the generality of the method of choosing restraints described here.

A detailed comparison of the met and azidomet complexes is beyond the scope of this paper and will be reported elsewhere.

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Analysis of the Thermal Parameters of the Water Molecule in Crystalline Hydrates Studied by Neutron Diffraction

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Abstract

A survey is given of the thermal parameters of 150 water molecules in crystalline hydrates determined by neutron diffraction. The accuracy of the thermal parameters has been examined and rigid-bond tests revealed systematic errors for approximately 25% of the molecules. Considering only the most precise and accurate studies, good agreement is obtained between vibrational amplitudes derived from diffraction and spectroscopy. The influence of the immediate environment on the vibrations of the water molecule has also been investigated. A positive correlation is found between H···O hydrogen-bond distances and librational amplitudes. The coordination geometry around the O atom is shown to influence the vibrational amplitudes of the O atom.

Introduction

Several attempts have been made in the past to test the validity of diffraction-obtained thermal parameters. Particularly relevant is the study of hexamethylene-tetramine by Willis & Howard (1975), who showed that the neutron-diffraction thermal parameters were in close agreement with those obtained independently from the phonon-dispersion curves. Their result was a very important one since it is difficult to determine the accuracy of the absolute magnitudes of neutron-diffraction-obtained vibrational amplitudes. It was also most encouraging, especially since an earlier IUCr project (Hamilton & Abrahams, 1970) had created a rather depressing picture of the accuracy of thermal parameters.

Recently, Trueblood & Dunitz (1983) have used

diffraction data to obtain torsional amplitudes and force constants for internally librating groups in molecules. They used 'vibration parameters derived within the last decade from diffractometer data of relatively high precision'. Their study confirms the impression of a general improvement in data collection and treatment procedures which has led to higher precision and accuracy in the resulting thermal parameters.

Water is that molecule studied most extensively by neutron diffraction. Chiari & Ferraris (1982) have published an extensive survey of the geometry and environment of 183 water molecules. Their survey is based on papers published up until 1980. To date (March 1983), some 250 water molecules have been investigated by neutron diffraction. Moreover, spectroscopic studies (IR, Raman) and normal coordinate calculations (see, for example, Falk & Knop, 1973; Pedersen, 1975; Eriksson & Lindgren, 1978a) have provided information on vibrations localized to the water molecule in a crystal. On the whole, the situation would seem particularly favourable to embark upon an analysis of the vibrational parameters for the water molecule.

This paper surveys neutron-diffraction-determined vibrational parameters for the water molecule in crystalline hydrates. We discuss their reliability, and put forward some criteria by which to judge accuracy and select water molecules for further analysis. The magnitudes of the vibrational amplitudes and their dependence on the geometry and type of water-molecule environment are presented. Comparisons are made with results from spectroscopy and normal coordinate calculations.

Geometry and vibrations of the water molecule in hydrates

Chiari & Ferraris (1982) found the average neutron-diffraction-determined geometry of the water molecule in crystalline hydrates to be $0 \cdot 963$ Å for the O—H distance and $107 \cdot 0°$ for the H—O—H angle.

Almost all water molecules donate two hydrogen bonds, the majority of the hydrogen-bond acceptors being O atoms. According to Chiari & Ferraris (1982) the average $O(W) \cdots O$ and $H \cdots O$ distances are $2 \cdot 81$ and $1 \cdot 86$ Å, respectively.

Following the classification of Ferraris & Franchini-Angela (1972) the majority of hydrate water molecules belong to coordination class 2, i.e. tetrahedral environment (see Fig. 1a). Chiari & Ferraris (1982) found that 102 of their 183 water molecules studied belong to class 2 while 41 belong to class 1 (triangular environment, Fig. 1b) and 39 to class 1' (one coordination bond approximately in the direction of one lone pair of the water O).

The internal vibrations of the bonded water molecule have been studied extensively (Falk & Knop, 1973). Two vibrations, well described as O—H stretchings, have wavenumbers in the region 3100–3600 cm^{-1} (2300–2650 cm^{-1} for D_2O); stronger hydrogen bonds give lower wavenumbers. A bending vibration is found around 1650 cm^{-1} (1200 cm^{-1} for D_2O).

Of the external vibrations, three librational modes have wavenumbers between 300 and 900 cm^{-1} ($\sim$220–650 cm^{-1} for D_2O). For the C_{2v} site symmetry, the librations are restricted to motion around the x, y and z axes (see Fig. 1c) through the centre of mass and are commonly called wagging, twisting and rocking, respectively. This notation is frequently used as a conceptual basis for other site symmetries for which, in fact, mixing of these types of vibration can occur (Eriksson & Lindgren, 1978a,b).

The water molecule also performs translational vibrations. Such vibrations have been found at lower wavenumbers (<250 cm^{-1}) but sometimes as high as 400 cm^{-1} (Ichida, Kuroda, Nakamura & Kubo, 1972). Although wavenumber shifts following isotopic substitution show translational modes well localized to the water molecules themselves, there are other vibrations where translational displacements of the water molecules are connected with substantial motion of their environment (for example, the acoustic modes).

