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A Bent Hydrogen Bond Model for the Structure of Ice-I

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A bent–hydrogen-bond model for the structure of ice-I is proposed which uses a value for the H–O–H angle close to the vapour value of $104\frac{1}{2}$°. It is shown that while it is at least as consistent with the neutron-diffraction data of Peterson & Levy as the 'half-hydrogen' Pauling model, it is to be preferred from bond energy and spectroscopic considerations.

Recent studies on the structures of hydrated crystals by neutron diffraction and proton magnetic resonance indicate that the water molecule, when hydrogen-bonded into the structure, is not much distorted from its vapour configuration. Thus in oxalic acid dihydrate (Garrett, 1954) and sodium sesquicarbonate (Bacon & Curry, 1956), where the angles subtended at the donor water oxygen by the acceptor oxygens are respectively 84° and 114°, the corresponding H–O–H angles have been determined as 106° and 107°. This is to be expected, for it can be shown that the energy changes involved in the deformation of the H–O–H bond angle from the equilibrium value are at least several times higher than those involved in the formation of bent O–H $\cdots$ O hydrogen bonds. Hence, it would appear unlikely that in ice–I the H–O–H angle should increase by about 5° from the vapour value of $104\frac{1}{2}$° to *exactly* the tetrahedral value, in order that linear O–H $\cdots$ O hydrogen bonds may be formed.

The main reason for the assumption in recent literature (for example, Frank, 1958) of a tetrahedral value for the H–O–H angle in ice is the neutron-diffraction investigation of hexagonal D_2O ice by Peterson & Levy (1957), who have shown that their diffraction data are in good agreement with the 'half-hydrogen' model of Pauling (1935). It is the purpose of this paper to suggest a modification of the Pauling model which uses a value for the H–O–H angle close to $104\frac{1}{2}$°; to show that it is also consistent with the neutron-diffraction data; and then to advance some arguments in its favour.

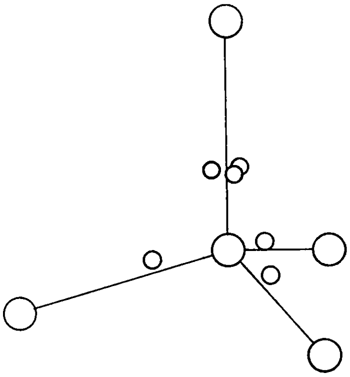

Fig. 1. Illustration of the splitting of a 'half-hydrogen' position into three 'one-sixth hydrogen' positions: ○–O, ○–$\frac{1}{6}$ H. (The splitting has been heavily exaggerated.)

If we suppose that the H–O–H angle is smaller than the tetrahedral value (*without being necessarily equal to the vapour value*), the so-called 'half-hydrogen' position will be split into three 'one-sixth hydrogen' positions distributed at the vertices of an equilateral triangle perpendicular to the O $\cdots$ O line, which will pass through the centroid of the triangle (Fig. 1). Here we have assumed that O $\cdots$ H–O–H $\cdots$ O lie in one plane (a reasonable assumption because for a given H–O–H angle this involves the minimum non-linearity in the hydrogen bonds) and that the non-linearity in the two hydrogen bonds from each oxygen is the same. It may be noted that this model retains the mean statistical space group D_{6h}^4–$P6_3/mmc$ of the 'half-hydrogen' Pauling model for hexagonal ice. If O–H = 1 Å and the angle H–O–H = $104\frac{1}{2}$°, each 'one-sixth hydrogen' position is shifted from the O $\cdots$ O line by

0·044 Å. Along each O · · · O line there are two triangles representing the splitting of the two 'half-hydrogen' positions. In hexagonal ice these triangles are related by a mirror plane for O · · · O lines parallel to the *c* axis and by a centre of symmetry for the others. Thus there is a distinction here between the two sets of O · · · O lines which may have some bearing on the lowering of the *c*/*a* ratio from the ideal value of 1·633 (LaPlaca & Post, 1960).

We will now show that in a neutron-diffraction structure analysis of hexagonal D_2O ice on the basis of the 'half-hydrogen' model, the splitting postulated above, if it exists, will be accommodated as part of the thermal motion of the D atoms perpendicular to the O · · · O line. The structure factors for the 'one-sixth hydrogen' model, calculated using the parameters O–D = 1 Å, $D\text{–}\hat{O}\text{–}D = 104\tfrac{1}{2}°$, $f_D = 0{\cdot}65$, $f_0 = 0{\cdot}58$ and the unit-cell constants $a = 4{\cdot}516$ Å, $c = 7{\cdot}357$ Å corresponding to −50 °C. (Lonsdale, 1958), are given in the second column of Table 1. The reflections used are those mentioned by Peterson & Levy to be especially sensitive to the model assumed. The third column gives the structure factors for the corresponding 'half-hydrogen' model and the last column those when an anisotropic temperature factor for a thermal vibration of r.m.s. amplitude 0·031 Å perpendicular to the O · · · O lines has been applied to the 'half-deuteriums'. (The values given here should not be compared with the experimentally observed ones because true temperature factors have not been applied). The excellent agreement between the second and last columns proves that the present model cannot be ruled out on the basis of neutron-diffraction data. In fact, even without the application of a differential anisotropic temperature factor the *F* values for the 'half-hydrogen' model given in the third column are very close to those for the 'one-sixth hydrogen' model.

Table 1. *Comparison of structure factors computed for the 'one-sixth hydrogen' and 'half-hydrogen' models*

$h0l$	$F_{(1/6)}$	$F_{(1/2)}$	$F'_{(1/2)}$
$10\bar{1}3$	−1·69	−1·69	−1·69
$20\bar{2}3$	1·30	1·30	1·30
$30\bar{3}1$	−0·35	−0·35	−0·35
$30\bar{3}2$	−1·22	−1·25	−1·22
$30\bar{3}3$	−1·03	−1·05	−1·04
$30\bar{3}5$	−1·66	−1·69	−1·66
$40\bar{4}4$	−0·07	−0·05	−0·05
$40\bar{4}5$	−1·09	−1·05	−1·07
$10\bar{1}9$	0·69	0·66	0·69
$0,0,\bar{0},10$	1·43	1·48	1·42
$50\bar{5}5$	0·34	0·31	0·35

In this context, it is pertinent to mention that a similar inability to distinguish between true and statistical centring by neutron diffraction has been encountered in the problem of proton location in short O–H · · · O hydrogen bonds (≃ 2·50 Å), where the diffraction data alone could not decide whether the proton is at the midpoint of the bond or occupies two half-positions separated by about 0·35 Å (Bacon & Pease, 1953; Peterson & Levy, 1958).

On the other hand, the following arguments are in favour of accepting the model postulated above:

(1) As mentioned in the first paragraph, energy considerations favour formation of bent O–H · · · O bonds to deformation of the H–O–H angle.

(2) The very small change in the H–O–H deformation frequency (1595 cm.$^{-1}$ in the vapour to 1640 cm.$^{-1}$ in ice) indicates a correspondingly small change in the H–O–H angle (Ockman & Sutherland, 1958).

(3) While the above arguments are in favour of any model which assumes an H–O–H angle close to $104\tfrac{1}{2}°$, a non-polar disordered model, using Rundle's suggestion (1953) of one linear and one bent O–H · · · O bond from each oxygen (e.g., Shimaoka, 1960), should also involve a 'rocking' disorder associated with the two ways of bonding a donor oxygen to the same two neighbours and hence an additional residual entropy of $R \ln 2$. But the experimental value of residual entropy is completely accounted for in terms of the Pauling disorder, which alone exists in the model postulated above.

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