Furthermore, with the establishment of **F**, there are some procedures with which the eigenvalues $\Lambda_{\rm Int}$ 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 $\Lambda_j = 5\cdot89146\omega_j^2$. 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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(1957); Saito, Machida & Uno (1971); Duncan (1971); Shteinberg, Mushkin & Finkelshtein (1972) and Hadži, Kidrič, Kneževic & Barlič (1976). Saito, Machido & Uno (1971) made an assignment of all 18 internal modes based on the observed infrared spectra of urea, urea-d_4 and partially deuterated ureas. Shteinberg, Mushkin & Finkelshtein (1972) also made an assignment of all internal modes, except for one frequency of the A_2 species. The other authors only made assignments of the in-plane modes (A_1 and B_2 species). The measured frequencies and assignments of the in-plane modes of all the authors are nearly identical. However, the frequencies and assignments of the out-of-plane modes (A_2 and B_1 species) of Shteinberg, Mushkin & Finkelshtein (1972) differ from those of Saito, Machida & Uno (1971). Our calculations are based on the assignment of the latter. In order to estimate the errors introduced by uncertain assignments, we also performed one calculation based on the assignment of Shteinberg, Mushkin & Finkelshtein (1972).

In our calculations, 16 force constants of a Urey–Bradley force field were used. The values of ten force constants for the in-plane modes were taken from Saito, Machida & Uno (1971), and the values of the other six constants were determined from the best agreement between observed and calculated frequencies (Table 1). For the determination of the force constants, frequencies and eigenvectors, we used the program of Shimanouchi (1968). For calculating the mean-square amplitudes of the internal modes Shimanouchi's program was extended corresponding to equation (13) of Scheringer & Fadini (1979).

3. Vibration tensors of the internal modes

The calculated vibration tensors of the internal modes are given in Table 2 for 0, 100 and 300 K. The tensors are referred to a Cartesian coordinate system; because of site symmetry $2mm$ for C and O, and m for N and H, we have $U_{12} = U_{23} = 0$ for all atoms and $U_{13} = 0$ for C and O.

To represent the temperature dependence of the vibration tensors more concisely, we have calculated two averages. One is taken over the diagonal components of the atoms C, O, N(1), N(2), the other over the diagonal components of the four H atoms. The average values were calculated for nine temperatures between 0 and 300 K, and obtained by interpolation for the other temperatures (Fig. 1). The assumption that the vibration tensors of the internal modes do not depend on the temperature in this region is justified for urea. The reason is that the internal modes have high frequencies (the lowest is 500 cm^{-1}, Table 1) and, thus, 300 K is a low temperature for the internal modes. To a good approximation, we could use the tensors for $T = 0$ K in the 0–300 K region (Fig. 1). This implies that the high temperature approximation $\bar{E} = k_B T$ is not appropriate for the internal modes. From $\hbar\omega = k_B T$ we obtain $\omega = 208$ cm^{-1} for $T = 300$ K, a value which is far below the values of the observed frequencies. For an internal frequency of 3000 cm^{-1} we would obtain 4337 K as a high temperature. The inexpediency of the high temperature approximation was also found for the internal modes of benzene, naphthalene and anthracene (Scheringer, 1972).

The vibration tensors of the internal modes of the H atoms are about 18 times larger than the tensors of C, N and O. The mass ratio is (on average) 1:14. Large mean-square amplitudes for the light atoms were also found for many other molecules where a force constant analysis was performed; see the compilation in Table 1 of Scheringer (1973). In a rough approximation, the trace of the vibration tensor of the internal modes is found to be inversely proportional to the mass of the corresponding atom.

4. Estimate of errors

In order to estimate the effect of measuring errors on the vibration tensors we carried out three test cal-

Table 1. *Observed and calculated frequencies* (cm^{-1}) *obtained with the Urey–Bradley force field*

Assignment of Saito, Machida & Uno (1971).

	obs	calc		obs	calc
A_1	3485	3472	B_1	785	785
	3352	3366		719	719
	1678	1646		500	500
	1615	1614			
	1153	1146	B_2	3485	3469
	1003	1010		3352	3365
	558	557		1615	1640
				1463	1464
A_2	719	719		1153	1161
	555	555		575	562

Table 2. *Vibration tensors* ($U_{ij} \times 10^6$ *in* Å^2) *of the internal modes in urea*

(*a*) 0 K, (*b*) 100 K, (*c*) 300 K. x axis parallel to C=O, y axis perpendicular to the plane of the molecule. $U_{12} = U_{23} = 0$.