Isotopic-substitution techniques (Falk & Knop, 1973) have shown that there is generally little mixing between the above-mentioned four types of vibration of the
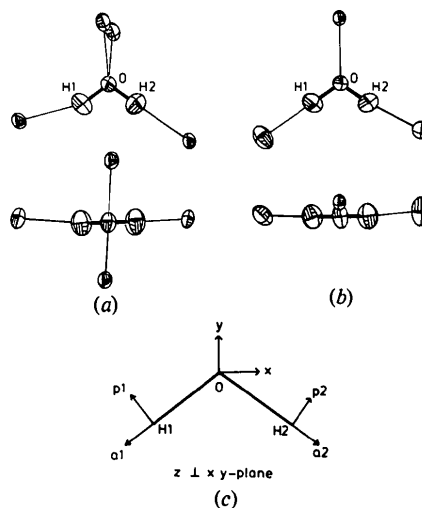

Fig. 1. (a) The water molecule in $NaHC_2O_4 \cdot H_2O$ (Tellgren, Thomas & Olovsson, 1977) with tetrahedral coordination (class 2) viewed in two perpendicular directions. (b) One of the water molecules in $Al(NO_3)_3 \cdot 9D_2O$ (Hermansson, 1983) with triangular coordination (class 1). (c) Definition of directions of vibrational amplitudes. x is parallel to the H(1)—H(2) direction, a is along an O—H bond and p is perpendicular to an O—H bond and in the molecular plane. Note that the directions defined are not necessarily related to a certain nucleus.

Table 1. *Calculated vibrational m.s. amplitudes of the water molecule in crystalline hydrates*

Nucleus and direction (see Fig. 1c)	Contributing vibrational modes	M.s. amplitude for H_2O (Å²)	M.s. amplitude for D_2O (Å²)
O,x ⎫ O,y ⎬ O,z ⎭	Translations*	–	–
H,a	Stretchings	0·005	0·003
	Translations*	–	–
H,p	Bending	0·005	0·003
	Rocking†	0·009–0·044 0·009–0·028	0·007–0·039 0·006–0·020
	Translations*	–	–
H,z	Wagging†	0·009–0·040 0·008–0·026	0·005–0·031 0·005–0·016
	Twisting†	0·010–0·046 0·009–0·029	0·007–0·042 0·007–0·022
	Translations*	–	–

* The values of the amplitudes arising from translational motion cannot be calculated from the simple model used. However, the difference between an H_2O and a corresponding D_2O translational m.s. amplitude is expected to be less than 5% of the amplitude itself.

† The intervals given for the librational modes correspond to the wavenumber interval 900–300 cm⁻¹. The upper line is valid for room temperature and the lower for low temperature (100 K).

water molecule: stretching, bending, libration and translation. If not stated otherwise, this is assumed in the following.

Normal coordinate calculations based on a relatively simple vibrational model (Eriksson & Lindgren, 1978a), followed by the application of the equation

$$\langle Q_i^2 \rangle = (h/8\pi^2 c \nu_i) \coth(hc\nu_i/2kT) \qquad (1)$$

(Q_i normal coordinate, ν_i wavenumber, T temperature) and appropriate mass-weighting, give the contribution to the total mean-square (m.s.) amplitudes from a specified normal vibration. Table 1 lists the essential contributions in certain specified directions.

The magnitudes of neutron-diffraction-observed amplitudes

In this investigation, all published water molecules with O—H distances determined with standard deviations smaller than 0·010 Å are considered. Disordered water molecules are not included, neither are a few compounds for which thermal parameters were not

Table 2. *Hydrate structures analysed in this survey*

The entries are: reference (year, journal, volume, page), compound name, neutron data collection temperature, number of crystallographically independent water molecules. The studies marked with an asterisk fulfil certain precision and accuracy tests (see text).

