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Temperature Factors for Internuclear Density Units. II. Considerations with Respect to Experimental Accuracy

By C. Scheringer

Fachbereich Geowissenschaften der Universität Marburg, D-3550 Marburg/Lahn, Germany (BRD)

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A simple two-parameter approximation for the vibration tensors of internuclear density units is introduced and numerical values are calculated. The approximation is used to estimate the errors in electron density distributions which are due to incorrect vibration tensors of the internuclear density units. It is concluded that, at the present state of experimental accuracy, the errors due to simple approximations for the temperature factors are hardly significant.

Introduction

In the preceding paper (Scheringer, 1977*a*) – hereafter referred to as SCHE – expressions for the temperature factors of internuclear density units were derived in the harmonic approximation. The application of these expressions in the experimental determination of electron density distributions is impaired by two facts. Firstly, neither the temperature factors for internuclear density units nor the coupling tensors can be determined by diffraction experiments. Secondly, the coupling tensors for the internal modes of molecules can only be calculated from a complete force-constant matrix, which is unknown in most cases. In view of these obstacles it is desirable to know approximate values for the vibration tensors of internuclear density units. The simplest approximation is the average of the vibration tensors of the adjacent nuclei. In this paper we establish a better approximation, and calculate the differences in the densities which we obtain with the average approximation and with our approximation. This difference is regarded as being representative of the magnitude of the errors which one encounters with the average approximation. We compare this difference (error) with the experimental errors in density distributions, and thus obtain a clue as to what accuracy for the vibration tensors of internuclear density units can be regarded as sufficient. We restrict our analysis to molecular crystals since these, at present, are the main objects of electron density determinations.

The reason why the vibration tensors of internuclear density units cannot be determined from X-ray data

Since the vibration tensors of internuclear density units appear in the structure factor, one would assume that they can be determined from the X-ray data. However this is usually impossible, mainly because of a too high correlation of the vibration components with other parameters. The structure factor, SCHE (2.10), contains the product $T_k(\mathbf{h})g_k(\mathbf{h})$ of the temperature factor and the Fourier transform of the kth density unit. The charge clouds between the nuclei are usually so diffuse that their Fourier transform $g_k(\mathbf{h})$ has already disappeared at small values of $\sin\theta/\lambda$; *i.e.* at about 0·6 Å^{-1} (Fritchie, 1966; Coppens, 1969; Scheringer, 1977*b*). Hence, with $g_k(\mathbf{h})\simeq 0$, $T_k(\mathbf{h})$ cannot be refined with the high-angle data. With the low-angle data, which one is forced to use, very high correlations of the vibration components to the shape parameters of the charge clouds appear and prevent a simultaneous refinement of the vibration and shape parameters. Thus, either one can only determine the whole product $T_k(\mathbf{h})g_k(\mathbf{h})$, or one has to keep the temperature factors $T_k(\mathbf{h})$ constant in order to be able to refine the shape parameters.

Our statement appears to contradict Hirshfeld (1976), who proposed the refinement of temperature factors and shape parameters simultaneously. However, Hirshfeld only considers the case of refining the temperature factors of the atomic cores. These cores are rather 'hard' and chemically constant, and their Fourier transforms do not disappear for $\sin\theta/\lambda > 0{\cdot}7$. In this case the high-angle data can be used to refine temperature factors of the atomic cores, and the low-angle data to refine the shape parameters of the charge distribution.

Obviously it is not a matter of principle that the temperature factors of internuclear density units cannot be determined from X-ray data. If we know the electron density distribution of a molecule exactly, and can introduce it into the refinement as a fixed quantity, then the X-ray data alone can be used to refine the temperature factors of all density units. This procedure establishes a possibility of determining the coupling tensors $\mathbf{U}_{rr'}$ from X-ray data. These tensors are needed, *e.g.* for calculating the thermal-motion bond-length correction (Scheringer, 1972*a*). In this context, the internuclear density units appear to be suited to the investigation of the dynamic relation of adjacent nuclei. With small molecules whose density distributions can be calculated quite accurately by quantum-chemical methods, the two-centre orbital products can be used as internuclear units whose vibration tensors are determined from the X-ray data.

