Acta Cryst. (1982). A**38**, 138–142

The Use of Spectroscopic Data in the Least-Squares Refinement of Diffraction-Obtained Structure Parameters. An Example: $K_2C_2O_4.H_2O$

By Anders Eriksson, Kersti Hermansson, Jan Lindgren and John O. Thomas

Institute of Chemistry, University of Uppsala, Box 531, *S*-751 21 *Uppsala, Sweden*

(*Received* 27 *August* 1981; *accepted* 22 *September* 1981)

Abstract

A method is presented in which parameters obtained from vibrational spectroscopy are used in the least-squares refinement of positional and thermal parameters obtained from diffraction data. The method involves the calculation of those contributions to the temperature factors not well described by the second-rank tensor approximation conventionally used in crystal structure determinations. Expressions are given for the temperature-factor contributions from vibrational motion on an arc and from anharmonic linear motion. The method is applied to the water molecule in dipotassium oxalate monohydrate, $2K^+.C_2O_4^=.H_2O$. Refinements using vibrational data are compared with a conventional refinement; the latter are shown to give considerable systematic errors in the geometrical parameters for the water molecule.

Introduction

The conventional approach to the treatment of thermal vibration in crystallographic work is to associate with each atom a second-rank vibrational tensor. The components of the tensor (B's or β_{ij}'s) are generally derived from a least-squares refinement procedure. It is not uncommon, however, that inadequacies in this approach become apparent in accurate work. Two major inadequacies are neglect of non-rectilinear and of anharmonic vibrational motion (Fig. 1). Both tend to be present to a non-negligible extent for molecular crystals, and various approximations have been suggested to take these into account, *e.g.* the use of **TLS** tensors (Schomaker & Trueblood, 1968), higher cumulants (Johnson, 1969), *etc.* These have proved useful in some cases, but inapplicable in others: typically, the rigid-molecule assumption can be at fault in the use of **TLS** tensors, or troublesomely high correlations can be encountered in the refinement of higher cumulants.

Particularly severe demands are imposed on the adequacy of the vibrational description of a molecule in electron density work, where an accurate vibrational model is essential to a successful separation of thermal and valence density effects in the data (see, for example, Harel & Hirshfeld, 1975). This introduces special complications for the case of the *water molecule* in crystal hydrates, where rigid-molecule assumptions are patently inappropriate.

We examine here, therefore, the technical possibility of making use of vibrational spectroscopic data for the water molecules in a crystal hydrate system to ascertain their vibrational motion, and of subsequently including this description in a least-squares refinement. We illustrate the method in the refinement of single-crystal neutron diffraction data for $K_2C_2O_4.H_2O$. It is planned to include this procedure in a later electron density study of this same compound.

The method

We consider here two types of vibrational motion where the assumptions implicit in the use of the second-rank **β**-tensor formalism break down: rotational motion where the nucleus moves on an arc and anharmonic linear motion. The principle of the method here is to derive an explicit description of these two types of motion from a normal coordinate analysis (NCA) of the vibrational motion of the molecule. The NCA makes use of wavenumbers assigned on the basis

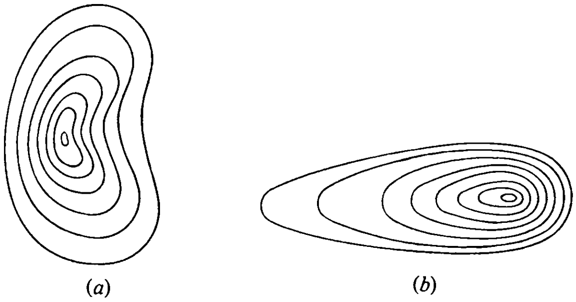

(*a*) (*b*)

Fig. 1. Probability densities for (*a*) non-rectilinear motion and (*b*) linear anharmonic motion. Both these types of motion are convoluted with translational motion to give a two-dimensional density.

0567-7394/82/010138-05$01.00

of vibrational spectroscopic data. The result from the NCA is primarily the normal modes of vibration. From these, vibrational amplitudes are easily calculated (see, for example, Cyvin, 1968).

