

On the Geometry of O-H...O Hydrogen Bonds

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The asymmetry of hydrogen bonds arises from the repulsion between the O atoms forming the bonds. A bond-valence analysis of the repulsion leads to the conclusion that strong and weak hydrogen bonds are different in kind, the stronger ones (O-O less than 2.7 Å) involve strain and are linear while the weaker ones (O-O greater than 2.7 Å) have an extra degree of freedom and are generally bent. The strength of the hydrogen bond is determined by a number of factors such as the requirement that the bond valences around each atom add up to the atomic valence, a tendency for the O-O distance to be close to 2.7 Å, and by crystal-packing considerations which often lead to the formation of bent, and hence weaker, hydrogen bonds. The bond-valence analysis correctly predicts the observed correlations between H...O distance and O-H-O angle. The frequency with which various hydrogen-bond configurations are observed in crystals is used to propose a method for determining hydrogen-bond energies. This analysis of hydrogen bonding leads to an understanding of the lengthening of hydrogen bonds in high-pressure ices and to proposals for hydrated ion structures which can be used, for example, to predict the acid strengths of anions and to show that in neutral aqueous solutions the oxygen atoms of complex anions each hydrogen-bond to two or three water molecules.

Introduction

The term 'hydrogen bond' is given to the system of two bonds, a donor Y-H and an acceptor H...Y' (where Y and Y' are two electronegative atoms), in which the donor bond is shorter, and hence presumably stronger, than the acceptor bond. The strength of the interaction between Y and Y' is determined by the weaker (acceptor) H...Y' bond and there is a strong positive correlation between the Y-Y' distance and the H...Y' distance (Ferraris & Franchini-Angela, 1972). Very short Y-Y' distances (2.4-2.7 Å) correspond to strong Y-H...Y' interactions (strong hydrogen bonds) while longer Y-Y' distances (2.7-3.1 Å) are called weak hydrogen bonds. In a review of the spectroscopic studies, Novak (1974) concludes that a qualitative change occurs in the character of the hydrogen bond over the range 2.6 to 2.7 Å, but Megaw (1973) believes the differences to be only ones of degree. Hamilton (1962) has shown that there is a correlation between the Y-Y' distance and the Y-H...Y' angle, the angle decreasing from 180° for strong hydrogen bonds to around 130° for the weakest ones (Pedersen, 1974). Various authors (Hamilton, 1962; Falk & Knop, 1973; Baur, 1972) have proposed criteria for the upper limit to the length of a weak hydrogen bond although all realise the arbitrary character of this limit.

Baur (1965) found he could predict the positions of the H atoms in crystalline hydrates using an electrostatic model provided he knew the positions of the neighboring atoms. Later he (Baur, 1972) used Pauling's concept of electroneutrality to make predictions concerning the positions of non-hydrogen atoms and he discussed seven factors that influence the geometry of hydrogen bonds. Donnay & Allman (1970) have used the electroneutrality principle in a different way

when assigning hydrogen bonds in crystals. From observed bond lengths they used empirical correlations to calculate bond valences which have the property that their sum around each atom is equal to the atomic valence. Brown & Shannon (1973) used the more general correlation

$$S = (R/R_0)^{-N}, \quad (1)$$

where S = bond valence, R = bond length and R_0 and N are universal parameters fitted empirically for a given atom pair. They showed that the sums of the bond valences around many cations including hydrogen [when determined by neutron diffraction, see Hamilton & Ibers (1968)] were within 0.04 valence units (v. u.) of the atomic valence in oxides.

In the discussion below bond valences are used to make predictions about the geometry of hydrogen bonds and these are then compared with observations. The energy of various hydrogen-bond configurations is discussed and finally the ideas that have been developed are applied to the structures of ice and the solvation of ions in aqueous solution.

Structure of O-H...O hydrogen bonds

For simplicity, the following discussion of hydrogen bonding is confined to those bonds for which the terminal atoms are both O since these have been most extensively studied. The principles will apply equally to other types of hydrogen bond.