Year	Journal	Vol.	Page	Compound	Temp	N
83	ACCCA	39´	925	$Al(NO_3)_3.9D_2O$	RT	9*
78	ACBCA	34	2290	$BaCl_2.2H_2O$	RT	2
68	JCPSA	48	1883	$Ba(ClO_3)_2.H_2O$	RT	1
82	JCPSA	76	5508	$Ba(NO_2)_2.H_2O$	RT	1
					102 K	1
					20 K	1
69	ACBCA	25	310	$BeSO_4.4H_2O$	RT	1
69	ACBCA	25	2442	α-$(COOD)_2.2D_2O$	RT	1
69	ACBCA	25	2442	β-$(COOD)_2.2D_2O$	RT	1*
69	ACBCA	25	2437	α-$(COOH)_2.2H_2O$	RT	1
80	R. Feld, thesis; Marburg				100 K	1
73	ACBCA	29	876	$C_3H_7NO_3.2H_2O$	RT	1
67	JCSIA	1967	1862	$C_4H_7NO_8.2H_2O$	RT	2
72	ACBCA	28	3006	$C_4H_8N_2O_3.H_2O$	RT	1*
72	ACBCA	28	2083	$C_4H_9ClN_2O_3.H_2O$	RT	1
76	INOCA	15	3057	α-$C_6H_4(COOH)SO_3H.3H_2O$	RT	1
78	ACBCA	34	2551	$C_6H_{12}O_5.H_2O$	RT	1*
72	ACBCA	28	3207	$C_6H_{15}ClN_2O_2.2H_2O$	RT	2
77	ACBCA	33	654	$C_6H_8N_2O_2.HCl.H_2O$	RT	1
79	ACBCA	35	1388	$C_6H_8N_3O_6.H_2O$	80 K	1
77	ACBCA	33	2490	$C_{12}H_{22}O_{11}.H_2O$	RT	1
78	ACBCA	34	2737	$Ca(C_3H_2O_4).2H_2O$	RT	2
82	ACBCA	38	1074	$CaSO_4.2H_2O$	RT	1*
76	ACBCA	32	2803	$Cd(C_6H_8N_3O_2)_2.2H_2O$	RT	1
75	ACBCA	31	1895	$Co(NH_4)_2(BeF_4)_2.6H_2O$	RT	3*
72	JCPSA	56	4352	$CuF_2.2H_2O$	RT	1
80	ZEKGA	152	161	$Cu(HC_3O_4)_2.2H_2O$	RT	1*
72	CSCMC	1	185	$CuK_2(SO_4)_2.6H_2O$	RT	3
69	ACBCA	25	676	$Cu(NH_4)_2(SO_4)_2.6H_2O$	RT	3*
72	CSCMC	1	367	$CuRb_2(SO_4)_2.6H_2O$	RT	3
75	ZEKGA	141	330	$CuSO_4.5H_2O$	RT	5
75	ZEKGA	141	330	$CuSO_4.5D_2O$	RT	5
73	ACBCA	29	2393	$Cu_2(CH_3COO)_4.2H_2O$	RT	1
76	ACSAA	30	735	$HgCl_2.2KCl.H_2O$	RT	1
75	ZEKGA	142	129	$HgCrO_4.\frac{1}{2}H_2O$	RT	1
78	ACBCA	34	1408	$HgSeO_4.H_2O$	RT	1*
76	ZEKGA	144	1	$Hg_3(OH)_2(SO_4)_2.H_2O$	RT	1
74	ACBCA	30	1421	α-$KC_6H_{11}O_7.H_2O$	RT	1
74	ACBCA	30	1421	β-$KC_6H_{11}O_7.H_2O$	RT	1
80	ACBCA	36	2869	$KI_3.H_2O$	RT	1
72	ACAPC	26	1358	$KMnCl_3.2H_2O$	RT	2
75	INOCA	14	2653	$KPtCl_3(C_2H_4).H_2O$	RT	1
70	ACBCA	26	77	$K_2C_2O_4.H_2O$	RT	1
82	ACBCA	38	15	$LiClO_4.3H_2O$	RT	1*
74	FEREL	6	191	$LiHCOO.H_2O$	RT	1*
80	ACBCA	36	1032	$LiNO_3.3H_2O$	RT	2*
					120 K	2*
82	ACBCA	38	2555	$LiOH.H_2O$	RT	1
83	JCPSA			$Li_2SO_4.H_2O$	RT	1
					80 K	1*
					20 K	1*
73	JCDTB	1973	816	$MgSO_4.7H_2O$	RT	7
82	ACBCA	38	1799	$MgS_2O_3.6H_2O$	RT	3
					120 K	3
71	ACBCA	27	66	$MnCl_2.4H_2O$	RT	4*
72	ACBCA	28	3340	$(NH_4)_2C_2O_4.H_2O$	RT	1
72	ACBCA	28	3340	$(ND_4)_2C_2O_4.D_2O$	RT	1
82	ACBCA	38	401	$Na_3AsS_4.8D_2O$	RT	8
79	ACBCA	35	1679	$NaBr.2H_2O$	RT	2*
82	ACBCA	38	2874	$Na_2CO_3.NaHCO_3.2H_2O$	RT	1
77	ACBCA	33	3500	$NaHC_2O_4.H_2O$	RT	1*
83	(Private communication)				120 K	1
76	ACBCA	32	987	$NaH_2PO_4.2H_2O$	RT	2
78	ACBCA	34	3502	$Na_2B_4O_5(OH)_4.8H_2O$	RT	4*
82	ACBCA	38	2671	$Na[S_2CN(CH_3)_2].2H_2O$	RT	2
75	ACBCA	31	890	$Na_2CO_3.H_2O$	RT	1
77	ACBCA	33	558	$Na_2[Pt(CN)_4Br_2].2H_2O$	RT	1
78	ACBCA	34	1975	$Na_2S_2O_3.5H_2O$	RT	5*
79	ACBCA	35	19	$Na_3SbS_4.9D_2O$	RT	3*
					105 K	3
83	(Private communication)			$NaH(CHCOO)_2.3H_2O$	120 K	3*
80	ACBCA	36	1387	$Ni(C_2H_4D_2N_2O)_2.DCl.D_2O$	RT	1
71	JCPSA	54	3990	$Ni(C_4H_{11}N_2O)_2.HCl.H_2O$	RT	1*
77	BCSJA	50	3167	$SnCl_2.2D_2O$	88 K	2
71	INOCA	10	323	$UO_2(NO_3)_2.2H_2O$	RT	2
79	ACBCA	35	2317	$Y(C_2H_5SO_4)_3.9H_2O$	110 K	2
75	JCDTB	1975	2072	$Zn(NO_3)_2.2Hg(CN)_2.7H_2O$	RT	4

Journal codes
ACAPC *Acta Chem. Scand.*
ACBCA *Acta Cryst. Sect. B*
ACCCA *Acta Cryst. Sect. C*
ACSAA *Acta Chem. Scand. Ser. A*
BCSJA *Bull. Chem. Soc. Jpn*
CSCMC *Cryst. Struct. Commun.*
FEREL *Ferroelectrics*
INOCA *Inorg. Chem.*
JCDTB *J. Chem. Soc. Dalton Trans.*
JCPSA *J. Chem. Phys.*
JCSIA *J. Chem. Soc. A*
ZEKGA *Z. Kristallogr.*

available. Altogether, 150 water molecules are used in this survey. The relevant compounds are listed in Table 2. The separation of the water molecules into protonates and deuterates, and room- and low-temperature studies is shown in Table 3.

