

## On the Contributions of the Internal Modes of Molecules to the Debye–Waller Factors

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A method is described which allows one to estimate the contributions of the internal modes of a molecule to the Debye–Waller factors of the individual atoms. The contributions obtained are the average of the isotropic mean-square amplitudes over all atoms in the molecule having the same mass. For evaluating the contributions one needs to know only the frequencies of the internal modes of the molecule, as determined from infrared and Raman data, but not the force constants. Furthermore, a rough formula is derived which allows one to estimate the contributions of the internal modes to the vibrations of a given atom only from the number of the atoms in the molecule and from the mass of the respective atom. Numerical results are presented for the structures of benzene, naphthalene, and anthracene.

### 1. Introduction

Structures which contain nearly rigid molecules are often refined with thermal rigid-body parameters. These parameters can be determined either from the vibration tensors of the individual atoms of the molecule or – *via* the vibration tensors – from intensity data. However, there are not only the external modes of the molecules which contribute to the vibration tensors of the atoms but also the internal modes and thus the question arises to what extent the determination of the thermal rigid-body parameters from the vibration tensors will be disturbed or rendered inappropriate. The contributions of the internal modes of molecules are commonly judged to be small and thus liable to be neglected. Many successful refinements of structures with thermal rigid-body parameters seem to have confirmed this opinion. Furthermore, Higgs (1955) has calculated the contributions of the internal modes to the vibration tensors of the carbon atoms of naphthalene from a force-constant model and found them to amount to only about 3.2%. Recently Johnson (1970) has calculated the mean-square amplitudes of the internal modes for the benzene and cyclobutane molecule from a complete force-constant model. He found that the mean-square amplitudes of the carbon atoms are small enough to be neglected whereas those of the hydrogen atoms are large. They amount to more than 10% of the contributions of the external modes. Some authors have determined the mean-square amplitudes of the internal modes by using approximate force-constant models, and subtracted these amplitude values from the vibration tensors of the individual atoms before the rigid-body vibration tensors were calculated. Becka & Cruickshank (1963) calculated the mean-square amplitudes of the internal modes for the carbon and nitrogen atoms in hexamethylenetetramine by assuming a force constant model with rigid CH<sub>2</sub> groups. Johnson (1970) used the force constants of the benzene molecules to correct for the contributions of the internal modes in phenyl groups, and Ellison,

Johnson & Levy (1971) used the force constants of the methylene chloride molecule to correct for the contributions of the internal modes in glycolic acid. Recently Pawley (1971), inspired by Johnson's (1970) calculations on benzene, took into account the contributions of the internal modes to the hydrogen atoms of pyrene by refining a common temperature factor for the hydrogen atoms. He applied the same procedure to the deuterium atoms of deuterated naphthalene and anthracene. In this procedure Pawley used three anisotropic components which were fitted to the anisotropy of the motions of the hydrogen atoms in the benzene molecule. These three additional parameters proved to be highly significant in the least-squares refinement which suggests that for these molecules the contributions of the internal modes to the hydrogen and deuterium atoms are substantial.

Unfortunately, the force constants of the internal vibrations are unknown for most molecules. As a rule there are more force constants than normal frequencies for a molecule so that the number of spectroscopically measured frequencies will not be sufficient to determine all the force constants. Only for highly symmetrical molecules is the number of force constants so greatly reduced that they can be determined from the spectroscopic data. In this situation we have lowered the aim and searched for a method which only requires one to know the normal frequencies and not the force constants. The correct assignment of frequencies to the measured infrared and Raman data is still a great task for large molecules but it has been achieved in a number of cases. We shall show that by using the normal frequencies of the internal modes one is able to determine the average of the isotropic mean-square amplitudes for each type of atom in the molecule. Thus our approach does not allow one to determine the exact values of the internal mean-square amplitudes for each atom, but we obtain averages which are correct to about 10% of the order of magnitude. These isotropic averages can then be compared with the standard errors of the components of the

vibration tensors of the atoms. In this way we find a basis on which to judge whether a determination of the thermal rigid-body parameters from the uncorrected vibration tensors of the atoms is appropriate.

We first discuss the physical assumptions which we make and the mathematical methods which we use. Then we derive a rough formula which allows us to estimate the contributions of the internal modes to the vibrations of a given atom only from the number of atoms in the molecule and from the mass of the respective atom. Finally we present numerical results for the structures of benzene, naphthalene and anthracene.

