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The Water Molecule in Crystalline Hydrates Studied by Neutron Diffraction

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Abstract

A survey of the geometry and environment of water molecules in crystalline hydrates is presented. Histograms and correlation analyses are based on 97 crystal structures accurately determined by neutron diffraction, and include data from 183 water molecules, each donating two hydrogen bonds. The sample is analyzed according to the nature of the hydrogen-bond acceptors and of the coordinated cations. Cases of bifurcated hydrogen bonds are also discussed. The hydrogen bonds tend to be linear and the acceptors tend to be located close to the water plane. The tendency of coordination bonds to be collinear with the direction of one of the lone pairs of the O or their bisector increases with the strength of the bonds. The length of the $W-H$ bond, which, on average, is shorter than in the gas phase, is correlated to the strength of the donated hydrogen bond and to the nature of the acceptor as well as to the type of coordination. On average, $W-H$ is shorter for weaker hydrogen bonds, lower electronegativity of the acceptors and a triangular (as opposed to tetrahedral) type of coordination. The $H-W-H$ angle is, on average, about 2.5° wider than in the gas phase; this widening is correlated to the type of coordination (larger for triangular), to the strength of the hydrogen bond, and to the $A \cdots W \cdots A$ angle between acceptors. Differences between the dimensions of water molecules in gas and solid phases are shown to be effective and not due to uncorrected thermal effects.

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Introduction

Since the survey published by Ferraris & Franchini-Angela (1972) (FF hereafter), the structures of crystalline hydrates studied by neutron diffraction have quadrupled in number, and data for about 200 such structures are now available. Meanwhile, following previous work (Hamilton & Ibers, 1968; Vinogradov & Linnel, 1971), several reviews based on neutron diffraction data have been published (Falk & Knop, 1973; Fuess, 1979; Lundgren, 1974; Olovsson & Jönsson, 1976; Speakman, 1972, 1973, 1974, 1975, 1976). All these works, however, are not specifically concerned with hydrates, and an up-to-date investigation of these compounds seemed, therefore, worthwhile. In particular, the larger number of structures now available also allows one to take into consideration, in some cases, the nature of the hydrogen-bond acceptors A , and of the cations C coordinated to the water molecule. Because of the larger sample, selection criteria even stricter than those used by FF were applied. Compounds with any kind of disorder, symmetry ambiguities, uncertainties in the hydrogen-bonding scheme or in coordination, gross inaccuracy or some other flaws have been excluded. Unfortunately for our purposes, several structures had been selected for neutron diffraction studies in order to clarify order/disorder problems, and so about half of the papers scrutinized were not included in the present investigation, which was eventually based on 97

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hydrates. These are displayed in Table 1 according to accuracy and types, and listed in Table 2 together with references abbreviated according to the method of Brown, Brown & Hawthorne (1977).

The relevant bond lengths and angles were recalculated for every structure as a check and have been deposited together with references and information about accuracy, conformation of water molecules, chemical nature of the acceptors *A* and of the

coordinated cations *C*; angular coordinates (θ and φ , Fig. 1) of *A* and *C* are also reported.* For *A*, θ and φ are referred to a Cartesian system with origin at H, in which the *z* axis coincides with the corresponding *W*-H direction, and the *x* axis lies in the water plane and is chosen so that the *x* coordinate of the other H atom, not bonded to that particular *A*, is positive (Fig. 1a). For *C* atoms the origin is at *W*, the *z'* axis coincides with the external bisector of the H-*W*-H angle, and the *x'* axis lies in the water plane and is chosen so that the H atom with the shorter *W*-H distance has a positive *x* coordinate (Fig. 1b).† φ_1 and φ_2 for the *A* atoms are restricted between 0° ($+x$) and 180° ($-x$); φ_3 and φ_4 for *C* atoms are restricted

Table 1. Water molecules distributed according to accuracy and type of structures

	Non-molecular compounds		Molecular compounds	
	Number of structures	Number of H ₂ O	Number of structures	Number of H ₂ O
$\sigma_{(W-H)} < 0.01 \text{ \AA}$	34	74	22	29
$0.01 \leq \sigma_{(W-H)} \leq 0.02 \text{ \AA}$	16	34	4	6
$\sigma_{(W-H)} > 0.02 \text{ \AA}$	17	33	4	7
Total	67	141	30	42

* These data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36778 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† H₁ and H₂, throughout this paper, are distinguished on the basis of the *W*-H bond, so that *W*-H₁ \leq *W*-H₂. A₁ and A₂ receive hydrogen bonds from H₁ and H₂ respectively. C₁ and C₂ are chosen so that *W*...C₁ \leq *W*...C₂.

Table 2. List of the compounds investigated in this work, with their references abbreviated according to the given code

No star, one star and two stars refer to good, medium and low accuracy of structure determinations as defined in Table 1.