The thermal parameters originate from published second-rank tensor components (β_{ij}'s or U_{ij}'s) obtained from least-squares fits. The observed distribution of the m.s. amplitudes in certain directions (as defined in Fig. 1c) is shown in Fig. 2. The directions of the principal axes of the thermal ellipsoids are often found to be close to these selected directions.

On comparing the amplitude distributions for the H_2O and D_2O molecules, one should notice that they generally originate from different compounds. A comparison between room-temperature and low-temperature values is subject to the same limitation. This, and the expected amplitude intervals given in Table 1, should be kept in mind when some general trends observed in Fig. 2 are pointed out. These trends can be summarized as follows:

(1) Out-of-plane amplitudes are larger than in-plane amplitudes.

(2) The magnitudes of the H amplitudes are larger than those for O. This can be explained by the participation of the H nuclei in internal vibrations and librations. The relatively large scatter in the H amplitudes in the p and z directions compared to the a direction arises, at least partly, from the librations.

(3) Amplitudes for D are smaller than those for H in the z direction and, to a lesser extent, in the p direction.

(4) The ratios between the mean values of the room-temperature and low-temperature m.s. amplitudes are larger for O (2·5–2·6) than for H (1·6–2·1). In the temperature interval considered (0–300 K), a temperature dependence of the m.s.
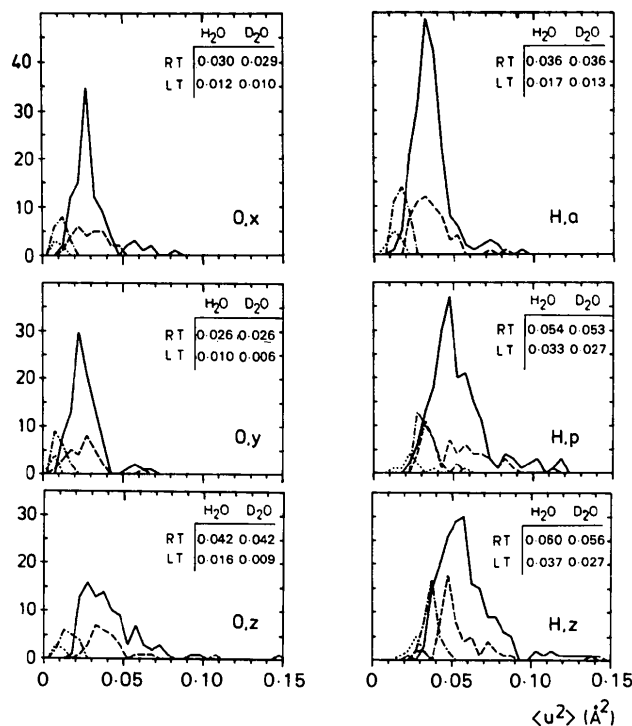

Fig. 2. Frequency functions for the m.s. amplitudes of the 150 water molecules. The class width is 0.005 Å^2. Mean values are given for each direction (RT: room temperature, LT: 20–120 K). Solid line: H_2O, RT. Dashed line: D_2O, RT. Dashed–dotted line: H_2O, LT. Dotted line: D_2O, LT. The standard deviations for individual observations are 0.0001–0.004 Å^2 for O and 0.0005–0.007 Å^2 for H. Three observations between 0.15 and 0.18 Å^2 are excluded for the H nuclei in the p directions and two in the z direction.

amplitudes larger than 10% is expected only for vibrations below ~ 600 cm^{-1}. Thus, the H amplitudes contain a temperature-independent component from the internal vibrations and possibly also from the librations.

(5) The temperature dependence is larger for D_2O amplitudes than for H_2O amplitudes. This is explained by the fact that the D_2O vibrations have smaller wavenumbers than the corresponding H_2O vibrations [equation (1)]. The unexpectedly large differences observed at low temperature between H_2O and D_2O oxygen amplitudes may be coincidental, and arise from the small number of compounds in the sample.

Accuracy test of the thermal parameters

In order to be able to extract information of a chemical nature from the thermal parameters, it is necessary to exclude observations which are too affected by systematic errors. A criterion for such an exclusion will not be decisive if the random errors are too high. Therefore, the set of water molecules was first limited to

Table 3. *Number of water molecules satisfying certain requirements*

RT: temperature between 290 and 300 K.
LT: temperature between 20 and 120 K.
$\sigma(R_{OH})$: standard deviation of O–H distance.
U_{ii}: any diagonal element of a second-rank vibrational tensor.
$\sigma(U_{ii})$: standard deviation of U_{ii}.

Requirement	H_2O RT	H_2O LT	D_2O RT	D_2O LT	Total
$\sigma(R_{OH}) < 0.010$ Å	99	17	29	5	150
All $\sigma(U_{ii})/U_{ii} < 0.05$	35	8	22	0	65
Rigid-bond test satisfied	87	15	13	2	117
All above requirements satisfied	28	6	12	0	46
Used in final analysis:					
Total	32	7	13	0	52
Of class 1	5	0	7	0	12
Of class 1'	7	0	0	0	7
Of class 2	20	7	6	0	33

those for which all nine of the $\sigma(U_{ii})/U_{ii}$ ratios were less than 0·05 (see Table 3). This condition is fulfilled for 65 water molecules; 45 of the molecules have ratios in the range 0·05–0·10; the remaining 40 molecules have ratios larger than 0·10.