## 2. The contributions of the internal and external modes

In the preceding paper (Scheringer, 1972) we derived a lattice-dynamical matrix representation of the anisotropic vibration tensors of the atoms in the unit cell in which not only the single atom but all atoms of the cell are considered. We obtained equations which relate the mean-square amplitude matrix of the vibration tensors to the dynamical matrices of the crystal. We shall use these equations in order to derive the relations needed for this investigation, between the mean-square amplitudes and the frequencies. We consider the case  $T > 0^\circ\text{K}$  and apply equation (12) of the preceding paper which we list for reference as

$$\mathbf{D} = \frac{k_B T}{2N} \sum_{\mathbf{q}} (\mathbf{R}\mathbf{\Lambda}^{-1}\mathbf{\Gamma}\tilde{\mathbf{R}} + \mathbf{R}^*\mathbf{\Lambda}^{-1}\mathbf{\Gamma}\tilde{\mathbf{R}}^*), \quad (1)$$

where the factor  $k_B T$  has been extracted. For each wave vector  $\mathbf{q}$  we have

$$A_j^{-1} = \frac{1}{\omega_j^2}; \Gamma_j = \frac{\hbar\omega_j}{2k_B T} \coth\left(\frac{\hbar\omega_j}{2k_B T}\right). \quad (2)$$

The notation is as used in the preceding paper (Scheringer, 1972). For  $Z$  molecules in the unit cell, each consisting of  $n$  atoms, the matrices in equation (1) are of the order  $3nZ$ .  $\mathbf{R}$  is unitary, *i.e.*  $\tilde{\mathbf{R}} = \mathbf{R}^{-1}$ , and  $\mathbf{\Lambda}$  and  $\mathbf{\Gamma}$  are diagonal; their elements are defined in equation (2). Since  $\mathbf{R}$  is unitary we can gain the essential relation for our problem by applying the theorem of the trace invariance for unitary transformations. For each wave vector in equation (1) we have

$$\sum_{j=1}^{3nZ} A_j^{-1} \Gamma_j = \text{trace}(\mathbf{R}\mathbf{\Lambda}^{-1}\mathbf{\Gamma}\tilde{\mathbf{R}}) = \text{trace}(\mathbf{R}^*\mathbf{\Lambda}^{-1}\mathbf{\Gamma}\tilde{\mathbf{R}}^*). \quad (3)$$

With equations (1) and (3) we obtain

$$\text{trace}(\mathbf{D}) = \frac{k_B T}{N} \sum_{\mathbf{q}} \sum_{j=1}^{3nZ} (A_j^{-1} \Gamma_j)_{\mathbf{q}}. \quad (4)$$

In the following we want to separate the contributions of the internal and external modes, which appear simultaneously in equation (4). In this regard we assume that the forces among the molecules in the

crystal can be neglected in comparison with the forces among the atoms within the molecule. Thus we assume that the internal modes of a molecule in the crystal are the same as those of a molecule in the gaseous state. This assumption is largely confirmed by the fact that the infrared and Raman frequencies of a molecule are only slightly split when the molecules condense into a crystal. Taking the assumption as valid, we can replace the average over all wave vectors  $\mathbf{q}$  in equation (4) by one member with  $\mathbf{q} = 0$  for the internal modes of the molecules. Then we obtain

$$\text{trace}(\mathbf{D}) = k_B T \sum_{j=1}^{Z(3n-6)} (A_j^{-1} \Gamma_j)^{\text{int}} + \frac{k_B T}{N} \sum_{\mathbf{q}} \sum_{j=1}^{6Z} (A_j^{-1} \Gamma_j)_{\mathbf{q}}^{\text{ext}}. \quad (5)$$

Now we want to transform equation (5) so that we obtain the contribution of only one molecule. Since we assume that the  $Z$  molecules are (chemically) equivalent the internal modes for the  $Z$  molecules are the same. The contributions of the external modes are equal for the  $Z$  molecules if the molecules are in symmetrically equivalent positions. If there is more than one molecule in the asymmetric unit, the contributions of the external modes need not be exactly the same. However, they tend to be the same to a sufficient approximation since the summation is taken over all modes  $\mathbf{q}j$ . Thus we obtain from equation (5)

$$\frac{1}{Z} \text{trace}(\mathbf{D}) = \sum_{r=1}^n m_r (U_r^{11} + U_r^{22} + U_r^{33}) = C^{\text{int}} + C^{\text{ext}}, \quad (6)$$

where

$$C^{\text{int}} = k_B T \sum_{j=1}^{3n-6} (A_j^{-1} \Gamma_j)^{\text{int}} \quad (7)$$

represents the contribution of the internal modes of a molecule, and

$$C^{\text{ext}} = \frac{k_B T}{NZ} \sum_{\mathbf{q}j=1}^{6ZN} (A_j^{-1} \Gamma_j)_{\mathbf{q}}^{\text{ext}} \quad (8)$$

represents the contribution of the external modes of a molecule in the crystal. If we denote the isotropic average of the  $r$ th atom by

$$U_{r,\text{iso}} = \frac{1}{3}(U_r^{11} + U_r^{22} + U_r^{33}), \quad (9)$$

valid for internal and external modes, we obtain from equations (6), (7), and (9)

$$C^{\text{int}} = 3 \sum_{r=1}^n m_r U_{r,\text{iso}}^{\text{int}} \quad (10)$$

for the internal modes of the molecule.  $m_r$  is the mass of the  $r$ th atom.