The asymmetry of an O-H...O hydrogen bond results from the repulsion of the terminal O atoms. The van der Waals radius of O is 1.40 Å so that any oxygen atoms that are closer than 2.80 Å can be considered to be in contact. Accordingly, hydrogen bonds whose O-O distance is shorter than 2.80 Å should be strained

and relatively unstable while those longer than 2.80 Å will not involve O–O repulsion and will be unstrained. However, oxygen atoms bonded to the same cation can approach much closer than the van der Waals distance, (e.g. 2.1 Å in NO_3^-) and hydrogen atoms might also be expected to bring the oxygen atoms closer together.

A more sensitive approach is to treat the O atoms as

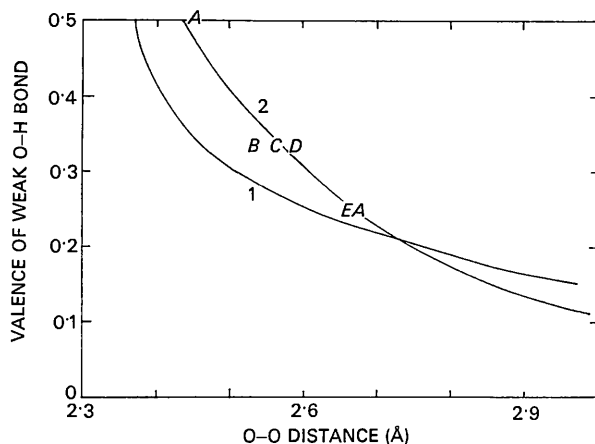


Fig. 1. Relationship between O–O distance and H–O(acceptor) bond valence. (1) Calculated from the O–H curve of Brown & Shannon (1973). (2) R_m , the minimum non-bonded O–O distance. The letters corresponds to observed O–O distances for A, $(\text{H}_3\text{O}_2)_2\text{SO}_4$, Taesler & Olovsson (1969); B, $(\text{H}_3\text{O})\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3$, Lundgren & Williams (1973); C, $(\text{H}_3\text{O})\text{O}_3\text{SC}_2\text{H}_4\text{SO}_3$, Mootz & Wunderlich (1970); D, H_3OHSO_4 , Taesler & Olovsson (1968); E, $\text{Be}(\text{H}_2\text{O})_4\text{SO}_4$, Sikka & Chidambaram (1969).

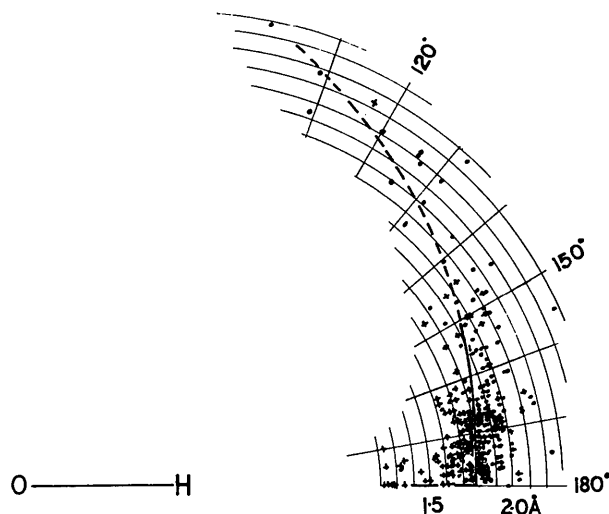


Fig. 2. Hydrogen-bond geometry. The position of the O acceptor atom is indicated relative to the O(donor)–H bond in the plane of the three atoms. The crosses are observed hydrogen bonds formed by O–H groups, the dots by H_2O groups (neutron diffraction data taken from Table 1). The coordinates are H...O length and O–H...O angle. The predicted positions are given by the solid line. The dashed line is the extrapolation of this line through the experimental points.

soft spheres and to assume that as the forces holding the O atoms to a central atom (X) are increased the O atoms can be brought closer together. The minimum possible O–O distance (R_m) can be found from the maximum oxygen coordination numbers observed around different cations. Values of R_m can be expressed in terms of an effective valence (S') by analogy with equation (1) as

$$S' = (R_m/P)^{-M}, \quad (2)$$

where M and P are fitted constants and S' is the component of the valence of the X–O bond, S , along the O–O vector given by

$$S' = S \cos \alpha, \quad (3)$$

α being the angle between O–O and X–O. For a given atom X, the average X–O bond valence, S , will be the atomic valence divided by the coordination number and from this R_m can be calculated (2 and 3) as well as the expected O–O distance (R_{OO}) [calculated from R found using (1)]. This coordination number is only expected to occur if $R_{\text{OO}} \geq R$. The values $P=2.22$ and $M=7.4$ give a good prediction of the maximum cation coordinations observed with O.