An approximate formula for the vibration tensors of internuclear density units

A main result in SCHE was that the vibration tensors of internuclear density units $\mathbf{U}_k$ are always smaller than the average of the tensors $\mathbf{U}_r$ and $\mathbf{U}_{r'}$ of the adjacent nuclei. Let us denote this average by

$$\mathbf{U}_M=\alpha_1\mathbf{U}_1+\alpha_2\mathbf{U}_2, \qquad (1)$$

where $\alpha_1+\alpha_2=1$, *cf.* SCHE (2.4), and we obtain the tensor $\mathbf{U}_k$ for the density unit between the nuclei 1 and 2 by subtracting the positive definite tensor $\mathbf{A}_{12}$ from $\mathbf{U}_M$, *cf.* SCHE (2.13). Our approximation consists in introducing one, and later two, parameters K (instead of the six components of $\mathbf{A}_{12}$), and instead of SCHE (2.13) we write

$$\mathbf{U}_k=K\mathbf{U}_M, \quad K\le 1. \qquad (2)$$

The main content of this section is to estimate numerical values of K for different temperatures.

We can simplify our task at once, since a good approximation is known for the components of $\mathbf{U}_k$ in the direction of the bond vector $\mathbf{d}$:

$$K(\|\mathbf{d})=1, \ \mathbf{U}_k(\|\mathbf{d})=\mathbf{U}_M, \ \mathbf{A}_{12}(\|\mathbf{d})=\mathbf{0}. \qquad (3)$$

(3) is established by Hirshfeld's (1976) 'rigid-bond' criterion. (It was used by Hirshfeld to estimate the correctness of the refined vibration tensors.) The 'rigid-bond' approximation means that in the direction $\mathbf{d}$ of the bond only rigid translations occur. In physical terms, this approximation means that the stretching modes of the molecules are neglected, and only the bending modes are taken into account. Applying (2) and (3), we obtain the simplification

$$\mathbf{U}_k(\perp\mathbf{d})=K(\perp\mathbf{d})\mathbf{U}_M(\perp\mathbf{d}), \qquad (4)$$

i.e. we need only search for values of K in the directions perpendicular to the bond vector.

We shall determine $K(\perp\mathbf{d})$ separately for the external and internal modes of the molecules because the two types of modes can be separated for most molecules to a good approximation, and because they depend in different manners on the temperature. For the internal modes we make the further assumption that they do not depend on the temperature in the range from 0 to 300 K. Let us denote the contribution of the external modes to the vibration tensors by β and with (2) we can write

$$K=\beta K^{\rm ext}+(1-\beta)K^{\rm int}. \qquad (5)$$

In principle, $K^{\rm ext}$ and $K^{\rm int}$ have different values for each nucleus and each density unit in the molecule. We ignore this and assume an average value, valid for all density units. We look for values of β, $K^{\rm ext}$ and $K^{\rm int}$ in the following.

One possibility for determining β, which we do not use here, consists in determining **TLS** and some internal-mode parameters from the vibration tensors of the nuclei, as was done by Pawley (1971), Scheringer (1972*b*), Willis & Howard (1975). Here we try to determine β by analyzing the vibration tensors of crystal structures which have been determined at several temperatures. With benzene, naphthalene, and anthracene at room temperature, we conclude from an analysis of the internal frequencies that β should be larger than 0·9 for the C atoms, and $\beta\simeq0{\cdot}9$ for the H atoms (Scheringer, 1972*b*). From vibration tensors of cyanuric acid (Verschoor & Keulen, 1971) we conclude that for the transition from 300 to 100 K, the vibration components decrease by about a factor of three. With *p*-nitropyridine *N*-oxide Wang, Blessing, Ross & Coppens (1976) report a decrease by an average factor of six for the transition from 300 to 30 K. If we generalize these results for molecular crystals with essentially van der Waals binding forces and assume $\beta=0{\cdot}92$ for $T=300$ K, then we deduce $\beta=0{\cdot}75$ for 100 K, and $\beta=0{\cdot}5$ for 30 K. A value of about $\beta=0{\cdot}5$ for 30 K can also be obtained by considering the large standard deviations in the rigid-body (**TLS**) analysis performed by Wang *et al.* (1976). The large contribution of internal modes at 30 K prevents a good fit of the **TLS** components to the observed vibration tensors and results in the large value of $\sigma=0{\cdot}0015$ Å^2 for the calculated tensors. $3\sigma=0{\cdot}0045$ Å^2 is already more than 50% of the diagonal components of the observed tensors. If we assume the contribution of the internal modes to be approximately equal to 3σ, then we obtain $\beta\simeq0{\cdot}5$ for $T=30$ K.