If only rigid-body vibrations are present, the difference in amplitude between any two nuclei is zero in the internuclear direction. If this is the case, or if the difference arising from the internal vibrations is known, we have a method to reveal certain systematic errors in the amplitudes ('the rigid-bond test', Hirshfeld, 1976; Rosenfield, Trueblood & Dunitz, 1978). It must be stressed, however, that the application of the method cannot prove the absence of such errors.

For water, in the a directions, the O—H stretchings give comparatively large differences between H and O amplitudes due to the large mass difference. Using simple harmonic force fields, this difference is calculated to be 0·0044–0·0050 Å^2 corresponding to the wavenumber interval 3600–3200 cm^{-1} and is valid for all temperatures below 300 K. Similarly, the amplitude difference is obtained as 0·0029–0·0031 Å^2 for O—D stretchings. The bending vibration gives, in all cases, a negligible contribution in the a directions ($<0·0002$ Å^2). The rigid-bond test was applied to the water molecules in the present survey and those molecules were excluded for which the difference between the H and O amplitudes in the a directions deviated by more than $3\sigma_{combined}$ from 0·0050 Å^2 for O—H and 0·0031 Å^2 for O—D. Of the 65 molecules with all $\sigma(U_{ii})/U_{ii}$ less than 0·05, it was found that 19 did not fulfil this test. In the x direction [the H(1)—H(2) direction], an amplitude difference close to zero is expected for the H nuclei if the bending vibration is not considerably mixed with the rocking libration. This test gave exactly the same exclusions as the test for the a directions.

the result, especially since the O—H stretching vibrations are known to have relatively large anharmonic contributions (Berglund, Lindgren & Tegenfeldt, 1978). To study this, we calculated the probability density along the O—H bond for an H nucleus using the method reported by Eriksson, Berglund, Tegenfeldt & Lindgren (1979). The magnitude of the anharmonicity was varied within the limits given by Berglund et al. (1978). A Gaussian function, corresponding to the density arising from harmonic motion and thus simulating the second-rank tensor vibrational model, was then fitted to the various probability densities, and the variation of its width was studied. For a given wavenumber, the half-width of the fitted Gaussian function was _smaller_ the larger the anharmonicity. The maximum reduction of the m.s. amplitudes was as small as 0·0005 Å^2 compared to the harmonic case. It is also relevant to investigate how librational motion can influence the measured m.s. amplitudes in the a directions. For this purpose, we considered the case of $K_2C_2O_4 \cdot H_2O$ (Eriksson, Hermansson, Lindgren & Thomas, 1982). In this study, the contribution of the librations to the amplitudes was removed from the β-tensor refinement; no change in $\langle u^2 \rangle_{H,a}$ or $\langle u^2 \rangle_{O,a}$ resulted. We conclude that the second-rank tensor model does not in itself imply serious systematic errors in the vibrational amplitudes along covalent bonds.

It is well known that the presence of extinction can strongly influence the refined thermal parameters. The extinction problem has, in general, been recognized in the papers which form the basis of this survey. A correction has often been applied in the least-squares refinement; sometimes more than one model was tried. In many cases, certain extinction-affected reflections have been omitted from the refinements. We have not found that the extinction problem has been severely mistreated in the cases where the rigid-bond tests fail.

Possible sources for systematic error

In principle, the second-rank tensor vibrational model is not very well suited for the description of anharmonic linear motion or of large-amplitude librational motion where the nuclei move on arcs rather than along rectilinear paths. It is expected, however, that this inadequacy will affect the determination of absolute amplitudes rather than be of importance in assessing trends such as those discussed in the last sections of this paper. In extreme cases, however, the values of the thermal parameters can be less meaningful. For example, a double-minimum potential unresolved by the diffraction experiment is poorly represented by the harmonic model.

There is a general trend for the amplitude difference in the a directions to be too large (Fig. 3). It is important to investigate how anharmonicity can affect
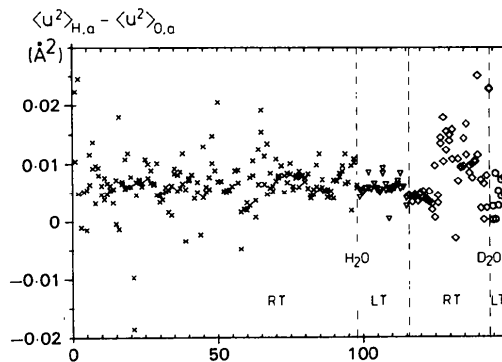
Fig. 3. The difference between H and O m.s. amplitudes in the a directions (rigid-bond test) for the 150 water molecules. Each position on the horizontal axis corresponds to one water molecule and thus contains values for two O—H bonds. The standard deviations are 0·0002–0·01 Å^2. The mean value for O—H bonds is 0·0066 Å^2 and for O—D bonds 0·0077 Å^2.

In a case of particularly severe extinction, $LiOH.H_2O$ (Hermansson & Thomas, 1982), the extinction level was substantially reduced by shock-cooling, which resulted in up to 40% larger m.s. amplitudes compared to a crystal which had not been subjected to shock-cooling. The rigid-bond tests were still not fulfilled, however.

Thermal diffuse scattering (TDS) may also influence the thermal parameters. For the few hydrates where a TDS correction has been performed and reported, the values of the thermal parameters have been shown to increase by up to 10%. The effect on the amplitude differences discussed above was very small, however.