In a symmetric hydrogen bond the valence of both O–H bonds will be 0.5 valence units (v. u.) which will also be the effective valence (S') needed for calculating R_m . Using the values of P and M given above, $R_m = 2.44$ Å and using the values $R_0=0.86$ and $N=2.17$ in equation (1) (Brown & Shannon, 1973) it is found that $R_{\text{OO}} = 2.36$ Å so that a symmetric hydrogen bond is not expected to occur. If the bonding around H is made asymmetric R_{OO} increases, since the weaker bond is lengthened more than the stronger one is shortened. Fig. 1 (curve 1) shows R_{OO} as a function of the valence of the H...O (acceptor) bond. For linear coordination, the value of S' will be equal to the valence of the weakest link in the O–H...O chain, namely the valence of the H...O (acceptor) bond. The corresponding value of R_m is shown as curve 2 in Fig. 1. The closeness of curves 1 and 2 indicates that a wide range of hydrogen-bond lengths are possible with relatively little strain. However, two different regions are clearly defined, that in which curve 1 lies below curve 2 (O–O less than about 2.73 Å) and that in which curve 1 lies above curve 2 (O–O greater than about 2.73 Å). In the latter case it is possible for the oxygen atoms to be separated by the distance indicated by curve 2 (non-bonded contact) and, by bending the bond, to have the O–H distances at the values predicted by equation (1). For O–O distances less than 2.73 Å it is not possible to satisfy simultaneously the requirements for the O–H distances and O–O distance and in this region the bonds must be strained. Here the observed O–O distances (indicated by letters in Fig. 1) follow more closely the predicted non-bonded O–O distances (curve 2) than the sum of the predicted O–H distances (curve 1) indicating that the non-bonded repulsion is the dominant effect.

For weak hydrogen bonds, that is those longer than 2.73 Å, there is no resultant strain. The strongest bonding is found for these bonds when the O–O distance is 2.73 Å. Weaker bonds can occur either if the acceptor O atom has less than 0.2 v. u. available to form the hydrogen bond or if the bonding in a crystal requires that the O–H···O angle be less than 180°, for in that case the sum of the two O–H distances will be required by geometry to be greater than the O–O distance and the H···O (acceptor) bond will have to be weakened. Most longer hydrogen bonds result from this latter effect but an example of the former effect is found in $\text{Li}(\text{H}_2\text{O})_3\text{ClO}_4$ (Sequeira, Bernal, Brown & Faggiani, 1975) where the low formal charge on O results in a weak H···O bond (0.12 v. u., 2.044 Å). In this crystal the weak bond cannot be ascribed to bending since the O–H···O angle is 163° (see Fig. 2 below).

Strong hydrogen bonds only occur in cases where it is impossible or difficult to assign O–H(donor) bond valences that are as large as 0.8 v. u. For example, in H_3O^+ the valence of at least one O–H bond must be smaller than or equal to 0.67 v. u.

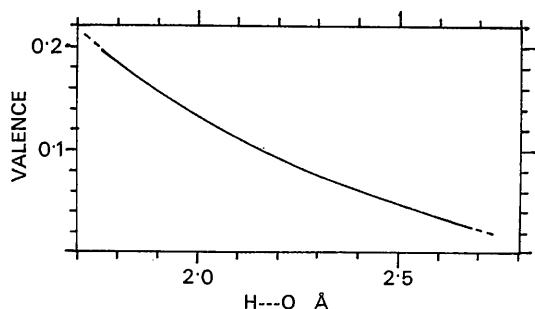


Fig. 3. Bond-valence-bond-length curve for O–H bonds.