78 ACBCA	34	2290	BaCl ₂ ·2H ₂ O	72 CSCMC	1	185	CuK ₂ (SO ₄) ₂ ·6H ₂ O	76 ACBCA	32	987	NaH ₂ PO ₄ ·2H ₂ O
68 JCPA	48	1883	Ba(ClO ₄) ₂ ·H ₂ O	75 CSCMC	4	709	CuK ₂ (SeO ₄) ₂ ·6H ₂ O	**78 SPCRA	23	343	NaNH ₂ SeO ₄ ·2H ₂ O
69 ACBCA	25	310	BeSO ₄ ·4H ₂ O	69 ACBCA	25	676	Cu(NH ₄)(SO ₄) ₂ ·6H ₂ O	**64 CJPSA	42	229	NaAl ₂ Si ₂ O ₇ ·2H ₂ O
69 ACBCA	25	2442	α -(COOD) ₂ ·2D ₂ O	72 CSCMC	1	367	CuRb ₂ (SO ₄) ₂ ·6H ₂ O	78 ACBCA	34	3502	NaB ₃ O ₆ (OH)·8H ₂ O
69 ACBCA	25	2442	β -(COOD) ₂ ·2D ₂ O	75 ZEKGA	141	330	CuSO ₄ ·5H ₂ O	75 ACBCA	31	890	Na ₂ CO ₃ ·H ₂ O
73 ACBCA	29	876	C ₂ H ₅ NO ₂ ·H ₂ O	*72 CSCMC	1	371	CuTi ₂ (SO ₄) ₂ ·6H ₂ O	**75 DANKA	224	580	Na ₂ Cr ₂ O ₇ ·2H ₂ O
*73 ACBCA	29	1167	C ₂ H ₅ NO ₂ ·S·H ₂ O	73 ACBCA	29	2393	Cu ₂ (O ₂ CCH ₃) ₄ ·2H ₂ O	**71 ACBCA	27	354	Na ₂ HAsO ₄ ·7H ₂ O
*77 ACBCA	33	1655	C ₂ H ₅ N ₂ O ₂ ·2H ₂ O	**66 JCPA	44	2230	Fe ₂ (PO ₄) ₂ ·4H ₂ O	*71 ACBCA	27	2269	NaH ₂ SiO ₄ ·5H ₂ O
67 JCSIA	A	1862	C ₂ H ₅ NO ₂ ·2H ₂ O	76 ACSAA	30	735	HgCl ₂ ·2KCl·H ₂ O	*77 ACBCA	33	1976	Na ₂ Pt(CN) ₄ ·3H ₂ O
72 ACBCA	28	3006	C ₂ H ₅ N ₂ O ₂ ·H ₂ O	78 ACBCA	34	1408	HgSeO ₄ ·H ₂ O	77 ACBCA	33	558	Na ₂ Pt(CN) ₄ ·Br ₂ ·2H ₂ O
72 ACBCA	28	2083	C ₂ H ₅ ClN ₂ O ₂ ·H ₂ O	76 ZEKGA	144	1	Hg(OH)(SO ₄) ₂ ·H ₂ O	78 ACBCA	34	1975	Na ₂ SO ₄ ·5H ₂ O
76 INOCA	15	3057	α -C ₂ H ₄ (COOH) ₂ SO ₃ H·3H ₂ O	*69 JCPA	47	1091	K[B ₂ O ₆ (OH) ₂] ₂ ·2H ₂ O	**74 ZSKSS	15	712	Na ₂ Zn(SO ₄) ₂ ·4H ₂ O
78 ACBCA	34	2551	C ₂ H ₅ O ₂ ·H ₂ O	74 ACBCA	30	1421	α -KC ₂ H ₁₁ O ₇ ·H ₂ O	79 ACBCA	35	19	Na ₂ SbS ₄ ·9D ₂ O
*73 JCPKB	1973	133	C ₂ H ₅ N ₂ O ₂ ·2H ₂ O	74 ACBCA	30	1421	β -KC ₂ H ₁₁ O ₇ ·H ₂ O	*77 DANKA	236	393	NbN ₂ H ₄ OF ₅ ·H ₂ O
72 ACBCA	28	3207	C ₂ H ₅ ClN ₂ O ₂ ·2H ₂ O	72 ACAPC	26	1359	KMnCl ₄ ·2H ₂ O	80 ACBCA	36	1387	Ni(C ₂ H ₅ D ₂ N ₂ O) ₂ ·2DCl·D ₂ O
77 ACBCA	33	654	C ₂ H ₅ N ₂ O ₂ ·HCl·H ₂ O	*77 ACBCA	33	3155	KNaPt(CN) ₄ ·3H ₂ O	71 JCPA	54	3990	Ni(C ₂ H ₅ N ₂ O) ₂ ·2HCl·H ₂ O
79 ACBCA	35	1388	C ₂ H ₅ N ₂ O ₂ ·H ₂ O	75 INOCA	14	2653	KPtCl ₃ (C ₂ H ₅) ₂ ·H ₂ O	75 CSCMC	4	713	NiK ₂ (SO ₄) ₂ ·6H ₂ O
77 ACBCA	33	2490	C ₁₂ H ₂₂ O ₁₁ ·H ₂ O	70 ACBCA	26	77	K ₂ C ₂ O ₄ ·H ₂ O	*72 PHYSA	57	215	Ni(IO ₃) ₂ ·2D ₂ O
78 ACBCA	34	2737	Ca(C ₂ H ₃ O ₂) ₂ ·2H ₂ O	*70 ACBCA	26	827	K ₂ CuCl ₄ ·2H ₂ O	78 CSCMC	7	127	Ni(NH ₄)(CrO ₄) ₂ ·6H ₂ O
*72 ACBCA	28	209	CaHAsO ₄ ·H ₂ O	*77 ACBCA	33	3933	La ₂ Mg ₃ (NO ₃) ₁₂ ·24H ₂ O	*66 ACCRA	21	705	NiSO ₄ ·6D ₂ O
**71 ACBCA	27	349	CaHAsO ₄ ·2H ₂ O	74 FEREL	6	191	LiHCOO·H ₂ O	*78 PRVBA	18	2179	RbFeCl ₃ ·2D ₂ O
*71 JCSIA	1971	3725	CaHPO ₄ ·2H ₂ O	80 ACBCA	36	1032	LiNO ₃ ·3H ₂ O	73 CMLTA	1973	1105	SnCl ₄ ·2D ₂ O
**74 ACBCA	30	921	CaSO ₄ ·2H ₂ O	**68 JCPA	48	5561	Li ₂ SO ₄ ·H ₂ O	*66 ACBCA	20	842	Th(NO ₃) ₆ ·5H ₂ O
**77 ACBCA	33	801	Cd(C ₂ H ₃ NO ₂) ₂ ·2H ₂ O	(Personal communication)	MgHPO ₄ ·3H ₂ O			*72 INOCA	11	1840	UO ₂ (H ₂ O)(CO(NH ₂) ₂) ₂ ·INO ₃
76 ACBCA	32	2803	Cd(C ₂ H ₅ N ₂ O ₂) ₂ ·H ₂ O	*64 ACCRA	17	863	MgSO ₄ ·4H ₂ O	*77 ACBCA	33	2997	UO ₂ (NH ₄) ₂ ·3H ₂ O
**69 ACBCA	25	1804	Cd(NO ₃) ₂ ·4D ₂ O	73 JCDTB	1973	816	MgSO ₄ ·7H ₂ O	**78 ACBCA	34	88	UO ₂ (NH ₄) ₂ ·4H ₂ O
75 ACBCA	31	1895	Co(NH ₄) ₂ (BeF ₄) ₂ ·6H ₂ O	71 ACBCA	27	66	MnCl ₂ ·4H ₂ O	71 INOCA	10	323	UO ₂ (NO ₃) ₂ ·2H ₂ O
**66 ACCRA	21	383	CoAl(SO ₄) ₂ ·12H ₂ O	72 ACBCA	28	3340	(NH ₄) ₂ C ₂ O ₄ ·H ₂ O	79 ACBCA	35	2317	Y(C ₂ H ₃ SO ₃) ₂ ·9H ₂ O
*78 PRVBA	18	2179	CsFeCl ₄ ·2D ₂ O	*67 ACCRA	22	182	NaAl(SO ₄) ₂ ·12H ₂ O	**77 KOKSA	3	1594	ZnF ₂ ·4H ₂ O
*77 ACBCA	33	1293	Cs ₃ [Pt(CN) ₄] ₂ ·H ₂ O	79 ACBCA	35	1679	NaBr·2H ₂ O	*79 SPCRA	24	336	Zn(HSeO ₃) ₂ ·2H ₂ O
**57 JCPA	26	220	CuCl ₂ ·2H ₂ O	77 ACBCA	33	3500	NaHC ₂ O ₄ ·H ₂ O	75 CSCMC	4	717	ZnK ₂ (SO ₄) ₂ ·6H ₂ O
72 JCPA	56	4352	CuF ₂ ·2H ₂ O	*74 AASTO	108	1	NaH ₂ AsO ₄ ·H ₂ O	73 INUCA	9	629	Zn(NO ₃) ₂ ·2Hg(CN) ₂ ·7H ₂ O
*72 CSCMC	1	189	CuF ₂ (SO ₄) ₂ ·6H ₂ O								

Journal codes

AASTO *Atti Accad. Sci. Torino Cl. Sci. Fis. Mat. Nat.*
 ACAPC *Acta Chem. Scand.*
 ACBCA *Acta Cryst. Sect. B*
 ACCRA *Acta Cryst.*
 ACSAA *Acta Chem. Scand. Ser. A*
 BCSJA *Bull. Chem. Soc. Jpn*
 CJPSA *Can. J. Phys.*
 CMLTA *Chem. Lett.*

CSCMC *Cryst. Struct. Commun.*
 DANKA *Dokl. Akad. Nauk SSSR*
 FEREL *Ferroelectrics*
 GEOCA *Geochemistry (USSR)*
 INOCA *Inorg. Chem.*
 INUCA *Inorg. Nucl. Chem. Lett.*
 JCDTB *J. Chem. Soc. Dalton Trans.*
 JCPKB *J. Chem. Soc. Perkin Trans. 2*