Let us consider the structure-factor expression as it is usually written in the neutron diffraction case:

$$F(\mathbf{H}) = \sum_{\text{nuclei } k} b_k \exp(i2\pi \mathbf{H}\mathbf{r}_k)\, T_k(\mathbf{H}), \qquad (1)$$

where b_k is the scattering length, $\mathbf{H}$ the scattering vector, $\mathbf{r}_k$ the position and $T_k(\mathbf{H})$ the temperature factor. Introduction of the second-rank $\boldsymbol{\beta}$-tensor formalism gives

$$T_k(\mathbf{H}) = \exp(-2\pi^2\, \mathbf{H}\boldsymbol{\beta}_k\, \mathbf{H}). \qquad (2)$$

Each normal mode contributes to the temperature factor such that it is possible to write the temperature factor for a given $\mathbf{H}$ as a product:

$$T_k(\mathbf{H}) = \prod_{\substack{\text{normal}\\ \text{modes } n}} T_{k,n}(\mathbf{H}). \qquad (3)$$

Our approach is to use the information from the NCA to calculate those $T_{k,n}(\mathbf{H})$ factors which do not satisfy the assumptions implicit in the use of the second-rank tensor approximation. This has to be done for certain nuclei and normal modes judiciously selected on the basis of the NCA. Contributions calculated in this way are multiplied into the $T_k(\mathbf{H})$ calculated using a conventional crystallographic computer program which refines $\boldsymbol{\beta}_k$ and $\mathbf{r}_k$. For clarity, the right-hand side of (3) can be split conveniently into three parts:

$$T_k(\mathbf{H}) = T_{k,\mathrm{ref}}(\mathbf{H}) \prod_{n_1} T_{k,n_1}(\mathbf{H}) \prod_{n_2} T_{k,n_2}(\mathbf{H}). \qquad (4)$$

$T_{k,\mathrm{ref}}(\mathbf{H})$ is refined in the normal way while the factors $T_{k,n_1}(\mathbf{H})$ (for motion on an arc) and $T_{k,n_2}(\mathbf{H})$ (for anharmonic linear motion) are calculated using the appropriate equations [see (5) and (8) below]. For the refinements we have used the computer program *UPALS* (Lundgren, 1979).

Let us now consider the specific contributions to the temperature factors from the two types of motion referred to above.

Motion on an arc

An expression for temperature factors has been given by Willis & Pryor (1975), equation (6.29). Let us consider here motion in only one plane, so their equation is reduced to

$$T_{k,n_1}(\mathbf{Q}) = (1 + iL_{11}\, aQ_3)^{-1/2} \times \exp\{L_{11}\, a^2\, Q_2^2/[2(1 + iL_{11}\, aQ_3)]\}, \qquad (5)$$

where $\mathbf{Q}$, with components Q_1, Q_2 and Q_3, is the scattering vector in an orthogonal coordinate system with nucleus k on axis 3 at a distance a from the rotational axis 1 (Fig. 2). L_{11} is the mean-square amplitude of the angle θ_1. The a values, L_{11} values and the coordinate transformations that give Q_1, Q_2 and Q_3 from h, k and l are obtained from the NCA. We have also applied the approximation to (5) given by Willis & Pryor (1975), equation (6.31), here simplified to be valid for motion in one plane only:

$$T_{k,n_1}(\mathbf{Q}) = \exp(-\tfrac{1}{2}L_{11}\, a^2\, Q_2^2)(1 - i\tfrac{1}{2}L_{11}\, aQ_3 + \tfrac{1}{2}L_{11}^2\, a^3\, Q_2^2\, Q_3). \qquad (6)$$

(In the book by Willis & Pryor there is a misprint in the last term: L_{11} appears instead of L_{11}^2.) The term $-i\tfrac{1}{2}L_{11}\, aQ_3$ (first order in Q) is shown by Willis & Pryor to give the correction to the positional parameters $\mathbf{r}_k$ in (1).

