} = (\mathbf{QQ}^T)^{-1}. \qquad (17)$$

Equation (17) may also be considered as a definition of the **B** matrix (Fadini, 1976, p. 43). [If **B** were a square (non-singular) matrix then (17) would be obtained by inversion of (8).] From (17), we deduce for the transformation of $\mathbf{G}^{-1}$ we are looking for,

$$(\mathbf{BQ})^T\mathbf{G}^{-1}\mathbf{BQ} = \mathbf{E}. \qquad (18)$$

Since **F** transforms in the same way as $\mathbf{G}^{-1}$, we now obtain for the secular equation instead of (9)

$$\det[(\mathbf{BQ})^T\mathbf{FBQ} - \Lambda_j\mathbf{E}] = 0, \quad j = 1,\dots 3n, \qquad (19)$$

with six eigenvalues $\Lambda_j = 0$. Obviously, $\mathbf{M}_{\text{int}}$ of (16) is identical with the transformed force constant matrix in (19). Hence, the eigenvalues $\boldsymbol{\Lambda}_{\text{int}}$ of (5) and (16), on the one hand, and of (9)–(11) and (19), on the other hand, are identical.

In order to perform the second part of our proof, we deduce from (11) $\mathbf{F} = \mathbf{L}^{T-1}\boldsymbol{\Lambda}_{\text{int}}\mathbf{L}^{-1}$, insert this expression into $\mathbf{M}_{\text{int}}$ of (16) and thus obtain for $\mathbf{M}_{\text{int}}$ of (5) and (16)

$$\mathbf{M}_{\text{int}} = (\mathbf{L}^{-1}\mathbf{BQ})^T\boldsymbol{\Lambda}_{\text{int}}\mathbf{L}^{-1}\mathbf{BQ}. \qquad (20)$$

A comparison of (5) and (20) shows that $\mathbf{R}_{\text{int}} = (\mathbf{L}^{-1}\mathbf{BQ})^T$, which completes our proof. Although neither $\mathbf{L}^{-1}$, nor **B**, nor **Q** are orthogonal, the product $(\mathbf{L}^{-1}\mathbf{BQ})^T$ is part of the orthogonal matrix **R**.

5. Calculation of the mean-square amplitudes with eigenvector routines

In order to avoid determining the eigenvalues of the **FG** matrix in the calculation of the mean-square amplitudes, Cyvin (1968, equation 7.53) and Øystein (1972) proposed series expansions. These series either converge poorly or not at all (Cyvin's series is only valid for frequencies with $\hbar\omega/2k_BT < \pi$). We shall show that it is not really necessary to use series expansions (or to search for better converging series) since, firstly, the eigenvalue problem can be more advantageously formulated than with the **FG** method and, secondly, there are certain methods for setting up the force constant matrix **F**, where the eigenvalues are known in advance.

Selecting the matrix **FG** for determining the eigenvalues is numerically inexpedient, since **FG** is not symmetric and **L** of (10) is not orthogonal. Thus, with the **FG** method, the inherent symmetry and orthogonality, which reduce the number of unknown elements, is not put to use. A matrix equivalent to **FG** which is at the same time symmetric, is obtained if first **G** is rewritten in the form $\mathbf{G} = \mathbf{CC}^T$. Methods for obtaining such a description are known, *e.g.* the Cholesky procedure (Zurmühl, 1964). Instead of **FG**, $\mathbf{C}^T\mathbf{FC}$ is now diagonalized and, instead of (10), we write

$$\mathbf{T}^T\mathbf{C}^T\mathbf{FCT} = \boldsymbol{\Lambda}_{\text{int}}. \qquad (21)$$

T is orthogonal and its columns contain the eigenvectors of $\mathbf{C}^T\mathbf{FC}$. Thus, **T** can be calculated with a standard eigenvector program. With (11) and (21) we finally obtain $\mathbf{L} = \mathbf{CT}$.

If one also wishes to avoid calculating **C**, one can use (instead of **C**) the matrix **BQ** and obtain (instead of $\mathbf{C}^T\mathbf{FC}$) $\mathbf{M}_{\text{int}}$ of (16). Diagonalization of $\mathbf{M}_{\text{int}}$ yields $\boldsymbol{\Lambda}_{\text{int}}$ and $\mathbf{R}_{\text{int}}$. **L** and $\boldsymbol{\Sigma}$ can no longer be calculated, but $\mathbf{U}_{\text{int}}$ can be according to (4*b*).

Furthermore, with the establishment of **F**, there are some procedures with which the eigenvalues Λ_{int} need not be determined. These are the '*Verfahren der nächsten Lösung*', the '*Kopplungsstufenverfahren*', the 'parameter representation of Pulay & Török' and the 'procedure of Mann, Shimanouchi, Meal & Fanö' (Fadini, 1976, Ch. 6 and 7). With these procedures, **F** is set up in such a way that, within the numerical accuracy, the eigenvalues of **FG** are exactly equal to the squares of the observed frequencies. This, incidentally, is a necessary condition, since in any fit of the force constants to the observed frequencies the optimal fit (here the exact equivalence) should be obtained. We remark that the *Kopplungsstufenverfahren* yields not only the force constant matrix **F** but also the matrix **L** of (10) and (11).

If one measures the observed frequencies ω_j in cm^{-1}, the eigenvalues are given by $\Lambda_j = 5{\cdot}89146\omega_j^2$. Thus, if one uses one of the above procedures for establishing **F**, there will be no difficulties in calculating the mean-square-amplitude matrix, since, on the one hand, the eigenvalues are known and, on the other hand, standard programs for evaluating the eigenvectors can be used.

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On the Contributions of the Internal Modes of Molecules to the Debye–Waller Factors. III. Urea

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Abstract

The contributions of the internal modes of urea molecules, CH_4N_2O, to the vibration tensors of their atoms are calculated at 0, 100 and 300 K. The calculations are based on IR and Raman data from the literature, and the force constants determined are of the Urey–Bradley type. The temperature dependence of the vibration tensors of the internal modes (diagonal components) is represented graphically in the 0–300 K region (interpolation over nine calculated points); in this region it is weak. Since, for urea, there are vibration tensors available which were determined by neutron diffraction, the contributions of the internal modes could be estimated. On average over the C, N, O atoms it is 1·8% at 300 K, 4·4% at 98 K and 5·8% at 60 K; on average over the H atoms it is 22·6% at 300 K, 39·9% at 98 K and 46·3% at 60 K.

1. Introduction

The determination of the contributions of the internal modes of urea to the Debye–Waller factors is a by-product of our experimental investigation of the electron density distribution in urea crystals. In this investigation temperature factors for internuclear charge clouds are needed; this necessitates an analysis of the internal modes of the urea molecules (Scheringer, 1977). Urea is a favourable example, since IR and Raman data are available for urea and deuterated urea and the vibration tensors of the nuclei have been determined from neutron diffraction data at 300, 98 and 60 K.

2. Origin of data, assignments and method of calculation

Measured IR and Raman data and assignments of the internal modes of solid urea are reported by Yamaguchi, Miyazawa, Shimanouchi & Mizushima

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