		U_{11}	U_{22}	U_{33}	U_{13}
C	(*a*), (*b*)	827	1569	946	0
	(*c*)	854	1701	989	0
O	(*a*), (*b*)	800	175	829	0
	(*c*)	843	191	949	0
N(1)	(*a*), (*b*)	705	467	920	−83
	(*c*)	762	519	993	−72
H(1)	(*a*)	11553	24464	7184	−3368
	(*b*)	11555	24481	7184	−3369
	(*c*)	12026	27586	7264	−3478
H(2)	(*a*)	5283	24018	13476	221
	(*b*)	5283	24031	13478	221
	(*c*)	5346	26898	13993	336

culations. (1) All frequencies were raised by 10 cm^{-1}, (2) all frequencies were lowered by 10 cm^{-1}, (3) the frequencies of Table 1 were alternately raised and lowered by 10 cm^{-1}. For (1) and (2), the average values of the vibration tensors are lowered and raised respectively by 1·5%. For case (3), an increase of 1·0% occurs. Hence, errors in measuring have little effect on the derived vibration tensors.

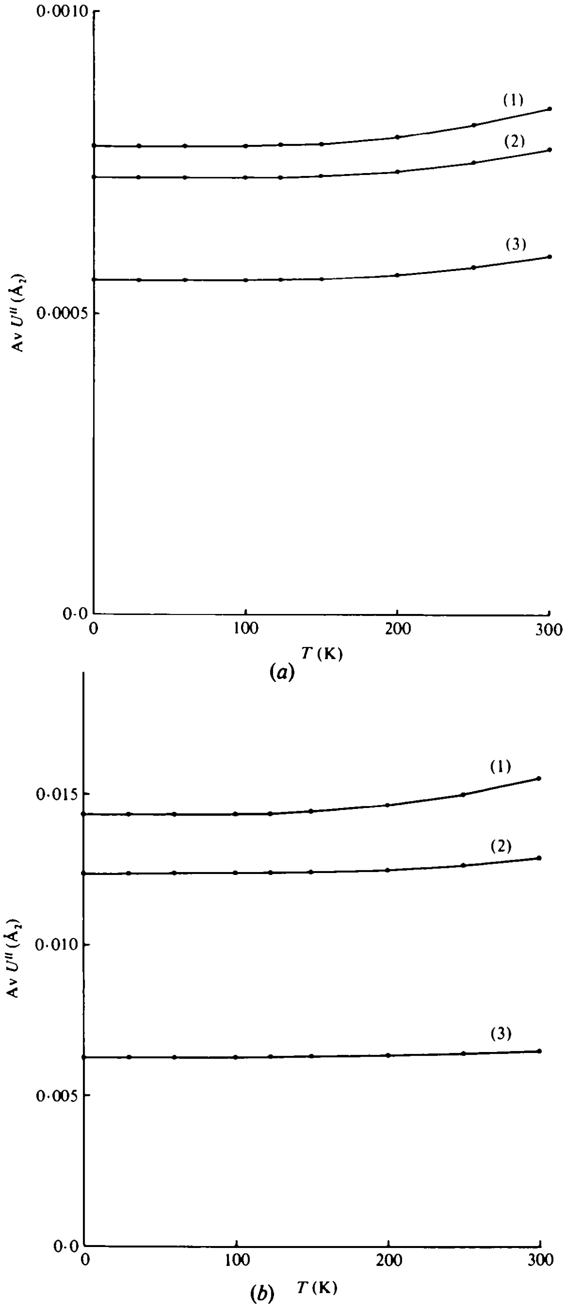

Fig. 1. Average values (Å^2) of the vibration tensors (diagonal components) of the internal modes in urea as a function of temperature. (*a*) Atoms C, N, O; (*b*) H atoms. (1) Assignment of Saito, Machida & Uno (1971), (2) assignment of Shteinberg, Mushkin & Finkelshtein (1972), (3) without the five low frequencies of the species A_2 and B_1.

Errors in the assignment are more important, particularly with the species A_2 and B_1 which contain the out-of-plane modes with low frequencies. In order to make such errors visible, we have calculated the averages shown in Fig. 1 with three different assignments of the A_2 and B_1 species. (1) Assignment of Saito, Machida & Uno (1971) with the five observed frequencies of 719, 555, 785, 719 and 500 cm^{-1}. (2) Assignment of Shteinberg, Mushkin & Finkelshtein (1972) with one calculated frequency of 1003 cm^{-1} and four observed frequencies of 720, 1075, 785 and 720 cm^{-1}. (3) Without the contributions of the species A_2 and B_1 (the five frequencies were set equal to 10^5 cm^{-1}). In (3), the average over the C, N, O atoms is reduced by 28·6% compared with (1), and the average over the H atoms by 57·2% (Fig. 1). The effect on the vibration tensors of the H atoms is so much larger because only the H atoms take part in the torsional modes (the torsional axes are the C—N bonds) and the NH$_2$ wagging mode. Fig. 1 shows that the correct assignment is essential for a reliable calculation of the vibration tensors of the internal modes.