Anharmonic linear motion

The temperature factor of a nucleus is given by the Fourier transform of its probability density function (Willis & Pryor, 1975, § 4.3):

$$T_k(\mathbf{Q}) = \int p_k(\mathbf{u}) \exp(i\mathbf{Q}\mathbf{u})\, \mathrm{d}^3\, \mathbf{u}, \qquad (7)$$

where $\mathbf{u}$ is a displacement vector and $p_k(\mathbf{u})$ is the probability density function for nucleus k along the vector $\mathbf{u}$. Performing the integration numerically for normal mode n_2, and choosing the coordinate system such that the displacement $\mathbf{u}$ is along axis 1, (7) is written

$$T_{k,n_2}(\mathbf{Q}) = \sum_{u=u_a}^{u_b} p_k(u) \exp(iQ_1\, u)\, \Delta u. \qquad (8)$$

Q_1 and u are the components of $\mathbf{Q}$ and $\mathbf{u}$ along axis 1, u_a and u_b are summation limits (Fig. 3). The probability

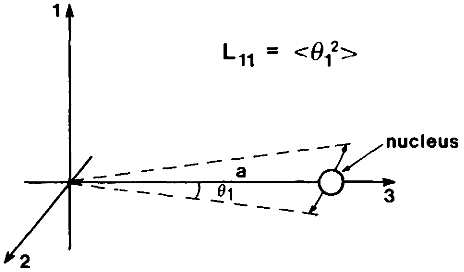


Fig. 2. Coordinate system for a nucleus vibrating on an arc. Axis 1 is the rotational axis.

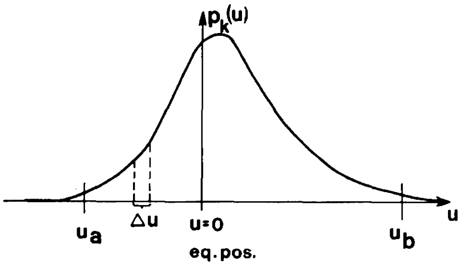


Fig. 3. Probability density function for a nucleus moving in an anharmonic potential.

density function for a hydrogen nucleus taking part in anharmonic stretching vibrations can be obtained using an equation given by Morse and modified by Ibers (1959). This function includes a harmonic wavenumber and an anharmonicity coefficient, the values of which are obtained conveniently from spectroscopic observations of X–H and X–D stretching vibrations of isotopically dilute molecules (Berglund, Lindgren & Tegenfeldt, 1978).

Application to the water molecule in $K_2C_2O_4.H_2O$

We have used the observed structure factors taken from the neutron diffraction study at 297 K by Sequeira, Srikanta & Chidambaram (1970) to carry out the refinements. Our attempt with the second-rank tensor approximation gave, within a standard deviation, the same result as obtained by Sequeira *et al.* The water molecule is on a C_2 site and its geometry and immediate environment are shown in Fig. 4.

The NCA was based on a model in which the water molecule was allowed to vibrate in a force field comprising its internal force field and an external force field from stationary surrounding atoms. The nine resulting normal modes can be described approximately as three internal, three rotational and three translational vibrations (Fig. 5). The details of the NCA have already been described by Eriksson, Hussein, Berglund, Tegenfeldt & Lindgren (1979).

From the form of the normal modes (Fig. 5) it was concluded that vibrations with considerable amplitudes and along arcs occur for the hydrogen nuclei in the bending vibration (at 1697 cm^{-1}) and in the three rotational vibrations, twisting, wagging and rocking (at 761, 756 and 656 cm^{-1}, respectively). The vibration at 99 cm^{-1} can be described as a translation out-of-plane coupled with a rotation around an axis parallel to the H—H direction. The individual nuclei move on arcs so that no fundamental difference in the treatment is needed. The contribution to the structure factors from each component of motion along an arc was calculated according to (5) and used in the refinement program as described above. Equation (6) was also applied with and without the third-order term.