With the external modes, $K^{\rm ext}<1$ arises only from the librations, *cf.* SCHE (2.13) and (4.2). For rigid-body translations (complete in-phase motions) we have for the two nuclei 1 and 2

$$\mathbf{U}_1=\mathbf{U}_2=\mathbf{U}_{12}=\mathbf{U}_k, \ \mathbf{A}_{12}=\mathbf{0}, \ K=1; \qquad (6)$$

i.e. the librations introduce an antiphase part into the coupling tensors and the tensors $\mathbf{A}_{12}$. We acquire the magnitude of this antiphase part, and hence values for $K^{\rm ext}$, from refined crystal structures for which a **TLS** analysis has been made. Using SCHE (2.13) and (4.2), for strong librations (50 degrees^2) and a bond length of $d=1{\cdot}3$ Å, we calculate values of $K^{\rm ext}$ between 0·8 and 0·9. Since the ratio of the libration tensor $\mathbf{L}$ to the nuclear tensor $\mathbf{U}$ varies only slightly with variations in temperature, *cf.* the data published by Verschoor & Keulen (1971), Scheringer (1973), Wang *et al.* (1976), the values of $K^{\rm ext}$ are essentially independent of the temperature.

With the internal modes of a molecule the antiphase part will, as a rule, dominate. A diatomic molecule has only one internal mode, and it is antiphase. With an increasing number of atoms in the molecule, a larger in-phase part will be introduced. Let us consider the cases of complete antiphase motion and equal in-phase and antiphase motion (uncorrelated motion), since these are the extremes between which the sum of the internal modes of a molecule must be located.

(1) *Complete antiphase motion*

$$\mathbf{U}_1=\mathbf{U}_2=\mathbf{U}_M,\ \mathbf{U}_{12}=-\mathbf{U}_1,\ \mathbf{U}_k=(2\alpha_1-1)^2\mathbf{U}_M. \quad (7)$$

For $\alpha_1=\frac{1}{2}$, $\mathbf{U}_k$ is zero and thus attains its minimum absolute value. A density unit at the midpoint between two nuclei remains fully at rest. This result agrees well with the exact calculation (within the limits of the Born–Oppenheimer approximation) for the H_2^+ ion: the dynamic density is found to be practically equal to the static density in the region between the two nuclei (Thomas, 1973).

(2) *Uncorrelated motion*

$$\mathbf{U}_{12}=\mathbf{0},\ \mathbf{U}_k=\alpha_1^2\mathbf{U}_1+\alpha_2^2\mathbf{U}_2=\mathbf{U}_M-\alpha_1\alpha_2(\mathbf{U}_1+\mathbf{U}_2). \quad (8)$$

For the midpoint position, $\alpha_1=\alpha_2=\frac{1}{2}$, we find $\mathbf{U}_k=\frac{1}{2}\mathbf{U}_M$, *i.e.* $K=\frac{1}{2}$.

With the antiphase part dominating in the internal modes, we expect the values of K^{int} to lie between 0 and 0·5. With an increasing number of atoms in the molecule, K^{int} will also increase. Thus, we estimate $K^{\text{int}}(\perp\mathbf{d})=0{\cdot}3$ for smaller molecules, and $K^{\text{int}}(\perp\mathbf{d})=0{\cdot}4$ for larger molecules.