Equation (10) has the disadvantage that it contains only the products  $m_r U_{r,\text{iso}}^{\text{int}}$ . In order to eliminate the mass  $m_r$ , we have to make a further assumption: the product  $m_r U_{r,\text{iso}}$  is constant for all atoms in the molecule. This does not hold exactly, but may be considered as a rule which is valid to about 10% relative

error. For a one-dimensional oscillator with constant frequency  $\omega$ , the rule is strictly valid as can be seen from  $U_r^2 m_r = \bar{E}/\omega^2$ . With many normal modes in a molecule the single atoms can take part in a particular mode in various ways; however, in the average over all modes these differences are annulled to a large degree so that the 'product rule' holds to a sufficient approximation. We can check it with Johnson's (1970) results for cyclobutane and benzene. Johnson's data (from his Fig. 9.2) for cyclobutane lead to the values of 0.0165, 0.0167, and 0.0166 mole.Å<sup>2</sup> of the products  $m_r U_{r,\text{iso}}^{\text{int}}$  for the atoms H<sub>1</sub>, H<sub>2</sub>, and C respectively. For the H and C atoms of benzene we find the values of 0.0140 and 0.0153 mole.Å<sup>2</sup> respectively, which differ by about 9%. Thus taking the 'product rule' to be valid we obtain for the isotropic average of the internal contributions for the atoms of mass  $m_r$

$$U_{r,\text{iso}}^{\text{int}} = \frac{C^{\text{int}}}{3nm_r}. \quad (11)$$

$U_{r,\text{iso}}^{\text{int}}$  can be calculated solely from the frequencies of the internal modes by using equations (2) and (7). The ratio of the internal contribution to the total (internal plus external) is then given by

$$V_{r,\text{iso}}^{\text{int}} = \frac{3U_{r,\text{iso}}^{\text{int}}}{U_r^{11} + U_r^{22} + U_r^{33}}, \quad (12)$$

where the  $U_r^{ii}$  are determined from diffraction data.

With the results obtained so far we can examine whether one is likely to determine too large values for the components of the rigid-body vibration tensors **TLS** from the vibration tensors  $U_r$  of the individual atoms, when the  $U_r$  were not corrected for the contributions of the internal modes. For this examination we have to know  $C^{\text{int}}$  and the components  $U_r^{ii}$  for all atoms of the molecule. On the one hand we obtain from equation (6)

$$C^{\text{ext}} = \sum_{r=1}^n m_r (U_r^{11} + U_r^{22} + U_r^{33}) - C^{\text{int}}. \quad (13)$$

On the other,  $C^{\text{ext}}$  can be calculated from the rigid-body vibration tensors as follows. If we assume the molecules to be rigid then equation (1) also holds for molecular crystals provided we attach the appropriate meaning to the symbols used: \* all matrices in equation (1) are of order  $6Z \times 6Z$ ,  $\Lambda$  contains the  $6Z$  frequencies of the external modes, and  $\mathbf{R}$  the  $6Z$  eigenvectors.  $\mathbf{D}$  is the mass-weighted mean-square amplitude matrix consisting of  $6 \times 6$  blocks. The  $Z$  diagonal blocks of  $\mathbf{D}$ ,  $\mathbf{D}_s$ ,  $s=1, \dots, Z$ , are obtained as follows: the vibration tensors **TLS** of the  $Z$  molecules are first expressed in the principal inertial system with origin at the centre of gravity. Then the tensors of the  $s$ th molecule are ordered into a  $6 \times 6$  matrix

$$\mathbf{G}_s = \begin{pmatrix} \mathbf{T} & \mathbf{S}^T \\ \mathbf{S} & \mathbf{L} \end{pmatrix} \quad (14)$$

\* A full proof of this statement will be given in a forthcoming paper.

and a mass-normalizing transformation

$$\mathbf{D}_s^{\text{mol}} = \mathbf{Q}^{-1} \mathbf{G}_s (\mathbf{Q}^T)^{-1} \quad (15)$$

is applied. (The superscript 'mol' indicates the molecular crystal.)  $\mathbf{Q}^{-1}$  is diagonal. The first three elements of  $\mathbf{Q}^{-1}$  are the total mass of the molecule,  $M$ , and the second three elements are the three principal moments of inertia,  $I_1, I_2, I_3$ , referred to the centre of gravity. Now, for the molecular crystal we obtain from equation (1)

$$\text{trace}(\mathbf{D}^{\text{mol}}) = ZC^{\text{ext}}. \quad (16)$$

If we assume the contributions of the external modes to be the same for each molecule, which always holds for symmetrically equivalent molecules, then

$$\text{trace}(\mathbf{D}_s^{\text{mol}}) = M(T^{11} + T^{22} + T^{33}) + I_1 L_{11} + I_2 L_{22} + I_3 L_{33} = C^{\text{ext}}. \quad (17)$$