5. Contributions of the internal modes to the Debye–Waller factors

Vibration tensors for urea at room temperature were determined by Pryor & Sanger (1970) and by Heger, Mullen & Treutmann (1979) (HMT) from neutron diffraction data. HMT also determined vibration tensors from neutron data at 98 and 60 K. We have used HMT's vibration tensors (Table 3) in order to determine the relative contributions of the internal modes at the three temperatures.

In order to express the contributions of the internal modes to the vibration tensors, we write $\mathbf{U} = \mathbf{U}_{\rm ext} + \mathbf{U}_{\rm int}$ and put

$$U^{ij}_{\rm ext} = \beta U^{ij}, \quad U^{ij}_{\rm int} = (1-\beta)\, U^{ij}$$

Table 3. *Average values* (Å^2) *of the vibration tensors* (*diagonal components*) *for the atoms* C, N, O *and the* H *atoms at* 60, 98 *and* 300 K

$1-\beta$ is the relative contribution of the internal modes and is calculated from the first six rows of the table respectively.

		C, O, N(1), N(2)	H
Internal modes	60 K	0·0008	0·0143
	98 K	0·0008	0·0143
	300 K	0·0008	0·0155
Neutron diffraction, HMT	60 K	0·0138	0·0309
	98 K	0·0180	0·0358
	300 K	0·0439	0·0686
$1-\beta$ (%)	60 K	5·8	46·3
	98 K	4·4	39·9
	300 K	1·8	22·6

(Scheringer, 1977). $1-\beta$ describes the relative contribution of the internal modes. In principle, $1-\beta$ is different for each component ij and for each atom, but in order to obtain representative results we consider only the averages already described (Table 3). At 300 K the $1-\beta$ values of the C, N, O atoms are small (1·8%). For benzene, naphthalene and anthracene values of 1·7, 3·2 and 6·8% respectively were found for the C atoms at 292 K (Scheringer, 1972). At 98 and 60 K the $1-\beta$ values of the C, N, O atoms in urea increase due to the decrease of the external modes, but they remain small (<6%). For the H atoms we find large relative contributions of the internal modes to the vibration tensors at all temperatures (Table 3). The reason for this is that the H atoms chiefly take part in the out-of-plane modes with low frequencies. The large $1-\beta$ values found for the H atoms in benzene, naphthalene and anthracene (11·8, 22·4 and 39·1% respectively at $T = 292$ K; Scheringer, 1972) seem to confirm our results for urea.

Scheringer (1977) estimated $1-\beta \simeq 25\%$ at 100 K for the first-row elements in molecules of medium size. This investigation shows that, for urea, this estimate is much too high. The discrepancy is partly due to the fact that the molecules considered earlier were larger than urea. The four relevant atoms, C, O, N(1), N(2), in urea form a very small unit in space, to the motions of which only the higher internal frequencies can contribute.

Since, for urea, the internal modes contribute little to the Debye–Waller factors of the C, N, O atoms, we conclude that the model of rigid-body motions will give a useful description for the motions of these atoms down to 60 K. The relative errors made with the rigid-body model will then be <10% of the vibration tensors of the C, N, O atoms. The rigid-body approximation obviously cannot be applied to the H atoms. Similarly, for larger molecules like anthracene, with some low-frequency internal modes, the rigid-body approximation will no longer be appropriate for any atom at 100 K.

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A Limited-Range Step-Scan Method for Collecting X-ray Diffraction Data

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Abstract

A limited-range, step-scan method for rapid diffractometer data collection is described. The data are reduced in a two-pass procedure. First, the step data from the more intense peaks are fitted by a Gaussian function $y_i = C_1 \exp[-(\bar{x}-x_i)^2/C_2^2]$, where C_1 is the peak maximum, C_2 is proportional to the peak width and C_1C_2 is proportional to the integrated intensity. Because the peak widths may vary appreciably over the range of data observed and cannot be determined very precisely for weak reflections, an empirical function is determined from the more intense reflections in the first pass and the calculated peak widths are used for all reflections in the second pass. Comparison of data

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