JCPA *J. Chem. Phys.*
 JCSIA *J. Chem. Soc. A*
 JINCA *J. Inorg. Nucl. Chem.*
 KOKSA *Koord. Khim.*
 PHYSA *Physica (Utrecht)*
 PRVBA *Phys. Rev. Sect. B*
 SPCRA *Sov. Phys. Crystallogr.*
 ZEKGA *Z. Kristallogr.*
 ZSKSS *Zh. Strukt. Khim.*

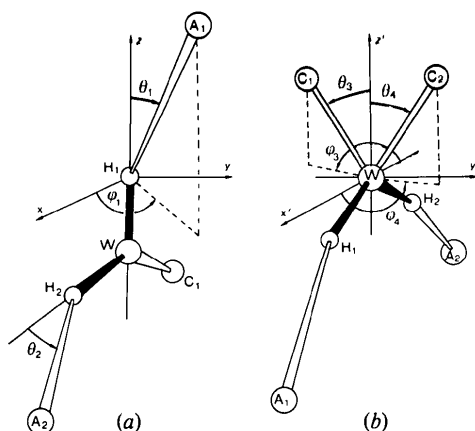


Fig. 1. Sketches of a water molecule with its environment. The reference systems for the polar coordinates θ and φ for (a) the acceptors, and (b) the coordinated cations are shown.

between 0° ($+x'$) and 90° ($+y'$). These limitations apply because the water molecules of different structures are referred to uncorrelated reference systems and, moreover, their absolute configuration is, in general, not determined. Within one molecule one can distinguish a *cis* or *trans* configuration for A (the same side or opposite sides of the water plane, respectively). For C , when there is only one C , a *cis* or *trans* configuration with respect to the two A can be established, provided that the latter are *cis* with respect to one another.

Fitting lines shown throughout this paper are linear-regression lines with the usual statistical meaning of the quantities. When applicable, the normality of the histograms with population K has been tested and the values E_i calculated from the estimated mean \bar{X} and the standard deviation σ are shown together with the observed frequencies (O_i) and an estimate $\Phi^2 = \sum_{i=1}^k [(O_i - E_i)^2 / E_i]$ (χ^2 distributed) of the goodness of fit. In evaluating correlations and, in general, in considering spread of values, it should be kept in mind that trends more than absolute values should be considered; in fact, uncorrected systematic errors can be as large as some hundredths of \AA for bond lengths, and some degrees for bond angles (Eriksson, Berglund, Tegenfeldt & Lindgren, 1979).

Classification of the water molecules

According to FF's classification, water molecules can be assigned to four classes which, in turn, are divided into several types according to the nature and geometry of the coordinated cations. To class 1 belong water molecules with only one coordination bond roughly along the bisector of the angle made by the lone pairs; to class 1' belong those with only one coordination bond directed toward one lone pair; water molecules

with two coordination bonds roughly along the two lone-pair directions are assigned to class 2. On the basis of the gap for θ_3 at about 25° in Fig. 3(a), 41 water molecules considered in the present paper are assigned to class 1 ($\theta_3 \leq 25^\circ$) and 39 to class 1' ($\theta_3 > 25^\circ$); 102, instead, belong to class 2 (see caption of Table 3).

Coordinations which do not belong to these classes are rare and in addition to the cases reported by FF (two of class 3 and one of class 4) only a few others can be added; these new cases, which are not further considered in this work, belong to class 3 (*i.e.* three-coordinated cations) and are found in the following compounds: $\text{LiKPO}_3\text{F} \cdot \text{H}_2\text{O}$ (74 ACBCA 30 697)* (structure determined by X-ray diffraction) of type O ; $\text{LiTi}(\text{H}_4\text{C}_4\text{O}_6) \cdot \text{H}_2\text{O}$ (78 FEREL 19 159) of type O ; $\text{KNa}[\text{Pt}(\text{CN})_4] \cdot 3\text{H}_2\text{O}$ (77 ACBCA 33 3155) of type O ; $\text{Cu}_6(\text{Si}_6\text{O}_{18}) \cdot 6\text{H}_2\text{O}$ (76 GEOCA 9 1328) of type P . It is also necessary to add (Table 3) two types in class 2 to the FF classification, *i.e.*: H' for the case with $C_1 = M^{2+}$ and $C_2 = M^+$; and H'' for the case with $C_1 = M^{n+}$ and $C_2 = \text{H}$. Instead, no examples for types C and I (only one monovalent cation) of classes 1 and 1', respectively, are present in the sample. In fact, the bond strength (Brown & Shannon, 1973) donated to W by one monovalent cation (normally about $\frac{1}{2}$ v.u.) is too small to compensate the bond strength 'removed' by two hydrogen bonds; of course H^+ (types F and K) with 'coordination' equal to two is an exception. C and I types could perhaps be found with water molecules which donate only one or two very weak hydrogen bonds.

Normal hydrogen bonds

Almost all water molecules are donors of two hydrogen bonds, with only few exceptions (for example, in zeolites or in the case of polyfurcated hydrogen bonds). Table 4 and Fig. 2 show the main features of the hydrogen bonds donated by water. If one wishes to distinguish these on the basis of the nature of the acceptors A , only the sample with $A = \text{oxygen}$ is large enough to be tested statistically with confidence. In this case, the upper and lower limits of the various magnitudes are very close to those reported by FF. The distribution of the number of hydrogen bonds *vs* the observed θ (which is supplementary to the bending angle $W-\text{H} \cdots A$) is shown both as observed (Fig. 2a) and after normalization ($n_{\text{max}} = 100$) to the solid angle as suggested by Pedersen (1974) and by Kroon & Kanters (1974) (Fig. 2b). The maximum value, which for the observed histogram belongs in the interval between 5 and 10° , is shifted to the interval between 0 and 5° after normalization. Recent theoretical com-

* See Table 2 for the code to reference abbreviations.

Table 3. Average, minimum and maximum values of bond lengths (Å) and angles (°) for water molecules, arranged according to the subdivision in classes

The water molecule of $K_2C_2O_4 \cdot H_2O$, which belongs to class 4, is not included.

	Class 1			Class 1'			Class 2							
	<i>D</i>	<i>F</i>	<i>M</i>	<i>J</i>	<i>K</i>	<i>N</i>	<i>A</i>	<i>B</i>	<i>E</i>	<i>G</i>	<i>H</i>	<i>H'</i>	<i>H''</i>	
No. of molecules	26	8	7	27	10	2	37	5	13	14	13	18	2	
No. of $A = O$	43	13	14	44	17	4	46	8	24	26	21	32	4	
$W-H$	Min.	0.916	0.909	0.930	0.930	0.923	0.951	0.891	0.959	0.944	0.925	0.959	0.934	0.983
	Av.	0.956	0.948	0.967	0.973	0.958	0.958	0.954	0.985	0.966	0.962	0.972	0.973	0.997
	Max.	1.003	0.988	1.001	1.014	0.993	0.964	1.005	1.021	0.982	1.007	1.001	1.019	1.012
$W \cdots O$	Min.	2.617	2.765	2.614	2.642	2.721	2.736	2.677	2.546	2.700	2.654	2.654	2.655	2.665
	Av.	2.835	2.823	2.763	2.740	2.834	2.841	2.858	2.712	2.821	2.862	2.791	2.750	2.683
	Max.	3.085	2.968	2.954	2.968	3.066	2.924	3.133	2.946	2.980	3.148	2.945	2.868	2.714
$H \cdots O$	Min.	1.656	1.817	1.636	1.680	1.765	1.790	1.699	1.520	1.747	1.742	1.650	1.679	1.668
	Av.	1.897	1.897	1.811	1.777	1.894	1.898	1.919	1.748	1.877	1.924	1.835	1.782	1.694
	Max.	2.176	2.059	2.132	2.069	2.137	1.982	2.242	1.827	2.099	2.258	2.034	1.952	1.742
$H-W-H$	Min.	103.2	104.9	106.3	100.4	102.4	106.2	101.0	104.4	103.5	102.5	104.0	104.7	106.0
	Av.	109.5	109.6	108.2	106.9	105.9	106.4	105.3	106.5	106.1	106.8	106.6	107.2	106.4
	Max.	113.2	113.9	111.1	109.9	108.7	106.4	109.8	111.3	109.5	110.7	109.7	114.0	106.8
$C-W-C$	Min.	-	-	-	-	-	-	80.1	89.1	83.0	90.1	103.2	90.7	94.6
	Av.	-	-	-	-	-	-	95.9	114.8	103.2	103.6	111.2	127.6	96.4
	Max.	-	-	-	-	-	-	125.2	139.9	119.3	129.5	131.6	139.0	98.1
$\langle A \cdots W \cdots A \rangle$ (average for each class)	Min.	-	82.2	-	-	83.5	-	-	-	-	68.9	-	-	
	Av.	-	109.7	-	-	105.9	-	-	-	-	107.4	-	-	
	Max.	-	147.8	-	-	129.9	-	-	-	-	146.5	-	-	