The differences in the a directions are especially large for certain O—D bonds (Fig. 3). We believe that this is due to incomplete deuteration of the D_2O samples. The scattering length used for D in deuterated samples was 6·67 fm for most of the structures in Table 2. This actually corresponds to 100% deuteration, while a more realistic degree of deuteration in many cases lies around 95%, which corresponds to an effective scattering length of 6·15 fm. This hypothesis was tested on a neutron data set for $Al(NO_3)_3.9D_2O$ (Hermansson, 1983). These data have previously been refined using an effective scattering length of 6·67 fm for D, even though the degree of deuteration had been determined rather reliably (both by IR spectroscopy and from the neutron diffraction data by an extra refinement cycle of the occupancy of the D nuclei) to 97%. The m.s. amplitude difference along the O—D bonds lay in the range 0·0054–0·0109 $Å^2$ for the eighteen bonds while the expected difference is ~0·0030 $Å^2$. A new complete least-squares refinement was carried out using a scattering length corresponding to 97% deuteration, i.e. 6·35 fm. The resulting thermal parameters for D were smaller and the rigid-bond test was fulfilled for all bonds (0·0018–0·0050 $Å^2$, see Fig. 3). The new thermal parameters have been used in the subsequent analysis.

We have pointed out above some possible sources for systematic error. The occurrence of misprints and other similar errors in the published papers must not be overlooked, however. During the course of our work several such errors were revealed and corrected (see also Trueblood & Dunitz, 1983).

Comparison with amplitudes derived from spectroscopy

In the following, we consider the 46 water molecules which fulfil both the $\sigma(U_{ii})/U_{ii} < 0.05$ criterion and the rigid-bond test. Moreover, six molecules which lie close to the limits and belong to compounds where the other molecules fall within the limits have been added. In total, 52 water molecules were thus selected for further analysis. The relevant compounds have been marked

with an asterisk in Table 2. The subdivision into different coordination classes according to Ferraris & Franchini-Angela (1972) is listed in Table 3.

In water, the differences between H and O amplitudes are expected to arise from internal vibrations and librations. In particular, the bending and rocking vibrations predominate the amplitude differences in the p directions. The expected difference (Table 1) is 0·014–0·049 $Å^2$ (0·009–0·042 $Å^2$ for D_2O). The plot in Fig. 4(a) shows that only one of the diffraction-obtained values is below this interval while three are above. For a symmetric case [C_{2v}, C_2 or $C_{\sigma(yz)}$ site symmetries], the observations are restricted to fall on the line drawn in Fig. 4(a) [corresponding to equal m.s. amplitudes for H(1) and H(2)]. In all other cases [$C_{\sigma(xy)}$ or C_1 site symmetries], deviation can occur from the line, in particular if there is a mixing between the bending and rocking vibrations. There is no clear spectroscopic evidence that such a mixing is frequent or can be large but, on the other hand, it is not straightforward to reveal this mixing with the standard techniques of vibrational spectroscopy. However, normal coordinate calculations show that the difference between H(1) and H(2) m.s. amplitudes due to mixing between bending and rocking can be up to 0·01 $Å^2$ in the p directions. About 70% of the points plotted in Fig. 4(a) deviate less than $3\sigma_{combined}$ from the symmetry line; only three molecules are constrained by symmetry to fall exactly on it. In view of the fact that 30% of the observations deviate by more than $3\sigma_{combined}$, we suggest that mixing between bending and rocking vibrations actually occurs in many cases.

The differences between out-of-plane H and O amplitudes arising from wagging and twisting libra-
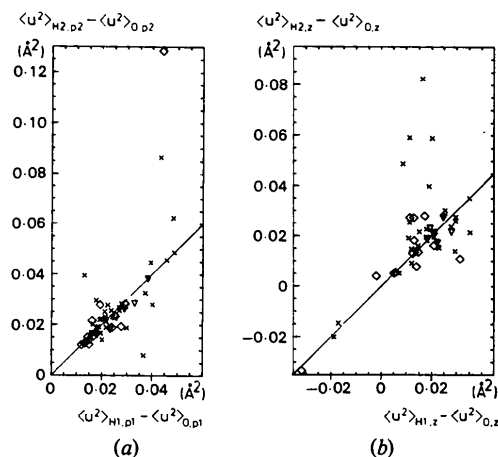

Fig. 4. The m.s. amplitude for H(1) vs the m.s. amplitude for H(2) (after the relevant O amplitudes have been subtracted) (a) in the p directions and (b) in the z direction. Crosses: H_2O, RT. Triangles: H_2O, LT. Squares: D_2O, RT. The solid lines correspond to the symmetric case. The standard deviations are 0·0004–0·004 $Å^2$ in each direction.

tions are expected to be 0·019–0·086 Å² (0·012–0·073 Å² for D_2O) (Table 1). It is found that about 40% of the diffraction-derived amplitudes lie below this interval; in a few cases they are even negative (Fig. 4b). This result is in agreement with normal coordinate calculations (Pedersen, 1975; Eriksson & Lindgren, 1978b) and vibrational spectroscopic measurements (Eriksson & Lindgren, 1978a), which have shown the possible existence of a low-wavenumber out-of-plane vibration in which the O amplitude is larger than those of the H atoms. This vibration can be described as a translation along the z axis coupled with a rotation around the x axis. The diffraction results indicate that

such a vibration occurs only for the coordination classes 1' and 1 (Fig. 5e). The water molecules investigated by Eriksson & Lindgren (1978a) are also of class 1.