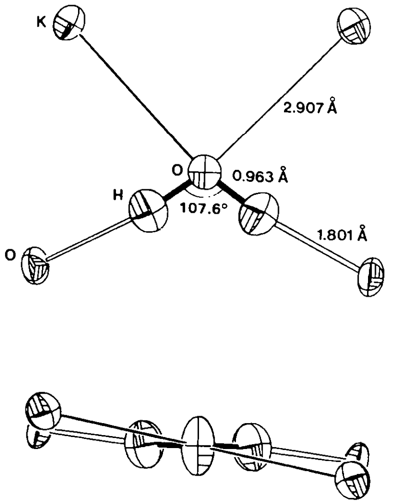


Fig. 4. The water molecule in $K_2C_2O_4.H_2O$ viewed perpendicular to the molecular plane and along the twofold axis. The hydrogen-bond-accepting oxygen atoms belong to oxalate ions.

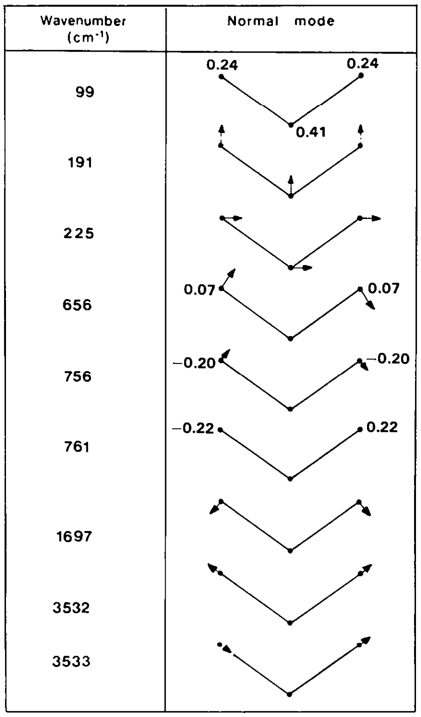


Fig. 5. Normal modes of the water molecule in $K_2C_2O_4.H_2O$. The displacement vectors are scaled to twice the root-mean-square amplitudes of vibration (in Å) at 300 K. The numbers indicated are out-of-plane components.

Anharmonic linear motion occurs for the O—H stretching vibrations at 3533 and 3532 cm^{-1} (Fig. 5). We used the probability density function given by Ibers (1959) with the harmonic wavenumber $\omega_e = 3532$ cm^{-1} and the anharmonicity coefficient $2\omega_e x_e = 283$ cm^{-1} (Eriksson, Berglund, Tegenfeldt & Lindgren, 1979) to calculate the contributions to the structure factors according to (8). The u_a, u_b and Δu values (Fig. 3) were chosen as −0·26, 0·37 and 0·01 Å, respectively. A maximum was found for $p_k(u)$ at $u \simeq 0{\cdot}015$ Å.

The geometrical parameters as obtained from the refinements are listed in Table 1. Model I employs the conventional second-rank tensor approximation, while in model II we have applied all the available spectroscopic information to calculate structure factors that are not well described by model I. The effects of the two different types of motion included in model II are apparent from the results of the application of models III and IV.

The thermal parameters obtained from the refinements with models I and II are depicted in Fig. 6. The ellipsoids in Fig. 6(*b*) thus show the influence of the normal vibrations not considered in the calculations using (5) and (8). Table 2 gives mean-square amplitudes of vibration for models I and II. There is a disagreement between the values for oxygen in Table 2 and the values given by Sequeira *et al.* (1970) (Table 4 in their paper); this is due to an error in their table. Nevertheless, their statement that there is excellent agreement between neutron and X-ray (Hodgson & Ibers, 1969) values for the thermal parameters of the oxygen atom still holds.

Discussion

Least-squares refinements using a third-rank tensor γ (Johnson, 1969) to describe the thermal vibrations are seldom reported in the literature. This is probably due to the fact that such refinements have not converged successfully, rather than that they have not been tried. Our refinement of ten γ values for hydrogen and four for oxygen in the water molecule of $K_2C_2O_4.H_2O$ resulted in large standard deviations and large correlations. The results of the refinement were not considered meaningful.