Table 4. Average, minimum and maximum values of bond lengths (Å) and angles (°) characterizing the hydrogen bonds donated by the water molecule to different types of acceptors

Acceptor	S	Br	N	Cl	O	F	
No. of bonds	7	5	14	27	298	15	
$W-H$	Min.	0.956	0.938	0.902	0.930	0.891	0.930
	Av.	0.960	0.950	0.945	0.954	0.965	0.967
	Max.	0.967	0.958	0.968	0.990	1.029	1.001
$W \cdots A$	Min.	3.319	3.339	2.817	3.086	2.546	2.563
	Av.	3.343	3.443	3.141	3.190	2.805	2.674
	Max.	3.358	3.586	3.419	3.321	3.148	2.906
$H \cdots A$	Min.	2.362	2.398	1.867	2.128	1.520	1.651
	Av.	2.394	2.560	2.235	2.254	1.857	1.716
	Max.	2.418	2.827	2.540	2.381	2.258	1.944
	Sum of van der Waals radii	2.85	2.95	2.50	2.80	2.40	2.35
No. of values	2	2	6	10	142	6	
$H-W-H$	Min.	106.7	102.5	102.2	100.4	101.0	106.2
	Av.	106.9	103.6	103.9	106.3	107.2	108.1
	Max.	107.1	104.7	105.5	110.0	114.0	110.6
$A \cdots W \cdots A$	Min.	107.3	80.5	76.5	84.7	68.9	96.5
	Av.	116.4	92.0	95.9	102.8	108.3	103.6
	Max.	125.6	103.5	109.5	120.4	147.8	114.5
$H \cdots H$	Min.	1.537	1.477	1.444	1.454	1.477	1.557
	Av.	1.539	1.496	1.486	1.524	1.554	1.569
	Max.	1.540	1.514	1.509	1.563	1.650	1.589

putations are in good agreement with these results (Ceccarelli, Jeffrey & Taylor, 1981; Newton, Jeffrey & Takagi, 1979), and clearly show the tendency for the hydrogen bond to be linear.

The isotropy of A around the $W-H$ direction is not as strict as pointed out by Pedersen (1974), even though his assumption is valid to a first approximation (Fig. 2c and d). In fact, there are clear maxima at $\varphi = 0$ and 180° , which can only be explained in part by crystallographic restrictions to these values (six and four $\varphi = 0$ and 180° , respectively). The histograms of

the angle γ between $H \cdots A$ and the water plane, and of the distance δ between A and the same plane (Fig. 2e and f) show a definite trend for A to be close to the H_2O plane; this surely causes bias to φ because small values of γ (and δ) require φ to be close to 0 or 180° when θ is large [$\sin \gamma = \sin \varphi \sin \theta$, and $\delta = (H \cdots A) \sin \gamma$]. On the other hand, maxima of θ and γ at about $7-8^\circ$, and $5-6^\circ$, respectively, are analytically related to the secondary maxima of φ around 60 and 120° .

According to φ of the hydrogen-bond acceptors, three types of configurations for the water molecule can be considered: group (I) (60 cases) for which both φ_1 and φ_2 relative to A_1 and A_2 are less than or equal to 90° ; group (II) (49 cases) for which $\varphi_1 \leq 90^\circ$ and $\varphi_2 \geq 90^\circ$, or *vice versa*; group (III) (74 cases) for which both φ_1 and φ_2 are in the range $90^\circ < \varphi \leq 180^\circ$. The unbalanced distribution of φ between the intervals $0-90^\circ$ and $90-180^\circ$, with 169 and 197 values respectively, is due to the predominance of group (III) molecules over group (I) [while group (II) obviously contributes equally to both intervals]. This distinction in groups according to φ is important for the discussion of the $A \cdots W \cdots A$ angle, as we shall see later.

There are 17 molecules for which at least one A lies in the water plane within the arbitrary limit of 0.01 \AA (five of class 1, one of class 1' and 11 of class 2). About 30 molecules can be considered planar within 0.1 \AA . The molecules with both A significantly out of the water plane are almost equally distributed between *cis* and *trans* configurations (16 *cis* and 20 *trans* for class 1; 16 *cis* and 22 *trans* for class 1'; 49 *cis* and 43 *trans* for class 2). For the 32 cases with only one C and the two A on the same side of the water plane, there is a preference for the C atom to be on the other side of that