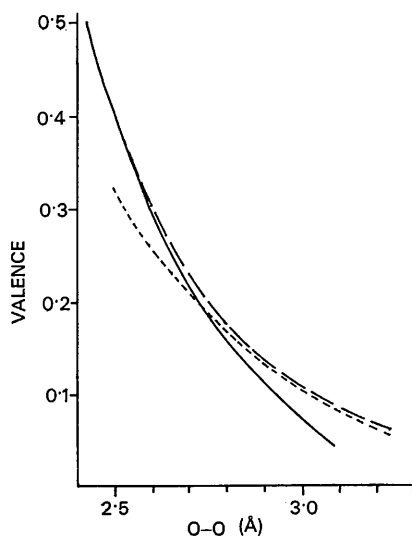


Fig. 4. Hydrogen-bond O–O distances versus valence of the H–O(acceptor) bond. Solid line: curve derived from Fig. 2; dashed line: curve given in Fig. 1; dotted line: curve of Lippincott & Schroeder (1955).

Comparison with observed configurations

Using the curves in Fig. 1 and assuming that weak hydrogen bonds result from a crystal packing requirement for bent bonds, it is possible to predict the H···O distances expected for various O–H···O angles and these are shown by the heavy line in Fig. 2 which plots the positions of the acceptor O atom relative to the O(donor)–H bond in the O–H···O plane. The experimentally observed positions taken from the neutron diffraction results summarized in Table 1 are indicated in Fig. 2 by the dots (H_2O molecules) and crosses (OH groups). The predicted O–H···O angle remains at 180° until an O–O distance of 2.73 Å is reached, but then decreases rapidly with further increases in the H···O distance. Because the prediction depends rather critically on the exact parameters used in equations (1) and (2) it is dangerous to extrapolate the curve very far but it gives a good description of the relationship between the O–O distance and O–H···O angle in the region where most hydrogen bonds are found.

One can extrapolate the curve in Fig. 2 to higher angles using the observed points rather than equations (1) and (2) (see dashed curve). At the weakest end this curve is tangential to the circle of radius 3.1 Å drawn with the donor O atom as centre, indicating that O–O distances beyond this length do not correspond to hydrogen bonds. By examining the valence-bond sums for crystals containing extremely weak H bonds it is possible to obtain a better bond-valence-bond-length curve than that given by Brown & Shannon (1973). The resultant O–H curve for weak bonds is given in Fig. 3 and the corresponding O–O curve is given in Fig. 4 where it is compared with the curve given in Fig. 1 (long dashes) and the curve of Lippincott & Schroeder (1955) as adapted to bond valences by Donnay & Allmann (1970) (short dashes).

Hydrogen-bond energies

An alternative way of interpreting the data given in Fig. 2 is to assume that where the density of points is large, the total binding energy is greater so that the observed distribution of acceptor O positions maps out the potential energy surface of hydrogen bonds in crystals. To obtain such a surface the observed density of acceptor O atoms ($\nu = \text{number}/\text{Å}^3$) is calculated in the recognition that Fig. 2 is a projection of a distribution with cylindrical symmetry (Pedersen, 1974). This distribution is then assumed to be related to the energy by a Boltzmann type function

$$\nu = \nu_0 \exp(-E/E_0) \quad (4)$$

where E_0 is an energy characteristic of that available for distorting the hydrogen bond. The resulting map (Fig. 5) shows not the true energy but a description of the observed distribution expressed as an 'energy' and only certain features can be expected to correspond to the true potential energy. The values of E/E_0 given

are only accurate to ± 0.5 to ± 1.0 and E_0 is probably different for strong and weak hydrogen bonds. In spite of these cautions, Fig. 5 shows even more dramatically than Fig. 2 the abrupt change in character of the hydrogen bond at an O...H distance of around 1.76 Å and shows also that the predicted curve lies very close to the 'energy' minimum trough.

A better energy description of normal and weak hydrogen bonds can be obtained by omitting the strong hydrogen bonds from consideration. Water molecules rarely form strong bonds; with two exceptions all the H...O (acceptor) distances formed with water as the donor are longer than 1.60 Å (Table 1). An 'energy' map calculated using only the water molecules (omitting the two short ones) is shown in Fig. 6. This figure, with the exception of the region containing strong H bonds around 1.6 to 1.7 Å, probably gives a better picture of the energy surface for normal and weak hydrogen bonds.