$C^{\text{ext}}$  of equation (17) can now be compared with  $C^{\text{ext}}$  of equation (13). In an actual structure determination the two values of  $C^{\text{ext}}$  should be equal within the limits of experimental error. If  $C^{\text{ext}}$  of equation (17) is found to be larger, the diagonal elements of  $\mathbf{T}$  and  $\mathbf{L}$  were incorrectly determined because the contributions of the internal modes were neglected. We finally remark that equations (13) and (17) are generally valid within the limits of the physical assumptions discussed and that  $C^{\text{ext}}$  of equation (17) does not depend on the particular method that has been used to determine the components of  $\mathbf{T}$  and  $\mathbf{L}$ .

The development of equation (1) has yielded three results: we were able to separate the mean-square amplitudes with respect to internal and external modes [equations (7) and (8)]; we were able to determine the isotropic average of the contributions of the internal modes of the molecule for each sort of atoms [equation (11)]; and we found a criterion to examine the components  $T^{ii}$  and  $L_{ii}$  for possible contributions of internal modes [equations (13) and (17)].

### 3. An approximate formula

Since there are many difficulties with large molecules in measuring and assigning all normal frequencies, it would be useful to gain approximate formulae for assessing the contributions of the internal modes without knowing the normal frequencies. The possibility of obtaining approximate formulae of this type arises from the fact that with equation (7) one does not need to know each single frequency but only the value of the sum of all frequency terms.

With increasing number,  $n$ , of atoms in the molecule the contributions of the internal modes to the vibration tensors increase rapidly. There are essentially two reasons: (1) the number of internal modes in the molecule is  $3n-6$ , and (2) new vibrations with low frequencies appear when  $n$  increases. It is particularly the

low-frequency vibrations which contribute to the vibration tensors. If one assumes to a rough approximation that the effect of the low-frequency vibrations increases with  $n$ , one obtains

$$C^{\text{int}} = (3n - 6)na \quad (18)$$

and, with equation (11),

$$m_r U_{r,\text{iso}}^{\text{int}} = (n - 2)a, \quad (19)$$

where  $a$  is a constant. The value of  $a$  can be determined from molecules whose normal frequencies are known. We have calculated  $a$  for benzene, naphthalene, and anthracene, *cf.* section 4, and found the average  $a = 0.0015 \text{ mole} \cdot \text{\AA}^2$ . With the known value of the constant  $a$ , equations (18) and (19) can be used to assess the contributions of the internal modes to the vibration tensors for other molecular crystals. Fialkovskaya & Nefedov (1968), who carried out comparative measurements on anthracene and acridine, point out that with molecules of lower symmetry the low frequency vibrations occur more frequently. The low frequencies are mainly attributed to the non-planar vibrations of the molecule. Thus it is quite possible that for molecules of lower symmetry than benzene, naphthalene, and anthracene, equations (18) and (19), with  $a = 0.0015 \text{ mole} \cdot \text{\AA}^2$ , will provide, for the contributions of the internal modes, an estimate which is too low.

#### 4. Numerical results

As examples we have used the structures of benzene, naphthalene, and anthracene. These structures are particularly suitable because they have frequently been studied by X-ray and neutron diffraction as well as by spectroscopic methods. With benzene, even the interatomic force constants are known and, for the internal vibrations, Johnson (1970) has calculated the atomic mean-square amplitude tensors which we shall use for comparison with our own results.

The temperature factors of benzene were determined by Cox, Cruickshank & Smith (1958), those of naphthalene by Cruickshank (1957*a*), and those of anthracene by Cruickshank (1956, 1957*b*). The vibration tensors of the hydrogen atoms could not be determined from the X-ray data; we have calculated them from the rigid-body vibration tensors **T** and **L**. This does not give completely correct values, however; in equation (6) the contribution of the hydrogen atoms amounts only to about 10% owing to the small mass of the hydrogen atoms. The normal frequencies for benzene were taken from a paper by Mair & Hornig (1949). For naphthalene we used the frequencies given by Luther & Drewitz (1962). A somewhat different assignment of the Raman frequencies was given by Suzuki, Yokoyama & Ito (1968); the use of their frequencies, however, did not lead to significantly different results. With anthracene, the assignment of the normal frequencies to the experimental data differs to

a large degree from author to author. We used the infrared frequencies from Chafik & Mecke (1968) and the Raman frequencies from Suzuki, Yokoyama & Ito (1968). We also tried the normal frequencies assigned by Brigodiot & Lebas (1969); the results obtained differ only slightly from those which we give below and so we do not present them here. It seems that the different assignment is only of minor importance, at least for the higher frequencies, since in equation (7) only the sum over all frequency terms is needed.