In this paper we have shown how explicit information from vibrational spectroscopy can be used to improve the thermal model for a water molecule, and in this way facilitate a more sophisticated analysis of diffraction-obtained geometrical and thermal parameters. The simple model used for the vibrations of the water molecule has earlier been shown to reproduce experimental wavenumbers and wavenumber shifts in connection with isotopic substitutions (Eriksson, Hussein, Berglund, Tegenfeldt & Lindgren, 1979), and to explain the temperature dependence of deuteron quadrupole splittings (Berglund, Eriksson, Lindgren & Tegenfeldt, 1979).

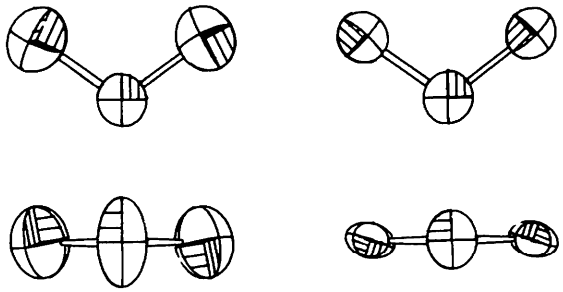
The geometry of the water molecule as obtained from model II and shown in Table 1 does not differ greatly from that obtained with model I. This is purely coincidental, however, as can be seen from the results of models III and IV. Two effects, an elongation due to

Table 1. *The geometry of the water molecule in* $K_2C_2O_4.H_2O$ *as refined using the different vibrational models (see text)*

Estimated standard deviations, which are given within parentheses, emerge from the diffraction experiment.

I: Conventional refinement; calculation of structure factors according to II: equations (5) and (8); III: equation (8); IV: equation (5); V: equation (6); VI: equation (6) without third-order term.

Model	R_{O-H} (Å)	R_{H-H} (Å)	α_{H-O-H} (°)
I	0·963 (3)	1·557 (5)	107·8 (4)
II	0·967 (2)	1·552 (4)	106·8 (3)
III	0·943 (3)	1·523 (4)	107·8 (3)
IV	0·988 (3)	1·586 (5)	106·8 (3)
V	0·988 (3)	1·586 (5)	106·8 (3)
VI	0·989 (3)	1·588 (5)	106·8 (3)



(*a*) (*b*)

Fig. 6. Thermal ellipsoids for the water molecule in $K_2C_2O_4.H_2O$ drawn at 50% probability level and viewed in two perpendicular directions. The figures show the result of a refinement according to (*a*) model I and (*b*) model II. *Note*: the ellipsoids in (*b*) do not include the vibrational motion that is calculated using equations (5) and (8) for the selected normal modes.

Table 2. *Mean-square amplitudes in* Å^2 *for models* I *and* II

Cartesian displacement coordinates have been chosen so that x is parallel to the H—H direction, y is along the twofold axis and z is perpendicular to the molecular plane. Estimated standard deviations from the refinements are given within parentheses.

	Oxygen model I This work	Oxygen model I Hodgson & Ibers (1969)	Oxygen model II This work	Hydrogen model I This work	Hydrogen model II This work
$\langle xx \rangle$	0·0219 (3)	0·0241 (1)	0·0219 (3)	0·0321 (3)	0·0228 (2)
$\langle yy \rangle$	0·0248 (11)	0·0247 (8)	0·0247 (10)	0·0385 (13)	0·0237 (10)
$\langle zz \rangle$	0·0743 (16)	0·0801 (19)	0·0322 (11)	0·0510 (15)	0·0128 (9)
$\langle xy \rangle$	0	0	0	0·0046 (3)	−0·0016 (2)
$\langle xz \rangle$	−0·0004 (2)	−0·0030 (2)	−0·0003 (2)	−0·0033 (2)	−0·0036 (2)
$\langle yx \rangle$	0	0	0	−0·0002 (12)	−0·0005 (8)

anharmonic stretching and a contraction due to rotational vibrations, almost cancel for the O—H and H—H distances. For a more weakly bonded water molecule, for which the rotational vibrations occur at lower wavenumbers, the neutron-diffraction-obtained O—H distance can differ by about 0·03 Å from the equilibrium position (Eriksson, Berglund, Tegenfeldt & Lindgren, 1979).