We now calculate values of K from (5), and use $K^{\text{ext}}=0{\cdot}9$, $K^{\text{int}}=0{\cdot}4$, and $\beta=0{\cdot}92$, 0·75, and 0·50 for $T=300$, 100, and 30 K respectively. We obtain $K(\perp\mathbf{d})=0{\cdot}86$, 0·78, and 0·65, *i.e.* we obtain reductions of the average tensor $\mathbf{U}_M$ of 14, 22 and 35% respectively.

Experimental data of high quality, such as those collected for *p*-nitropyridine *N*-oxide by Wang *et al.* (1976), will lead to standard deviations $\sigma(\mathbf{U}_r)$ which are equal to 3–4% of the diagonal components U_r^{ii}. If we assume the real error to be 3σ, then we obtain an error in the vibration tensors of 9–12% of their diagonal components. Hence, for room temperature, the deviation of the tensors $\mathbf{U}_k$ from the average tensor $\mathbf{U}_M$, with 14%, is nearly significant, whereas for the two low temperatures the deviations with 22 and 35% respectively are highly significant.

Vibration tensors in electron density determinations

Here we discuss two somewhat different cases: (1) The refinement of electron density models, and (2) the conversion of quantum-chemically calculated (static) densities into dynamic densities.

In the refinement of density models, incorrect temperature factors give rise to incorrect densities. In the following we shall consider the question of how large the errors will be in the densities, if the average approximation, $\mathbf{U}_k(\perp\mathbf{d})=\mathbf{U}_M(\perp\mathbf{d})$, *i.e.* $K(\perp\mathbf{d})=1$, is used. Here we adopt the point of view that our approximation, derived in the last section, gives the correct order of magnitude for the vibration tensor $\mathbf{U}_k$. The difference in the densities, obtained by using $\mathbf{U}_M$ and $\mathbf{U}_k$, is then regarded as the order of magnitude of the errors in the densities which one obtains when using the average tensor $\mathbf{U}_M$. We restrict our investigation to the heights of bond peaks and represent the peaks by Gaussian distributions (Scheringer, 1977*b*). The peak maximum which is obtained after deconvolution with the (too large) tensor $\mathbf{U}_M$ is higher than that obtained after deconvolution with the (correct) tensor $\mathbf{U}_k$. In the numerical calculations, we applied (3) and (4) with the values of β, K^{ext} and K^{int} given above. The calculation of the peak heights is described in detail elsewhere (Scheringer, 1977*b*). For the C–C valence peaks with an occupation of $q=0{\cdot}8$ electrons the differences in the peak heights are in the range 0·014–0·020 e Å^{-3}. For the sharper peaks of deformation densities with $q\simeq0{\cdot}2$ electrons, the differences are in the range 0·030–0·070 e Å^{-3}. These differences vary only slightly with the temperature because, with increasing temperature (and increasing vibration tensors), the factor K also increases and so compensates for the increase of the vibration tensors.

When converting quantum-chemically calculated densities into dynamic densities an error corresponding to the use of the average tensor can hardly be avoided. The reason is as follows: a large part of the overlap densities (about two thirds) already arises from the one-centre orbital products (Hase, Reitz & Schweig, 1976), and only the smaller part arises from the two-centre orbital products. Since the one-centre products also contribute density to the atomic cores, the vibration tensors of the respective nuclei are used for these products. Hence, the region of the bond is made dynamic with the average tensors to about two thirds, provided the correct tensors $\mathbf{U}_k$ are used for the two-centre orbital products. The error which arises is about two thirds of the error mentioned above, *i.e.* with deformation densities about 0·02–0·047 e Å^{-3} in the bond peaks of the static density which has been made dynamic.