The results of our calculations are presented in Table 1, with  $T = 292^\circ\text{K}$ . In the first row the values for  $C^{\text{int}}$  of equation (7) are listed in units of  $\text{mole} \cdot \text{\AA}^2$ ; the second row contains the corresponding values for the high temperature approximation,  $\Gamma_j = 1$ . The data show that the high temperature approximation is not appropriate and gives values which are rather too small. The reason is that at room temperature, the frequency obtained from  $\hbar\omega = k_B T$  is only  $202 \text{ cm}^{-1}$  which is much smaller than many of the normal frequencies of the molecules. Thus for small molecules particularly, the high temperature approximation does not hold.

Table 1. Contributions of the internal modes

	Benzene	Naphthalene	Anthracene	
$C^{\text{int}}$	0.526	1.197	2.661	$\text{mole} \cdot \text{\AA}^2$
$C^{\text{int}}_{T \rightarrow \infty}$	0.252	0.738	2.016	
$U^{\text{int}}_{\text{C,iso}}$	1.22	1.85	3.08	$\times 10^{-3} \text{\AA}^2$
$U^{\text{int}}_{\text{H,iso}}$	14.62	22.16	36.96	
$V^{\text{int}}_{\text{C,iso}}$	1.70	3.25	6.79	$\times 10^{-2}$
$V^{\text{int}}_{\text{H,iso}}$	11.84	22.39	39.14	
$I_1$	10.2	19.6	28.4	$\times 10^{-2}$
$I_2$	20.4	27.7	42.8	
$I_5$	37.1	41.5	56.2	
$I_{10}$	56.2	55.5	65.8	
$\bar{v}_1$	410	176	96	$\text{cm}^{-1}$
$\bar{v}_2$	410	285	136	
$n$	12	18	24	
$a$	1.46	1.39	1.68	$\times 10^{-3} \text{mole} \cdot \text{\AA}^2$

In order to compare our value of  $C^{\text{int}}$  of  $0.52628 \text{ mole} \cdot \text{\AA}^2$  for benzene with Johnson's results, we have calculated  $C^{\text{int}}$  from Johnson's (1970, Fig. 9.2) r.m.s. amplitude data by using equations (9) and (10). We obtained  $C^{\text{int}} = 0.52618 \text{ mole} \cdot \text{\AA}^2$  which is in very good agreement with our value, although our source of spectroscopic data (Mair & Hornig, 1949) is different from Johnson's (Miller & Crawford, 1946; Crawford & Miller, 1949).

In the next four rows of Table 1, the values of  $U_{r,\text{iso}}^{\text{int}}$  are listed for carbon and hydrogen atoms respectively. Our  $U_{r,\text{iso}}^{\text{int}}$  values for benzene compare well with those which we have calculated from Johnson's (1970, Fig. 9.2) data, namely  $0.00127$  and  $0.01397 \text{\AA}^2$  for carbon and hydrogen respectively. Our value of  $0.00185 \text{\AA}^2$  for the carbon atoms of naphthalene is a little larger than the mean value of  $0.00167 \text{\AA}^2$  which we have cal-

culated from Higgs's (1955) data. Higgs based his calculation on the high temperature approximation,  $\Gamma_j = 1$ , but our high temperature value of  $0.00114 \text{ \AA}^2$  is smaller than Higgs's value. Probably these discrepancies are to be attributed to deficiencies in Higgs's force constant model for the naphthalene molecule. The contributions of the internal modes to the vibration tensors are considerable for the carbon atoms in anthracene and for the hydrogen atoms in all three molecules. The contributions of the internal modes to the vibration tensors of the carbon atoms in naphthalene and anthracene are about as large as the standard deviations  $\sigma(U_r^{ii})$  obtained by Cruickshank. Cruickshank (1956) gives  $\sigma(U_C^{ii}) = 0.0025 \text{ \AA}^2$  for anthracene, which has been estimated from the X-ray data. This is somewhat smaller than the contributions of the internal modes of  $0.0031 \text{ \AA}^2$  so that these become important with respect to the accuracy obtained. This may explain why the fit of the thermal rigid-body parameters **T** and **L** to the vibration tensors **U**, is not convincing. Cruickshank calculates  $\sigma(U_C^{ii}) = 0.0043 \text{ \AA}^2$  from the r.m.s. difference between the  $U^{ik}(\text{obs})$  and  $U^{ik}(\text{calc TL})$  which is notably larger than  $0.0025 \text{ \AA}^2$ . For naphthalene, Cruickshank (1957a) does not give estimated standard deviations derived from X-ray data; however, since the *R* values for naphthalene and anthracene are about equal, we may also assume  $\sigma(U_C^{ii}) = 0.0025 \text{ \AA}^2$  for naphthalene. The contributions of the internal modes with  $0.0018 \text{ \AA}^2$  are comparatively small and thus do not seem to be very important. This is in agreement with the reasonable **TL** fit of  $\sigma(U_C^{ii}) = 0.0028 \text{ \AA}^2$ , obtained by Cruickshank.