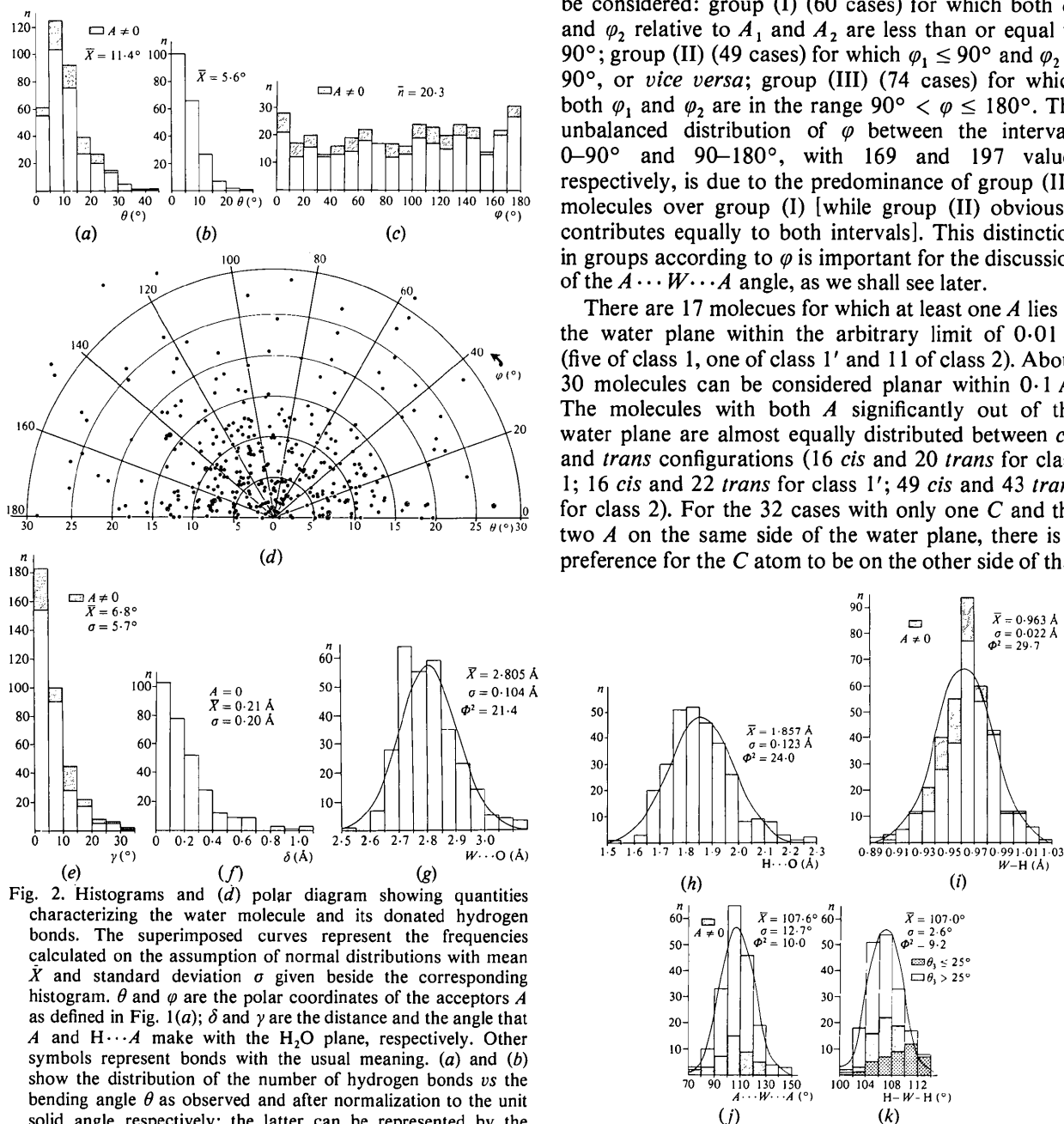


Fig. 2. Histograms and (d) polar diagram showing quantities characterizing the water molecule and its donated hydrogen bonds. The superimposed curves represent the frequencies calculated on the assumption of normal distributions with mean \bar{X} and standard deviation σ given beside the corresponding histogram. θ and φ are the polar coordinates of the acceptors A as defined in Fig. 1(a); δ and γ are the distance and the angle that A and $H \cdots A$ make with the H_2O plane, respectively. Other symbols represent bonds with the usual meaning. (a) and (b) show the distribution of the number of hydrogen bonds vs the bending angle θ as observed and after normalization to the unit solid angle respectively; the latter can be represented by the equation $n = 105 \exp(-\theta/110)^2$.

Fig. 2 (cont.)

plane for class 1' (13 out of 16 cases), while for class 1 the position of *C* is irrelevant (8 are in *cis* and 8 in *trans*). Particularly for non-molecular compounds, a tendency for the longest $W \cdots A$ bonds to be less linear and with *A* more distant from the water plane is observed, although no linear-regression line can be calculated, since both θ (or γ) and δ are not normally distributed.

Polyfurcated hydrogen bonds

With a van der Waals radius of 1 Å for H (Baur, 1972; Olovsson & Jönsson, 1976) it can be noted (Table 4) that the average and maximum length of the $H \cdots A$ bond are about 17 and 10% shorter, respectively, than the sum of the van der Waals radii for H and *A*, for all *A*. With *A* = O these shortenings are 23 and 6%, respectively.

In some cases, especially in the presence of weak acceptors, more than one $H \cdots A$ contact not longer than the corresponding sum of the van der Waals radii is found for a given H (with some allowance for the uncertainty of these radii; for example, for *A* = N the

limit in Table 4 is surely small). On the basis of the cases which have been investigated in this work, two types of multiple $H \cdots A$ contacts should be distinguished: (a) two $H \cdots A$ contacts with more or less the same features, *i.e.* differences in corresponding bond lengths and angles which are not larger than about 10 and 20% respectively; (b) a typical hydrogen bond plus one or, sometimes, more $H \cdots A$ contacts [*i.e.* in chlorates, as pointed out by Brown (1976)] which are longer and strongly bent. Cases (a) are summarized in Table 5 and, in our opinion, only situations like these should be called bifurcated (polyfurcated) hydrogen bonds, because only in these cases is the hydrogen bond clearly split into two bonds of comparable strength. For cases (b) of Table 6 it is preferable to say that for the H atom considered there is one hydrogen bond with its characteristics of directionality, plus one (second line in Table 6, for each water molecule) very weak contact [although not negligible on the basis of bond-strength computations (Brown & Shannon, 1973; Brown, 1976)] which is not considered here as a real hydrogen bond.

A case with only very weak contacts, at least on the basis of the van der Waals radius attributed to N, is

Table 5. Quantities (Å and deg) characterizing water molecules with bifurcated hydrogen bonds

Pairs of values in braces refer to bifurcated hydrogen bonds which involve all the $W-H$ on the second line plus two on the first line for each water molecule. The first water molecule of $K_3SO_3ON(SO_3)_2 \cdot 3/2H_2O$ is on a twofold axis. Stars have the same meaning as in Table 2.

	$(W-H)_1$ $(W-H)_2$	$(H \cdots A)_1$	$(H \cdots A)_2$	$(W \cdots A)_1$	$(W \cdots A)_2$	θ_1	θ_2	H-W-H	Coordination type
A_1 and $A_2 = O$									
* $MgSO_4 \cdot 4H_2O$ (64 ACCRA 17 863)	0.968 0.931	1.974	{ 2.388 2.587	2.835	{ 3.041 3.281	28.7	{ 52.9 48.3	111.0	D
$H_3PO_4 \cdot \frac{1}{2}H_2O$ (74 ACBCA 30 1470)	0.949 0.946	2.146	{ 2.205 2.388	2.993	{ 2.978 3.093	32.1	{ 41.7 48.9	106.0	E
$K_3SO_3ON(SO_3)_2 \cdot \frac{3}{2}H_2O$ (77 ACBCA 33 1591)	0.941	{ 2.299 2.368	{ 2.299 2.368	{ 2.957 3.206	{ 2.957 3.206	{ 53.5 31.8	{ 53.5 31.8	107.2	A
	0.941								
	0.946	2.022	{ 2.457 2.490	2.935	{ 3.192 3.211	18.4	{ 44.9 46.4	106.9	A
	0.940								
* $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$ (77 ACBCA 33 3933)	0.959 0.955	1.930	{ 2.382 2.235	2.866	{ 2.985 3.104	15.4	{ 59.3 29.2	101.7	E
$Ca(H_2PO_4)_2 \cdot H_2O$ (75 ACBCA 31 9)	0.976 0.962	1.824	{ 2.315 2.105	2.763	{ 2.917 2.963	19.6	{ 60.0 32.4	102.3	G
** $Na_3[Ru(NO_3)_4NOOH] \cdot 2H_2O$ (65 JINCA 27 309)	0.928 0.911	{ 2.224 2.544	{ 2.411 2.286	{ 2.913 3.308	{ 2.972 2.079	{ 49.1 40.2	{ 60.1 34.7	109.2	A
A_1 and $A_2 = Cl$									
$BaCl_2 \cdot 2H_2O$ (78 ACBCA 34 2290)	0.960 0.954	2.228	{ 2.488 2.672	3.179	{ 3.242 3.310	9.5	{ 44.1 55.3	102.7	B
$MnCl_2 \cdot 4H_2O$ (71 ACBCA 21 66)	0.967 0.944	2.226	{ 2.499 2.635	3.173	{ 3.281 3.295	14.2	{ 39.7 52.6	104.3	H
A_1 and $A_2 = N$									
* $KNa[Pt(CN)_4] \cdot 3H_2O$ (77 ACBCA 33 3155)	0.950 0.954	1.947	{ 2.477 2.554	2.895	{ 3.193 3.251	4.6	{ 48.3 50.0	104.7	A
A_1 and $A_2 = S$									
$Na_3SbS_4 \cdot 9D_2O$ (79 ACBCA 35 19)	0.957 0.927	2.338	{ 2.830 2.861	3.293	{ 3.590 3.594	4.2	{ 40.2 43.0	106.8	G

Table 6. Quantities characterizing water molecules with a second weak contact (second line for each water molecule) which has not been considered a hydrogen bond

Stars have the same meaning as in Table 2.