From the values of the bond valence marked along the O (acceptor) curve in Fig. 5 one can derive the correlation between bond valence and hydrogen-bond energy expressed in terms of E_0 . This is shown by the crosses in Fig. 7. The continuous line is the hydrogen-bond energy (in Kcal/mole) calculated for a straight hydrogen bond by Lippincott & Schroeder (1955). The two curves agree sufficiently well to suggest a value of about $2/3$ Kcal/mole for E_0 , an energy not far different from the van der Waals energies that are important in the structures of molecular crystals.

Chidambaram & Sikka (1968) have modified the Lippincott & Schroeder potential to calculate the energy of a bent hydrogen bond and their curves for $E=0$ and 2Kcal/mole, shown as dashed lines in Figs. 5 and 6, are in striking agreement with those derived in the present work.

Application to the structures of ice

Nowhere is the role of the hydrogen bond more important than in the structural chemistry of water and aqueous solutions. A complete description of liquid water remains elusive but a considerable amount is known of the structure of the various forms of ice and crystalline hydrates. In all of these the H-O-H angle is found to be close to 108° (Ferraris & Franchini-Angela, 1972) but a large range of O-H...O angles is found (see the dots in Fig. 2). The structures of ice are particularly interesting since they should show no tendency to form strong hydrogen bonds, that is bonds shorter than about 2.73 Å. Ice I contains normal hydrogen bonds (Peterson & Levy, 1957; Chidambaram, 1961) with an O-O distance of 2.76 Å.* This represents the strongest hydrogen bond that can be obtained without the strain introduced by the require-

ments of valence balancing, but such a bond must be nearly linear and leads to a relatively open and low-density crystalline structure. In the higher-pressure forms of ice the increase in density is associated with

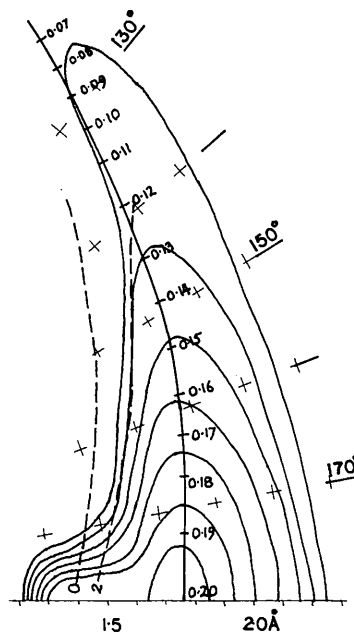


Fig. 5. 'Energy' function derived from the observed hydrogen-bond geometries. Contours in intervals of $E_0 \sim \frac{1}{3}$ Kcal mole $^{-1}$. The coordinates are H...O(acceptor) distance and O-H...O angle. The predicted curve is shown with bond valences. The dashed curves are the calculated energies (kcal/mol) of Chidambaram & Sikka (1968).

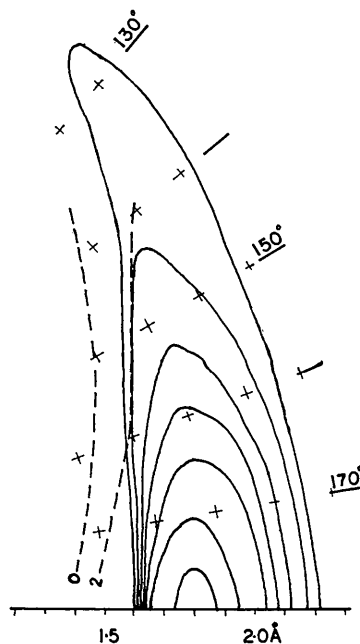


Fig. 6. 'Energy' function calculated as in Fig. 4 but using only hydrogen bonds formed by water molecules.

* The difference between the distance of 2.76 Å and the value of 2.73 Å suggested for a 'normal' hydrogen bond is not significant.