Pawley (1971) refined the contributions of the internal modes to the vibration tensors of hydrogen and deuterium atoms by using neutron diffraction data. He found the parameters describing these contributions to be statistically highly significant. It is thus interesting to compare Pawley's results with ours. From Pawley's anisotropic data for the deuterium atoms we have calculated the isotropic average and multiplied by 2 to obtain the isotropic average for hydrogen atoms. We obtain  $0.022$ ,  $0.020$  and  $0.017 \text{ \AA}^2$  for naphthalene, anthracene, and pyrene respectively. The naphthalene value is in full agreement with our value of  $0.022 \text{ \AA}^2$ , whereas Pawley's anthracene value of  $0.020 \text{ \AA}^2$  is significantly smaller, and so is his pyrene value of  $0.017 \text{ \AA}^2$  for which we obtain  $0.036 \text{ \AA}^2$  by using the approximate formula equation (19). These results seem to confirm that Pawley's refinement of the thermal parameters of naphthalene is the best on an absolute standard, reaching  $R = 3.3\%$ , whereas the refinements of the anthracene and pyrene parameters are not as convincing.

We have also made the comparison of the values of  $C^{\text{ext}}$  from equations (13) and (17). With the values of  $C^{\text{int}}$  listed in Table 1 we obtain

$C^{\text{ext}}$ [equation (13)]	16.64,	20.46,	20.46 mole. $\text{\AA}^2$
$C^{\text{ext}}$ [equation (17)]	17.31,	21.67,	23.04 mole. $\text{\AA}^2$

for benzene, naphthalene, and anthracene respectively. With all molecules  $C^{\text{ext}}$  [equation (17)] is larger than  $C^{\text{ext}}$  [equation (13)] by about the value of  $C^{\text{int}}$ . [The benzene data are the least reliable ones since the diagonal components of the **L** tensor cannot be uniquely determined from the **U** tensors of the carbon atoms. We have thus used the value of  $L_{11}$  estimated by Cox *et al.* (1958).]

The numerical data of this comparison clearly show that, with the usual least-squares determination of the components of **T** and **L** from the uncorrected components of the **U** tensors, the components  $T^{ii}$  and  $L_{ii}$  have been found to be too large. It seems that the  $T^{ii}$  are mainly concerned since in equation (17) the term  $M(T^{11} + T^{22} + T^{33})$  contributes about 75% of the total with all three molecules.

The next four rows in Table 1, marked by *I1*, *I2*, *I5* and *I10* are given to illustrate the large effect of the low frequencies on  $C^{\text{int}}$ . *I1* represents the part of  $C^{\text{int}}$  that arises only from the lowest frequency. *I2*, *I5*, and *I10* represent the parts that arise from the two, five and ten lowest frequencies respectively. In the two following rows, marked by  $\bar{\nu}^1$  and  $\bar{\nu}^2$ , the two lowest frequencies are listed in units of  $\text{cm}^{-1}$ . With anthracene the lowest frequency of  $96 \text{ cm}^{-1}$  already contributes 28.4% to  $C^{\text{int}}$ , and with all molecules the ten lowest frequencies contribute more than 55% to  $C^{\text{int}}$ . The final two rows in Table 1 list the number of atoms in the molecule, *n*, and the constant *a* of equations (18) and (19). *a* was calculated from the known values of  $C^{\text{int}}$  and *n* with the aid of equation (18). Of course, *a* is only approximately constant. We find that  $a = 0.00150 \text{ mole.}\text{\AA}^2$  with a mean deviation of  $0.00011 \text{ mole.}\text{\AA}^2$  for the three molecules. A further value of *a* can be obtained from Johnson's (1970, Fig. 9.2) r.m.s. amplitude data of the cyclobutane molecule. From Johnson's data we calculate  $C^{\text{int}} = 0.59638 \text{ mole.}\text{\AA}^2$  and with  $n = 12$  we obtain  $a = 0.00166 \text{ mole.}\text{\AA}^2$ . Finally, the constant *a* can also be calculated from Becka & Cruickshank's (1963) data of hexamethylenetetramine, although these authors have only applied an approximate force constant model by assuming rigid  $\text{CH}_2$  groups. We find  $U_{C,\text{iso}}^{\text{int}} = 0.0020 \text{ \AA}^2$  and  $U_{N,\text{iso}}^{\text{int}} = 0.0016 \text{ \AA}^2$ . With  $n = 22$  we obtain  $a = 0.00120 \text{ mole.}\text{\AA}^2$  from the carbon atoms, and  $a = 0.00112 \text{ mole.}\text{\AA}^2$  from the nitrogen atoms. These somewhat lower values of the constant *a* may be due to the high symmetry of the  $(\text{CH}_2)_6\text{N}_4$  molecule,  $\bar{4}3m$ , and/or to the inaccuracies of the force constant model used.