	H...A	W...A	θ
A = O			
MgHPO ₄ ·3H ₂ O	2.087 Å	3.007 Å	18.9°
[H. Bartl, M. Catti & W. Joswig (1981, personal communication)]	2.512	3.121	58.4
*MgSO ₄ ·4H ₂ O ^(a)	2.064	2.860	40.0
(64 ACCRA 17 863)	2.419	3.080	54.0
*Th(NO ₃) ₄ ·5H ₂ O ^(a)	2.067	2.946	32.1
(66 ACCRA 19 536)	2.414	3.096	54.0
A = N			
Ba[Pt(CN) ₄] ₄ ·4H ₂ O	2.218	2.941	47.7
(77 ACBCA 33 884)	2.611	2.990	75.6
	2.262	3.118	28.8
	2.696	3.084	74.4
*KNa[Pt(CN) ₄] ₃ ·3H ₂ O	2.310	3.103	40.4
(77 ACBCA 33 3155)	2.841	3.242	72.0
	2.548	3.210	30.0
	2.802	3.400	55.7
A = Cl			
MnCl ₂ ·4H ₂ O ^(a)	2.495	3.317	31.7
(71 ACCRA 27 66)	2.948	3.416	67.0
SnCl ₂ ·2D ₂ O	2.427	3.270	32.9
(77 BCSJA 50 3167)	2.778	3.420	50.7

(a) Considered bifurcated by FF.

found in Na₂[Pt(CN)₄]₃·3H₂O (77 ACBCA 33 1976): H...N = 2.754 and 2.990 Å, W...N = 3.318 and 3.786 Å, $\theta = 59.4$ and 34.2° .

From Table 5 it can be seen that only the group with both A = O is large enough to allow some comparison. The average values obtained for normal and bifurcated hydrogen bonds are, respectively: W-H = 0.960 and 0.939 Å, H...O = 1.979 and 2.353 Å; W...O = 2.878 and 3.075 Å; $\theta = 22.8$ and 45.4° . The significant shortening of the W-H distance for bifurcated bonds indicates, in terms of bond strength, that, on average, one normal hydrogen bond is stronger than the sum of two weak and strongly bent bonds; the H atom is therefore less bonded to W in the case of normal hydrogen bonds. It is worth noting also that H...A distances for bifurcated bonds are generally longer than the longest distance found for corresponding single bonds.

As a criterion for investigating the presence of polyfurcated hydrogen bonds, which cannot always be easily assigned, a careful examination of bond lengths is suggested. Particularly so when the hydrogen bonds already found show H...A or W...A lengths and θ angles at the upper limits in the corresponding histograms, indicating weak and bent hydrogen bonds. Without knowing the position of the H atoms it is

surely a risk to attempt the assignment of polyfurcated hydrogen bonds: see, for example, the case of Ba[Pt(CN)₄]₄·4H₂O where W...A of the rejected bond is shorter than the value for the accepted one; a similar case, not concerning water, is found in α -glycine (Jönsson & Kvik, 1972). Even greater care must be taken when one of the possible acceptors of a bifurcated hydrogen bond gives rise, with the other normal bond, to a standard environment for the water molecule.

Coordination bonds

Coordination bonds show a definite trend to be collinear with the lone-pair directions or their bisector; there is, in fact, a concentration of the coordinated cations near the Y'Z' plane (Fig. 3e), orthogonal to the

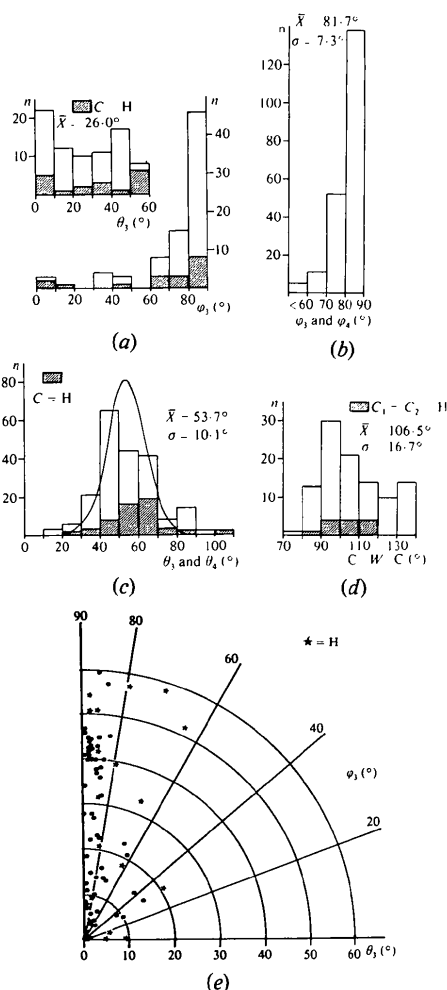


Fig. 3. Histograms of the quantities characterizing the coordination bonds of the water molecule for the case of one (a and e), and two coordinated cations (others). The polar coordinates are defined in Fig. 1(b); for (e), θ_1 refers to the coordinated cation in water molecules of classes 1 and 1'.