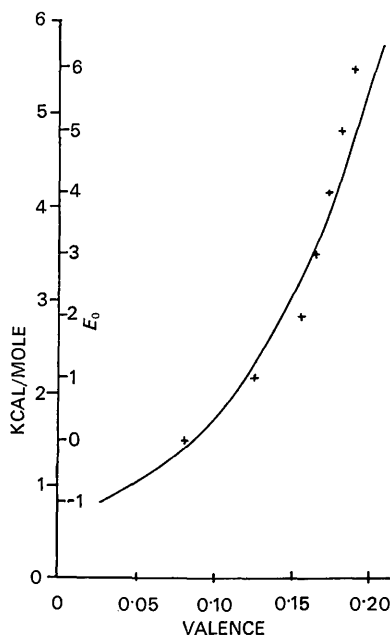


Fig. 7. Relationship between H-O(acceptor) bond valence and hydrogen-bond energy. Crosses are points derived from Fig. 6, the curve is from the calculations of Lippincott & Schroeder (1955).

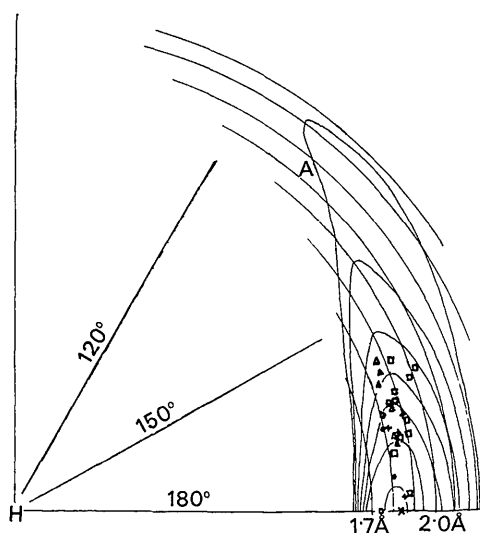


Fig. 8. Position of acceptor O atoms relative to H in various ice structures. The coordinates are the H...O(acceptor) distance and O-H...O angle. The contours given in Fig. 6 are shown for comparison. Key: \circ Ice I, disordered (neutron diffraction), Peterson & Levy (1957), Chidambaram (1961); $+$ Ice II ordered (neutron diffraction), Kamb, Hamilton, Laplaca & Prakash (1971); Δ Ice III disordered (X-ray diffraction), Kamb & Prakash (1968); \bullet Ice IX ordered (neutron diffraction), Laplaca, Hamilton, Kamb & Prakash (1973); \square Ice V partially ordered (neutron diffraction), Hamilton, Kamb, Laplaca & Prakash (1969); \times Ice VII disordered (X-ray diffraction), Kamb & Davis (1964); A , the position of the proton in ice VII if it were arranged to bond equally with all neighbours. The H atoms determined by X-ray diffraction have been moved to 0.96 Å from the donor O atom to facilitate comparison with neutron diffraction results.

a closer packing of the water molecules which requires bent and hence weaker bonds. The geometries of the H...O (acceptor) distances are shown in Fig. 8 together with the 'energy' contours of Fig. 6. They follow the same patterns as found in the crystalline hydrates (Fig. 2).

Coordination of cations by water

The ability of bond valences to give a quantitative description of the coordination water in crystalline hydrates (Brown & Shannon, 1973) suggests that they can also be used to discuss the coordination of ions in aqueous solution. Since water coordinates to cations through the O atom and to anions through the H atoms, it is convenient to discuss these separately.

Ideally, a water molecule will tend to form normal hydrogen bonds where the strong O-H bond is 0.8 v. u. and the weak one 0.2 v. u. The O atom therefore has 0.4 v. u. available for bonding to cations or for acting as an acceptor to other hydrogen bonds. If it is not able to use all this valence the donor O-H bonds will be further strengthened and the hydrogen bonding will be weakened. On the other hand, if it requires more than 0.4 v. u. to form a bond to a cation, the donor O-H bonds will be weakened and the hydrogen bonding will become stronger and strained as discussed above. Where possible the structure will adjust in order to avoid this situation.