The scatter from the symmetry line is larger for the z direction than for the p directions. Of the points plotted in Fig. 4(b), about 50% deviate more than $3\sigma_{combined}$ from this line. Again, this is in agreement with calculations (Eriksson & Lindgren, 1978b) and spectroscopic experiments (Thomas, Falk & Knop, 1974; Eriksson & Lindgren, 1978a). These studies have demonstrated that wagging and twisting vibrations quite frequently mix to form two normal vibrations
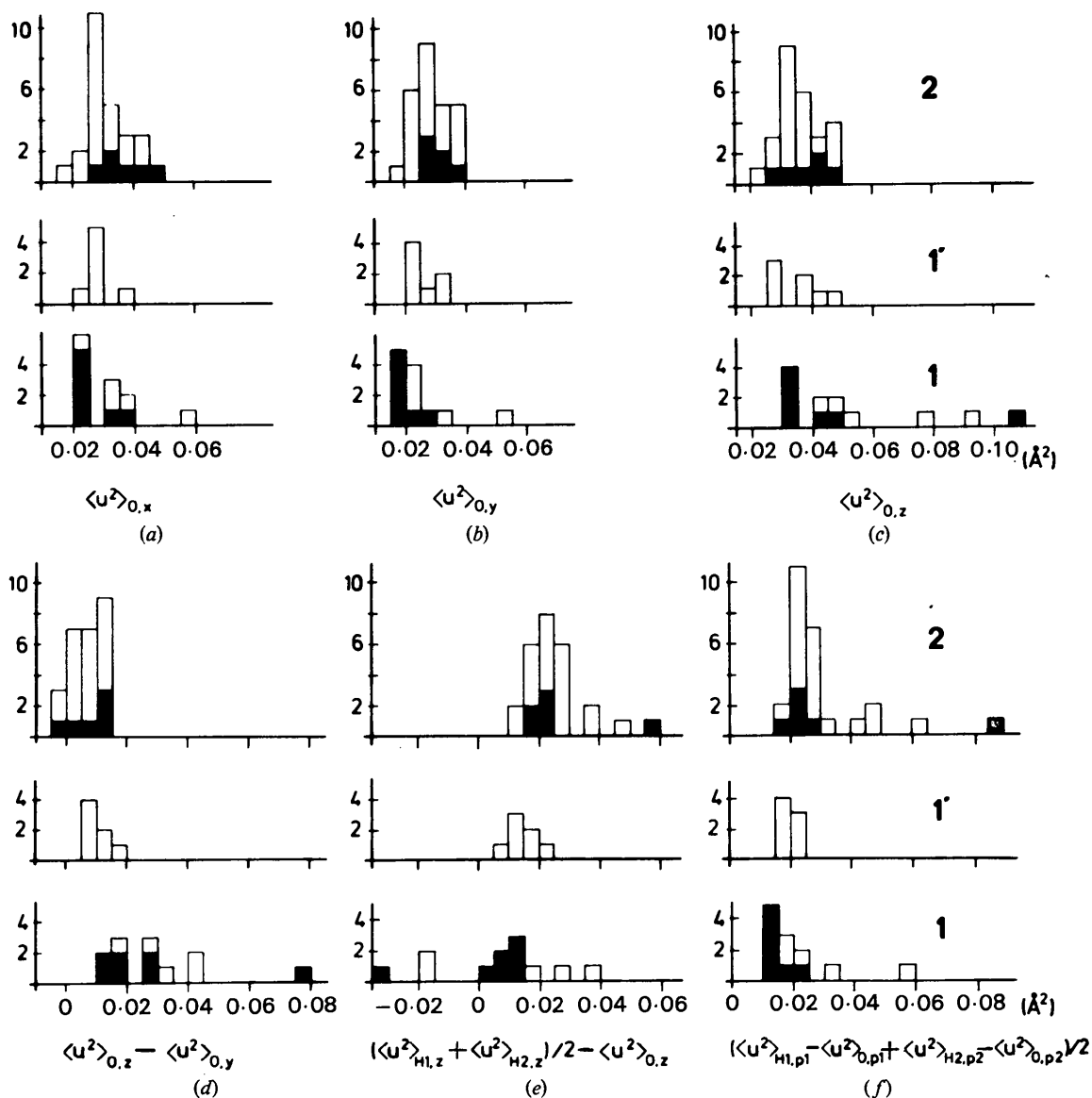

Fig. 5. Histograms of m.s. amplitudes divided according to coordination class. Only room-temperature data are included. Shaded columns are for D_2O molecules. The standard deviations are 0·0002–0·003 Å².

each of which has the character of one H nucleus being displaced more than the other. The amplitude difference between the two H nuclei produced in this way can be up to ~0·04 Å². It is seen from Fig. 4(b) that very few diffraction observations give larger differences.

Influence of the environment on the amplitudes

Oxygen coordination

We consider first the O amplitudes and their dependence on coordination class and geometry. The average out-of-plane amplitude is larger than the in-plane amplitudes (see Fig. 5a–c). Comparing the three coordination classes, it is found that the average amplitude in the z direction increases on going from class 2 to class 1, while that in the y direction decreases. The amplitude in the x direction does not vary appreciably with coordination class. In general, the vibrational behaviour is more anisotropic for class 1 water molecules (cf. Fig. 1a,b). This effect is more unambiguously shown in Fig. 5(d) where it is exemplified by the amplitude differences in the z and y directions. The result can best be interpreted in terms of the potential being steeper (larger force constant for translational displacement) in the direction of a coordinating species than in other directions.

The coordinating cation which occurs most frequently among the studied hydrates is the Na^+ ion; ten water molecules determined at room temperature are coordinated by two Na^+ ions (class 2). The relationship between the vibrational amplitudes of the O nuclei and the average of the two $O-Na^+$ distances was investigated but no correlation found.