In the ideal case in which all vibrations not satisfying the second-rank tensor approximation are instead described by our vibrational model, the remaining vibrations will be rigid translations of the water molecule. The associated thermal ellipsoids should thus be identical for the oxygen and hydrogen nuclei. Considering Fig. 6(*b*) and Table 2, the *in-plane* part of the ellipsoids could well be the result of translational vibrations only. However, a vibration involving some rotational character would seem to be necessary to explain the difference between the *out-of-plane* amplitudes for the oxygen and hydrogen nuclei. Although IR and Raman spectroscopic measurements show no such vibration other than those used in our calculations, it is nevertheless possible that such a vibration (or vibrations) with a non-zero wavevector can exist. In particular, if the rotational vibration at 99 cm^{-1} has lower wavenumbers for non-zero wavevectors, and has roughly the same form, the result of Fig. 6(*b*) is the expected one. Also, acoustic modes are not considered in our simple model.

It may also be that there are errors in the diffraction determination of the vibrational amplitudes. The accuracy of the thermal parameters obtained from diffraction has been questioned (see, for example, Willis & Pryor, 1975, § 4.7). In the case of $K_2C_2O_4.H_2O$, the vibrational amplitudes obtained for non-hydrogen atoms from neutron (Sequeira *et al.*, 1970) and X-ray diffraction (Hodgson & Ibers, 1969) are very similar, thus giving credibility to their claimed accuracy.

The method presented in this paper has been applied with some success to the case of $K_2C_2O_4.H_2O$. It is relevant to question whether the same treatment can be applied to a general water molecule in a hydrate. Several requirements have to be fulfilled. It is necessary for a successful normal coordinate analysis that extensive spectroscopic work (IR, Raman, isotopic substitution, polarized radiation) is done to assign the vibrations. Such an assignment is naturally more difficult for a hydrate containing more than one type of water molecule in the unit cell, and for hydrates with low site symmetry for the water molecule. In $K_2C_2O_4.H_2O$, it was possible to assign nine vibrations localized to the water molecule. For hydrates containing molecules or ions with masses comparable to that of water (*e.g.* $LiOH.H_2O$), difficulties are anticipated in finding such localized vibrations at low wavenumbers. The application of (5) also assumes that no correlation exists between certain rotational and translational vibrations, *i.e.* no screw motion occurs (Willis & Pryor, 1975, § 6.6).

It should finally be noted that the method need not be applied in its entirety; anharmonicity in the stretching vibrations of a water molecule can be considered in isolation, for example. Generally speaking, (5) and (8) can be applied to any molecule provided that the normal vibrations are known. This can sometimes be done without making a sophisticated normal-coordinate analysis, *e.g.* for X—H stretchings, $—CH_3$ and NH_3 twistings.

References

Berglund, B., Eriksson, A., Lindgren, J. & Tegenfeldt, J. (1979). *J. Mol. Struct.* **52**, 113–118.

Berglund, B., Lindgren, J. & Tegenfeldt, J. (1978). *J. Mol. Struct.* **43**, 169–177.

Cyvin, S. J. (1968). *Molecular Vibration and Mean-Square Amplitudes of Vibration.* Amsterdam: Elsevier.

Eriksson, A., Berglund, B., Tegenfeldt, J. & Lindgren, J. (1979). *J. Mol. Struct.* **52**, 107–112.

Eriksson, A., Hussein, M. A., Berglund, B., Tegenfeldt, J. & Lindgren, J. (1979). *J. Mol. Struct.* **52**, 95–105.

Harel, M. & Hirshfeld, F. L. (1975). *Acta Cryst.* B**31**, 162–172.

Hodgson, D. J. & Ibers, J. A. (1969). *Acta Cryst.* B**25**, 469–477.

Ibers, J. A. (1959). *Acta Cryst.* **12**, 251–252.

Johnson, C. K. (1969). *Acta Cryst.* A**25**, 187–194.

Lundgren, J.-O. (1979). Report UUIC-B13-04-04, Institute of Chemistry, Univ. of Uppsala.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Sequeira, A., Srikanta, S. & Chidambaram, R. (1970). *Acta Cryst.* B**26**, 77–80.

Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography.* Cambridge Univ. Press.