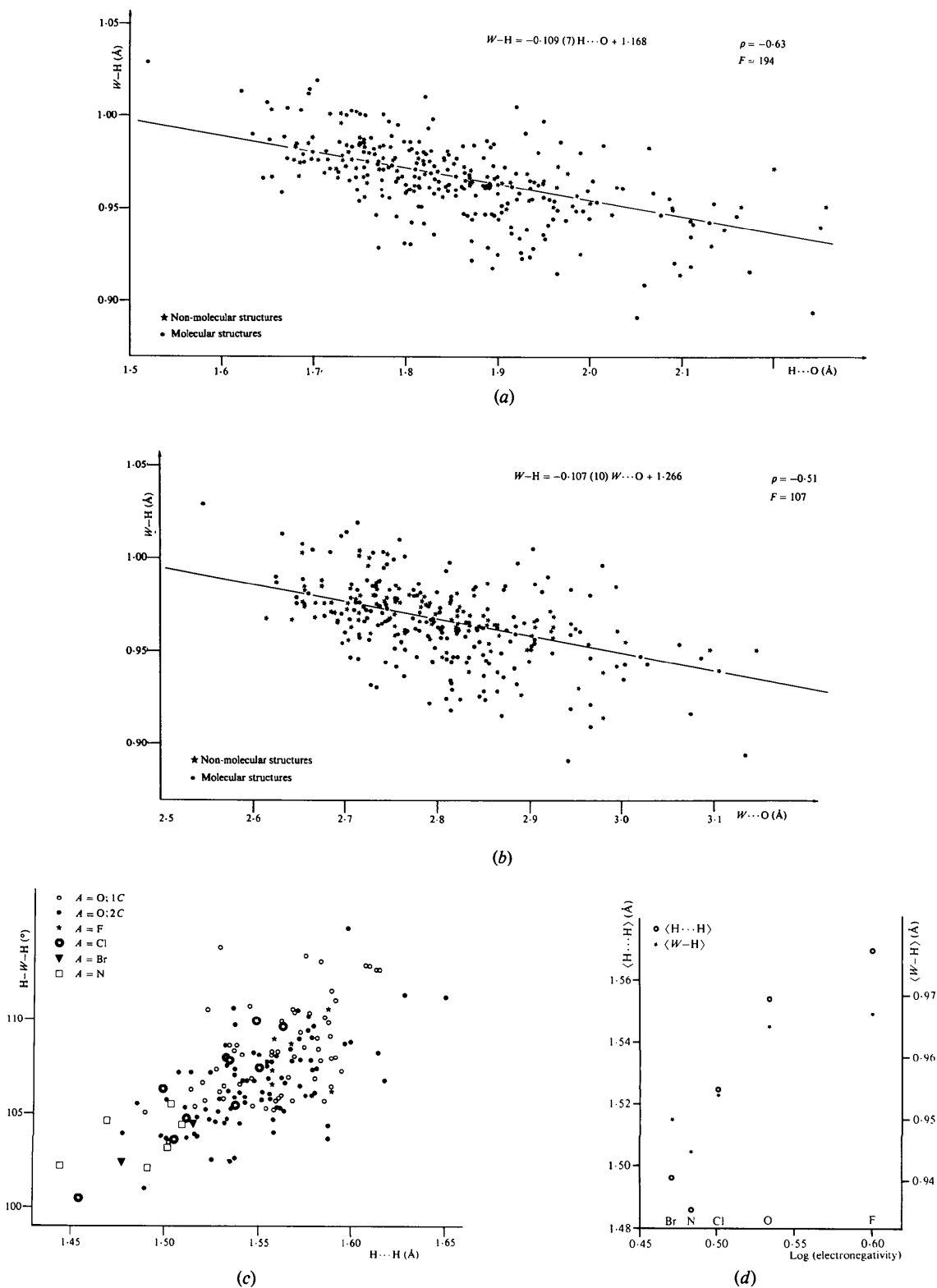


Fig. 4. Experimental values and regression lines, with their equations, for pairs of correlated quantities characterizing the water molecule and its environment. In (d) $H \cdots H$ values are averaged for each A ; in (e) the abscissa is the average $H \cdots O$ for each water molecule. In (f) the full line is the cumulative linear-regression line; dotted, dotted-dashed, and dashed lines are for groups (I), (II) and (III), respectively.

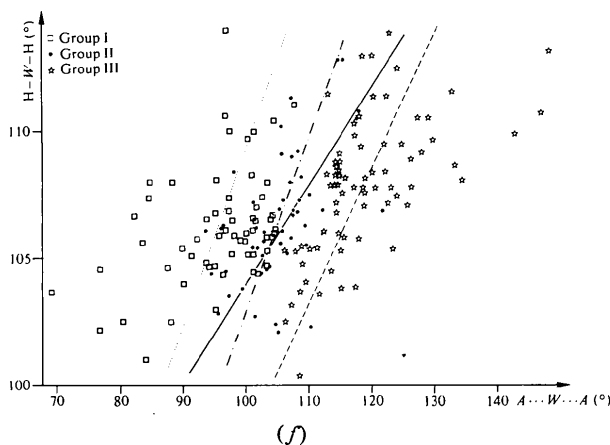
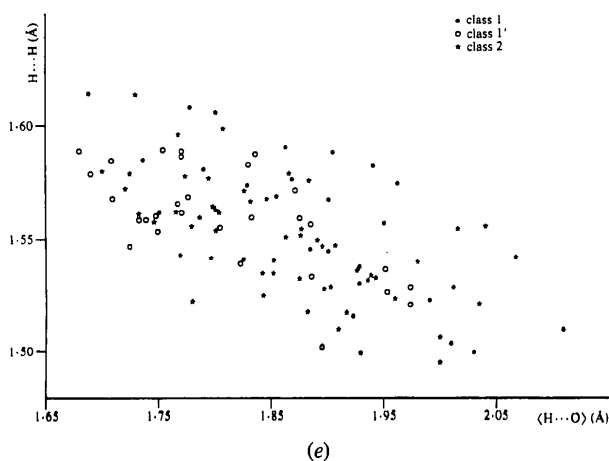


Fig. 4 (cont.)

water-molecule plane, as shown by the maxima in the φ distribution at around 90° (Fig. 3*a* and *b*; the structure of $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ with $\varphi_3 = \varphi_4 = 11.1^\circ$ is the most obvious exception). Furthermore, for molecules of class 2 (Fig. 3*c*) and of class 1' (Fig. 3*a*) there are clear maxima of the angle θ at about 50° , while for molecules of class 1 the maximum of θ is around 0° (Fig. 3*a*). The spread of values, however, is large, and indicates several exceptions; e.g. for $C_1 = C_2 = \text{H}$ the maximum of θ is found at about 65° (Fig. 3*c*, shaded area). This justifies what was pointed out by Olovsson & Jönsson (1976) and in *Hydrogen Bond Studies*. 100. *A Survey of the Hydrogen Bond Project* (1975), i.e. that in the case of hydrogen bonds donated to water, the influence of the lone pairs on the bond direction seems not to be essential. However (at least for H-, Cu-, Na- and K-coordinated cations in this study), stronger bonds seem to be preferentially directed towards a lone pair or the bisector of the water molecule. On average, the hydrogen bonds accepted by water are shorter for class 1 molecules than for class 1'. A study on the Ca-water interaction conducted on 150 examples, of which 90% were X-ray diffraction studies (Einspahr & Bugg, 1980), confirms the tendency for the Ca^{2+} cation, also, to lie near the plane bisecting the water molecule. In this case, too, the stronger $\text{Ca} \cdots \text{W}$ bonds tend to be nearly collinear with the water dipole.

The distribution of the $\text{C} \cdots \text{W} \cdots \text{C}$ angles is shown in Fig. 3(*d*) and Table 3. Owing to the higher interaction repulsion, the largest average values for these angles are observed when M^{2+} cations are present; in particular, type H' (M^{2+} and M^+ cations) show the highest values, even though the sample could be biased since most of the compounds of this type are isostructural, with formula $M^{2+}M_2^+(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. Cations with a large charge prefer (7 cases out of 11, Table 3) type M configuration with the coordination bond roughly along the water dipole.

Correlations between bond lengths and angles

There are definite negative linear correlations between $\text{W}-\text{H}$ and $\text{H} \cdots \text{A}$ (with any A); that involving the 298 cases with $\text{A} = \text{O}$ is shown in Fig. 4(*a*) ($\rho = -0.63$). This correlation can easily be understood qualitatively in terms of a simple electrostatic model of the hydrogen bond or, even, roughly quantitatively, on the basis of empirical bond strengths (Baur, 1970; Brown & Shannon, 1973; Ferraris & Catti, 1973). In fact, the closer the acceptor is to the H atom, the higher the bond strength brought away from the H atom and the longer, consequentially, is the $\text{W}-\text{H}$ bond. A similar correlation* (although weaker, $\rho = -0.51$; Fig. 4*b*) is also found for the same sample, between $\text{W}-\text{H}$ and $\text{W} \cdots \text{O}$, which is justified by the very strong correlation ($\rho = 0.98$) between $\text{H} \cdots \text{O}$ and $\text{W} \cdots \text{O}$. Taking into consideration the accuracy of the structure determination and the subdivision into molecular and non-molecular compounds, even better correlations [$\rho = -0.70$ and -0.60 for the 168 cases of structures with $\sigma_{(\text{W}-\text{H})} < 0.01 \text{ \AA}$; $\rho = -0.72$ and -0.64 for the 119 cases of accurate, non-molecular compounds] can be found for $\text{W}-\text{H}$ vs $\text{H} \cdots \text{O}$ and $\text{W} \cdots \text{O}$, respectively.