In order to show the dependence on coordination class for librational motion, the relevant amplitude differences are plotted in Fig. 5(e,f). The larger variation with class in the average amplitude for the z direction (Fig. 5e) has already been discussed and explained in the previous section. Since the O amplitudes in the z direction may contain a substantial contribution from rotational motion (at least for the classes 1 and 1'), the amplitude difference between H and O is not necessarily a good representation of the influence from wagging and twisting vibrations. For the rocking vibration, however, Fig. 5(f) should show the dependence on coordination class. There is a tendency for slightly smaller amplitudes for classes 1 and 1' than for class 2. This can possibly be related to the fact that rocking vibrations are usually found at higher wavenumbers for classes 1 and 1' (Thomas, Falk & Knop, 1974; Eriksson & Lindgren, 1978a).

Hydrogen bonds

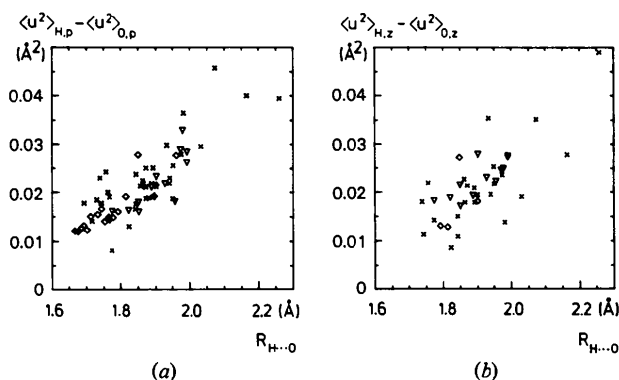The influence of the hydrogen-bond strength (length) on the amplitudes of the water molecule was then

Fig. 6. M.s. amplitude vs hydrogen-bond distance in the directions of librational motion. Only class 2 molecules are included in (b). The hydrogen-bond acceptors are O atoms and no bifurcated bonds are included. Crosses: H_2O, RT. Triangles: H_2O, LT. Squares: D_2O, RT. The standard deviations for the $H \cdots O$ distances are less than 0·01 Å and for the m.s. amplitudes 0·0002–0·003 Å².

considered, and limited to the cases with only O acceptor atoms (most abundant) and no bifurcated bonds. We found that the H amplitudes in the p and z directions tend to increase when the $H \cdots O$ distances increase. The dependence is seen more clearly if the relevant O amplitudes (contribution from translational motion) are first subtracted, and if only class 2 molecules are considered for the z direction (a consequence of the findings reported in the previous section, see also Figs. 4b and 5e). The correlation obtained (Fig. 6) is, to a large extent, due to the rigid-body librations which are localized to the water molecule itself, and therefore sensitive to the strength of its external bonds.

The O amplitudes show poor correlation with $H \cdots O$ distances. This is not unexpected since a large contribution arises from vibrations where the water molecule moves together with its nearest neighbours (e.g. the acoustic modes). If the $H \cdots O$ distances do not change during such vibrations, the bond strength is of no importance.

Although the $O-H$ stretching vibrations are known to be very sensitive to hydrogen-bond strength, the associated variation of the H amplitudes in the a directions is very small. Accordingly, no correlation is found between amplitudes in the a directions and $H \cdots O$ distances.

Conclusion

Of the 150 water molecules considered in this study, 33 (22%) do not fulfil the accuracy tests applied to the thermal parameters. Of the 65 molecules with low standard deviations of the thermal parameters $[\sigma(U_{tt})/$

$U_{ii} < 0.05$], 19 (29%) were discarded by the same accuracy test. This result indicates that the accuracy of the low-precision studies is lower than it is possible to judge from the individual studies themselves. Some possible sources of systematic error have been discussed. The effect of an improper choice of scattering length for D in not fully deuterated samples has been demonstrated.

The most precise and accurate observations of vibrational amplitudes made by neutron diffraction have been shown to be in good agreement with results from vibrational spectroscopy. The combination of neutron-diffraction results and experience from spectroscopic work give more comprehensive information about the form of the normal vibrations, especially the water librations.

The hydrogen-bond strength correlates to the librational amplitudes of the water molecule; the stronger the bond, the smaller the amplitudes. The vibrational amplitudes of the O nucleus of the water molecule depend on the coordination type so that a more anisotropic vibrational behaviour is found for class 1 molecules.

Even if the diffraction measurements and processing techniques have improved during the last decade, it is clear that the reliability of the diffraction-obtained vibrational parameters is in many cases far from satisfactory. In spite of this, it would seem that the enormous wealth of accumulated diffraction data should be used more often in solving problems related to vibrations in crystals.

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cis-Bis(bipyridyl)dichloroiron(III) Tetrachloroferrate(III), [Fe(bpy)₂Cl₂][FeCl₄]; Structure at 4·2 and at 115 K by Neutron Diffraction

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Abstract

The crystal structure of deuterated cis-[Fe^{III}(bpy)$_2$Cl$_2$][Fe^{III}Cl$_4$] has been determined by single-crystal neutron diffraction methods at 4·2 K. Crystals are orthorhombic, *Pccn*. At 4·2 K $a = 14·97$ (1), $b = 12·21$ (1), $c = 13·26$ (2) Å. Refinement of all 2895 measured unique reflections with anisotropic thermal motion [220 parameters (nv)] converged to $R(F^2) = 0·050$, $\chi = 2·6$. In addition, 869 reflections were