## 5. Conclusions

We have seen that the contributions of the internal modes to the vibration tensors **U** increase largely with increasing number, *n*, of the atoms in the molecule. With larger molecules, having  $n \geq 15$ , the contributions of the internal modes are already considerable, and with accurate values of the components  $U^{ik}$  they should not be neglected when determining the **TLS**

parameters. With modern experimental methods structures having molecules of the size of anthracene can be refined to give  $R$  values of 3.5–5.0%, *cf. e.g.* Pawley (1971). If we assume an  $R$  value of 6% to hold as a standard of quality, the standard deviations for carbon atoms will be about 0.0012 Å<sup>2</sup> for both X-ray and neutron data. According to Table 1, the contributions of the internal modes for carbon atoms are about 0.0018 and 0.0031 Å<sup>2</sup> for  $n=12$  and  $n=18$  respectively. For hydrogen atoms they are much larger with about 0.022 and 0.037 Å<sup>2</sup> respectively. Thus it is obvious that with very accurate data and for molecules having  $n \geq 15$  the contributions of the internal modes cannot be neglected and thus give rise to errors in the TLS components if these are determined from uncorrected  $U$  tensors. If the  $U$  tensors of hydrogen atoms are not corrected, one always obtains erroneous TLS components, even for small molecules ( $n < 15$ ).

As the comparison of the values of  $C^{\text{ext}}$  of equations (13) and (17) with benzene, naphthalene, and anthracene has shown, the least-squares method of determining the thermal rigid-body parameters from the uncorrected  $U$  tensors has to be applied with caution. It is likely that with the use of this method the contributions of the internal modes will always be added to the TLS components and that this does not necessarily result in a bad fit of the TLS parameters. This view has also been expressed by Milledge (private communication). The reasons why this can happen are as follows. With many internal modes the mean-square amplitudes may have such a form that they could also have arisen from the external modes. An example is the butterfly-type of vibration of a flat molecule whose mean-square amplitude could also be generated by a libration of the molecule about the corresponding axis. Thus a good fit of the TLS parameters to the uncorrected  $U$  tensors does not necessarily imply that the TLS parameters are correct, *i.e.* that they represent only the external modes of the molecule. A bad fit would indicate more appropriately the existence of the internal modes as a source of systematic error and perhaps yield TLS parameters which are physically more correct. However, it seems that in most cases the least-squares method, applied to the uncorrected  $U$  tensors, does not result in a bad fit so as to correspond to the contributions of the internal modes but rather it leads to a better fit resulting in erroneous components of TLS.

For very accurate determinations of the TLS parameters of molecules having  $n \geq 15$  it is thus necessary to take care of the contributions of the internal modes by some means or other. One way of doing this is by Pawley's (1971) approach of introducing appropriate parameters in the refinement. Another possibility is to employ approximate force constants and to calculate the contributions of the internal modes to the  $U$  tensors explicitly, *cf.* Becka & Cruickshank (1963); Ellison *et al.* (1971). Perhaps subtracting the isotropic

averages, as determined from equation (11), from the uncorrected  $U$  tensors would also lead to improved values of the TLS parameters, although in this case the certainly present anisotropy of the mean-square amplitudes of the internal vibrations and the specific location of the atoms in the molecule would be neglected. Perhaps the reduction of the TLS components by a factor of  $C^{\text{ext}}$  [equation (13)]/ $C^{\text{ext}}$ [equation (17)] would lead to reasonable results if the uncorrected  $U$  tensors are used. Milledge (private communication) proposes to keep the components  $U^{ii}$  (calculated TLS) always smaller than the components  $U^{ii}$  (observed), since the latter contain the contributions of the internal modes whereas the former should not. Which of these (approximate) procedures, or which combination of procedures, proves to give the most accurate results remains a question for future investigation.