At present electron density distributions determined by experiment have, at best, standard deviations of about 0·02–0·05 e Å^{-3} (Rees, 1976). With X–N maps one can assume that the errors are somewhat smaller since no model of the molecular density distribution is used. Thus, the errors in the X–N maps are only due to experimental and phase errors. The comparison of our approximation with the average approximation, $K(\perp\mathbf{d})=1$, shows that the errors in the densities due to the use of incorrect temperature factors are about as large as the experimental errors. Thus, at present, the average tensor $\mathbf{U}_M$ can probably be tolerated for most experimental investigations. Similarly, for a comparison with experimental densities, the error described in the conversion of quantum-chemically calculated densities can in most cases be tolerated. On the other hand, the approximation developed in this paper, $K(\parallel\mathbf{d})=1$, $K(\perp\mathbf{d})=0{\cdot}86$, 0·78 and 0·65 for $T=300$, 100, and 30 K respectively, is certainly better than the average approximation, and its application is comparatively easy. With more exact diffraction data, however, one will be forced to determine more exact temperature factors for internuclear density units.

Then the coupling tensors for the internal modes of the molecule have to be calculated from a complete force-constant matrix. We do not see a solution in which the quantum-chemically calculated static densities can correctly be converted to dynamic densities.

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X-ray Diffraction Study of the Structure of 1-Propanol at −25°C

BY A. MIKUSIŃSKA-PLANNER

Optics Section of the Institute of Physics, A. Mickiewicz University, Poznań 60–780, *Poland*

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Molybdenum *Kα* X-radiation, monochromated by an NaCl single crystal, was scattered in 1-propanol at −25°C. The angular distribution of the scattered X-ray intensity was determined and used for the calculation of the experimental pair function. On the basis of some models of the structure of liquid 1-propanol, the theoretical curves of pair functions were calculated and then compared to the experimental curve. The most probable model of the liquid is that of statistically distributed chains of 1-propanol molecules. Such chains are created by intermolecular bonds of the O–H···O type, the length of which is 2·65 Å. The angles between the O···O bonds have a value between 100 and 110°. In this model the oxygen and equivalent carbon atoms all lie in the same plane, and the carbon atoms of the individual molecules are in parallel planes, inclined at an angle of 80° to the oxygen-containing plane. The inhibited rotation of the $(CH_2)_2CH_3$ group around the O–C(1) bond and the free rotation of the CH_3 group around the C(2)–C(3) bond are possible.

Introduction

The first X-ray structural studies of aliphatic alcohols were carried out by Stewart & Morrow (1927). Methanol was the subject of the structural studies of Zachariasen (1935). According to the structural model proposed by Zachariasen, the methanol molecules conglomerate into associated polymer chains by hydrogen bonding. This model was later confirmed by Harvey (1938). Ethanol at 25°C and −75°C was also studied by Harvey (1939), while Prietzschk (1941) studied it in the super-cooled state at −150°C. Both these authors discovered the tendency of ethanol molecules to associate by the creation the hydrogen bridges of OH groups. The experimental results of Harvey and Prietzschk were confirmed theoretically by Jagodzinski (1947). The structural X-ray analysis of aliphatic alcohols was carried out by Ukrainian scientists (Golik, Skryshevskii & Adamienko, 1967; Golik, Skryshevskii & Ravikovich, 1954). Their studies confirmed the tendency of alcohol molecules to associate at room temperature as well as the increase of coordination number from 3 for amyl alcohol to 5 for decyl alcohol.

This paper shows the results of structural studies of 1-propanol at −25°C. 1-propanol at room temperature was investigated by Golik, Skryshevskii & Ravikovich (1954), but the plane model of the molecule suggested by them is not satisfactory and does not seem to be probable.

For a molecular liquid the interpretation of the maxima of the radial distribution function of electron density is rather difficult because it often happens that several interacting atom pairs with comparable interatomic distances can be attributed to one maximum. This is the reason why it is impossible to evaluate the coordination number only on the basis of the comparison between the surface areas of the distribution curve maxima and the surface areas calculated theoretically. In practice the pair function method, which is precise and approximation-free, is applied.

Experimental procedure

In the X-ray study of 1-propanol Mo *Kα* radiation, monochromatized by a ground crystal monochromator set in the primary beam, was used. Samples of the alcohol at −25°C were put into a liquid holder