From Table 3 some correlation between coordination bonds, on one side, and $\text{W}-\text{H}$ and donated hydrogen bonds, on the other, can be suspected. Unfortunately, only a few types of coordination bonds can be tested. For the 13 cases with $\text{C} = \text{Cu}$ and $\text{A} = \text{O}$, $\text{W} \cdots \text{Cu}$ increases, while $\text{W}-\text{H}$ decreases ($\rho = -0.39$); instead, $\text{H} \cdots \text{O}$ ($\rho = 0.65$) and $\text{W} \cdots \text{O}$ ($\rho = 0.71$) increase, as expected on the basis of the correlations with $\text{W}-\text{H}$ shown above. The correlation (however low) $\text{W} \cdots \text{Cu}$ vs $\text{W}-\text{H}$ is in agreement with

* A non-linear fitting line, as are the corresponding correlations including all $\text{O} \cdots \text{O}$ bonds (Olovsson & Jönsson, 1976; Ichikawa, 1978), may fit these data slightly better.

bond-strength theory; a similar correlation was pointed out between S—OH bonds and the corresponding O—H···O hydrogen bonds in tetrahedral oxyanions (Catti, Ferraris & Ivaldi, 1979). For cases with only one *C* there is a tendency for the *W*—H averaged for each molecule to be large when θ_3 is large (e.g., the average *W*—H for class 1 and 1' molecules is 0.957 and 0.968 Å respectively). This can be related to the kind of hybridization of *W*, as we shall see later.

For *A* = O, *W*—H and H···O seem not to be dependent on the coordination number of the acceptor. The correlations (Baur, 1970; Ferraris & Catti, 1973) of the difference between the Pauling bond strength of the donor *W* and that of the acceptor O (Δp) with *W*—H, H···O and *W*···O lengths give $\rho = 0.50$, -0.51 and -0.48 respectively.

H—*W*—H angle, H···H distance and comparison with the gas phase

The average H—*W*—H angle calculated for all the water molecules in the present study (107.0°) is larger than the value of 104.52° observed in the gas phase (Kuchitsu, 1971). The average opening of about 2.5° observed in the solid state can be attributed to a series of factors: the coordination bonds, the nature and geometrical disposition of the hydrogen-bond acceptors and, in general, to the force field in which the molecule is embedded in the crystals, as was proved with *ab initio* calculations by Almlöf, Lindgren & Tegenfeldt (1972).

The geometry of the coordination has the greatest influence on the opening of the H—*W*—H angle (Table 3). This fact must be related to the type of hybridization of *W*; as already pointed out by Coppens & Sabine (1969), a larger *p* character for the lone pairs and, therefore, a larger *s* character for the O bonding orbital is shown for triangular coordination. This corresponds to stronger *W*—H bonds, as pointed out before. In such a case (class 1 molecules), the average value of H—*W*—H is 109.3°; for tetrahedral configurations, instead, the same angle is 106.2° when two *C* are present (class 2) and 106.6° when only one *C* is directed along a lone pair (class 1'). The difference for the average H—*W*—H angle between classes 1 and 1', much larger than the difference between classes 1' and 2, shows that the geometry of the coordination is more important than the coordination number of *W* in influencing the H—*W*—H variations.

A second factor that could influence the H—*W*—H angle and, in general, the water geometry in the solid phase is the residual charge on the H atoms with the consequent mutual repulsion. Fig. 4(c) shows that there is a strong positive correlation between H—*W*—H and H···H [a regression line is not calculated since the average H···H values are quite different according to

the chemical nature of *A* (Table 4)]. Since the residual charges on the H atoms are not available, we used instead the average (for each molecule) length of the H···O bond (only for *A* = O is the group statistically representative) and the decimal logarithm of the electronegativity of *A* (Pauling's scale; McWeeny, 1979) to try to take into consideration the nature of *A*. The substitution of residual charge on H by electronegativity of the bonded *A* atom is certainly crude, especially since the electronegativities of non-bonded atoms were used; however, a division of *A* according to type of hybridization (McWeeny, 1979) would nullify the statistical significance of the samples. Fig. 4(d)* and (e) shows that H···H (and consequently H—*W*—H) are indeed positively correlated with the electron-withdrawal capacity of the acceptor (shorter H···O bond and larger electronegativity of *A* being associated with larger H···H). In conclusion, the fact itself that in the solid state the H atoms are engaged in hydrogen bonds can cause a widening of the H—*W*—H angle with respect to the gas phase, for which the residual charge of the H atoms is less pronounced.

Finally, there is a correlation (Fig. 4f) between H—*W*—H and *A*···*W*···*A* angles ($\rho = 0.52$ for all water molecules of the sample; $\rho = 0.69$ for the accurate non-molecular structures with *A* = O). In Fig. 4(f) the water molecules have been distinguished according to the three groups already defined above. One can easily see that the average *A*···*W*···*A* angles for the three groups are quite different (95.7, 105.4 and 118.7° respectively) and that the regression lines calculated for the three groups run almost parallel to each other [$\rho = 0.59$, 0.40 and 0.57 for groups (I), (II) and (III) respectively]. The corresponding H—*W*—H average values also increase from group (I) to group (III) (106.3, 106.6 and 107.9°), although within a smaller range. The opening of the H—*W*—H angle under the influence of *A*···*W*···*A* must be attributed to the general preference for almost linear hydrogen bonds already pointed out.

It should, however, be remembered that a comparison between the values that characterize the gas phase and the solid state is not straightforward, because distances and angles of the sample investigated were not corrected for thermal motion which surely causes systematic errors larger than the estimated standard deviations. According to some models, the measured bond lengths and angles are shorter and larger, respectively, than the real values (Busing & Levy, 1964; Pedersen, 1975). The last author has computed an average correction of 0.04 Å for *W*—H, which would cause the average observed value (0.963 Å) for *W*—H in hydrates to be longer than the corresponding value found in the gas phase (0.974 Å;

* For *A* = S there are only two cases of thiosulphates and the corresponding point (Table 4) is not reported in Fig. 4(d).

Kuchitsu, 1971); this would be in better agreement with the requirement of longer $W-H$ bonds with the increasing of the hydrogen-bond strength. It should also be noted that the bonding of H_2O in the crystalline state seems to cause a definite shortening of the $W-H$ bonds which is superimposed on the variation of this magnitude with $H \cdots A$. In particular, examination of the average $W-H$ values for different A (Table 4) and different types of coordination (Table 3) suggests that this shortening should be greater with monovalent cations and weak acceptors; the latter effect is confirmed by a positive correlation (Fig. 4d) between $\langle W-H \rangle$ and the decimal logarithm of the electro-negativity of the acceptors.

The average correction for $H-W-H$ according to Pedersen (1975) should be, instead, about -2° , which still seems too small to match the observed solid-state value (at least for class 1 molecules) with the corresponding value in the gas phase. On the other hand, Eriksson *et al.* (1979) have shown that, at least for $W-H$, both positive and negative terms are present in the computed correction and the sign of the total correction depends on the strength of the bonds. In such a case the average values could be less influenced by thermal motion than previously suspected and, therefore, differences between the average water molecule in crystalline hydrates and that in the gas phase should be real. It is also worth noting that while the magnitude of the thermal-motion correction is larger for weak bonds (Eriksson *et al.*, 1979), in this work it has been found that, on average, the observed $H-W-H$ angle is smaller when weak acceptors are present (Table 4).

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