*Note added in proof:* The constant  $\mathbf{a}$  has been calculated for some further molecules for which the mean-square amplitudes are known. We give the molecule, the value of  $\mathbf{a}$  in mole.Å<sup>2</sup>, and the reference in succession: cyclopropene 0.00211, cyclopropene -  $d_4$  0.00282, cyclopropane 0.00152, cyclopropane -  $d_6$  0.00203 (Cyvin & Hagen, 1970); 1,2,5-oxadiazole 0.00239, 1,2,5-thiadiazole 0.00259, 1,2,5-selendiazole 0.00299, furan 0.00178, furan -  $d_4$  0.00221, thiophene 0.00206, thiophene -  $d_5$  0.00235 (Cyvin, Cyvin, Hagen & Markov, 1969); propane 0.00211, propane -  $d_8$  0.00329, (Cyvin & Vizi, 1970) P<sub>4</sub>O<sub>6</sub> 0.00518, P<sub>4</sub>O<sub>10</sub> 0.00365, (Cyvin & Cyvin, 1971). It seems that a constant value of  $\mathbf{a}$  can only be used for certain types of molecules. Thus for hydrocarbons and CHON compounds, which possess a system of strong bonds,  $\mathbf{a}$  is approximately constant. The mean value of  $\mathbf{a}$  for the quoted compounds of that type is 0.00197 mole.Å<sup>2</sup> and is somewhat larger than that given in the paper. If, however, weaker bonds are formed with heavy atoms like sulphur and selenium or with inorganic compounds the mean-square amplitudes and thus the value of the constant  $\mathbf{a}$  are enlarged.

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## Elastic Properties of Ammonium Oxalate Hydrate, Ammonium Hydrogen Oxalate Hemihydrate, and Ammonium Tetroxalate Dihydrate

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The elastic constants of the two orthorhombic crystals  $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  and  $(\text{NH}_4)\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  were determined by diffraction of light by ultrasonic waves. These constants and those of the triclinic  $(\text{NH}_4)\text{H}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  previously measured are correlated with the crystal structure. All three crystals show extreme elastic anisotropy which may be explained by the layer-like packing of the oxalate groups. The minimum elastic stiffness is observed normal to the  $\text{C}_2\text{O}_4$  planes, whereas the direction of the maximum elastic stiffness may be correlated with the course of the periodic bond chains. It is shown that hydrogen bonds make a considerable contribution to the elastic properties of crystals. Correlations between elastic behaviour, morphology, and optical properties are discussed.

### Introduction

In the present paper the elastic properties of three ammonium salts of oxalic acid are investigated: ammonium oxalate hydrate  $[(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , point group 22], ammonium hydrogen oxalate hemihydrate  $(\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , point group *mmm*), and ammonium tetroxalate dihydrate  $[\text{NH}_4\text{H}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ , point group  $\bar{1}$ ], which for brevity will be referred to as AO, AHO and ATO respectively.

Because of its polar properties AO has attracted special attention. Vasilevskaya, Kuznetsova, Rez & Sonin (1968) have reported large electro-optical effects, Izraelenko, Orlov & Kopsik (1968) and Orlov (1969) have made use of AO in producing optical second-harmonic generation and, finally, Fournel & Vergnoux (1971) have performed infrared spectroscopic measurements. It seemed worthwhile to extend the measurements to the determination of the elastic constants of AO as these have not been measured previously.

There seem to be no reports on the physical properties of AHO in the literature.

The elastic constants of ATO have been measured by us (Küppers & Siegert, 1970). In the present paper an attempt will be made to give a structural interpretation of the anisotropic elastic properties of ATO as well as of the two other oxalates.

### Methods

Single crystals of AO and AHO were grown from aqueous solutions at 35°C (Küppers, 1972a).

Sound velocities were measured by the Schaefer-Bergmann method as improved by Haussühl (1956): standing ultrasonic waves of about 15 Mc/s were excited in rectangular specimens (average dimension 1 cm, tolerance 1  $\mu$ ). The ultrasonic wave causes the diffraction of a light beam from a mercury lamp ( $\lambda = 546.07$  nm). The beam is focused through the crystal onto a film placed at a distance of about 2 m. Measurement of the distance between the diffracted light spots yields the sound velocity.

In order to determine the elastic constants of the two orthorhombic crystals, the velocities of the longitudinal waves propagating along [100], [010], and [001] were measured. Transverse waves in these directions produce no measurable diffraction of light because the elastic displacement in this case is parallel to one of the principal axes of the elliptical section of the indicatrix (Küppers, 1966). Furthermore, the velocities of the quasilongitudinal and quasitransverse waves in the directions [110]', [101]', and [011]' (as related to a Cartesian coordinate system with axes  $\mathbf{e}_i$  parallel to  $\mathbf{a}_i$ ) were measured. The third wave in these directions is a purely transverse wave and is, for the same reasons