The strength of the O-cation bond will be approximately V/N where V is the cation valence and N the cation coordination number. As Baur (1970) has shown, strong hydrogen bonds will be formed by the water molecule when $V/N > 0.4$, that is for four coordinate divalent ions and four or six coordinate trivalent ions. If V/N becomes much greater than 0.5, water will tend not to bond unless the coordination sphere can distort in such a way as to provide relatively weak cation-O bonds of about 0.4 v. u. Examples of strong hydrogen bonds are found in $\text{Be}(\text{H}_2\text{O})_4\text{SO}_4$ (O-O = 2.62 Å) (Sikka & Chidambaram, 1969) and in the alums, e.g. $\text{CsAl}(\text{H}_2\text{O})(\text{SO}_4)_2(\text{H}_2\text{O})_6$ (Cromer, Kay & Larson, 1966) where the hydrogen bonds formed by the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion have O-O = 2.63 Å. The length predicted for such bonds from Fig. 4 is 2.65 Å. The hydrated $\text{B}(\text{H}_2\text{O})_4^{3+}$ ion by the same analysis would require hydrogen bonds with a valence split of 0.62:0.38 (O-O = 2.53 Å) and the $\text{Si}(\text{H}_2\text{O})_4^{4+}$ ion would show a split of 0.50:0.50 (O-O = 2.44 Å). Such bonds would have large strains which could be relieved if each water were to lose an H atom. The species $\text{Si}(\text{OH})_4$ could readily form normal hydrogen bonds with water, each oxygen acting once as donor and once as acceptor, and it would show little tendency to lose further H atoms to form the species SiO_4^{4-} . Silicon in aqueous solution is therefore expected to occur as $\text{Si}(\text{OH})_4$. Similar arguments can be used to predict possible hydration structures and hydrogen bond strengths around other cations including H^+ .

Table 2. *Dissociation constants and numbers of hydrogen bonds formed by anions*

Key	Species	pK^*	Average number of H bonds	No. of H bonds acceptor O	No. of H bonds donor O
B ⁰	BO ₃ ⁻	13.8	5.0	5.0	
B ¹	HBO ₃ ⁻	12.7	4.0	4.33	3.33
B ²	H ₂ BO ₃ ⁻	9.1	3.0	3.67	2.67
C ⁰	CO ₃ ⁻	10.5	3.3	3.3	
C ¹	HCO ₃ ⁻	6.4	2.3	2.67	1.67
F ⁰	HCO ₂ ⁻	3.7	2.5	2.5	
A ⁰	CH ₃ CO ₂ ⁻	4.7	2.5	2.5	
Si ⁰	SiO ₄ ⁻	12.0	5.0	5.0	
Si ¹	HSiO ₄ ⁻	12.0	4.2	4.45	3.45
Si ²	H ₂ SiO ₄ ⁻	11.7	3.5	4.0	3.0
Si ³	H ₃ SiO ₄ ⁻	9.7	2.8	3.55	2.55
P ⁰	PO ₄ ⁻	12.7	3.7	3.7	
P ¹	HPO ₄ ⁻	7.2	3.0	3.25	2.25
P ²	H ₂ PO ₄ ⁻	2.1	2.25	2.75	1.75
S ⁰	SO ₄ ⁻	1.9	2.5	2.5	
As ⁰	AsO ₄ ⁻	11.6	3.7	3.7	
As ¹	HAsO ₄ ⁻	6.8	3.0	3.25	2.25
As ²	H ₂ AsO ₄ ⁻	2.2	2.25	2.75	1.75
Se ⁰	SeO ₄ ⁻	1.9	2.5	2.5	
I ⁰	IO ₄ ⁻	1.6	1.25	1.25	
Te ⁴	H ₄ TeO ₆ ⁻	11.3	3.0	2.67	3.67
Te ⁵	H ₅ TeO ₆ ⁻	7.7	2.5	2.33	3.33

* pK for reaction $H_{n+1}XO_y \rightarrow H + H_nXO_y$ for species H_nXO_y . Values from *Handbook of Chemistry and Physics* (1970).

approach here but is dependent on making a specific assignment of charges to the various atoms in the ion. The approach described above is easy to apply and gives predictions that are generally as good as those of Kossiakoff & Harker and in some cases (e.g. formic acid) much better.

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