

## Rigid H<sub>2</sub>O Molecule Model of Anomalous Thermal Expansion of Ices

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Structural details of hexagonal *Ih* and cubic *Ic* ices, resulting from a combination between H<sub>2</sub>O molecular and ice-lattice dimensions, reveal new features of the proton dynamics in hydrogen bonds, applicable to all aggregates of water molecules. Coupling of proton transfers with reorientations of molecules induce systematic changes in the hydrogen-bond dimensions, e.g., a shortening of the O···O distances, and an anomalous thermal expansion of the ice crystals about 80 K. [S0031-9007(96)01671-7]

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Water is one of the most abundant substances and its role in many physical, chemical, or biological processes cannot be overestimated. The relatively simple H<sub>2</sub>O molecule is also a prototypic structure for studying a proton transfer, after *e* transfer the second most frequent chemical transformation in nature [1]. Properties of water and ices equally apply to simple hydrogen-bonded structures and to much more complex substances, proteins, DNA and other biopolymers, containing up to 60% of water [2]. Protons are the dominant charge carriers in hydrogen-bonded systems. Simple models, assuming a double-well potential of the H motion, well reproduce such a subtle property of ices, as a nonmonotonic function of temperature of the soliton mobility in ice *Ih* about 200 K [3]. A proton transfer across cellular membranes is associated with possible coherence features in the proton motion [4]. All the theoretical and experimental data indicate a strong coupling between H sites and lattice vibrations [5]. Water and ices, particularly naturally occurring on Earth ice *Ih* stable down to 0 K and to pressures of about 0.2 GPa, are the most intensively studied hydrogen-bonded materials [6,7]; however, certain of their structural properties still require explanation [8]. Three mechanisms of transformations of the hydrogen-bonded network in ice are considered in literature: intermolecular proton hopping [9], molecular reorientations [9,10], and intramolecular proton migrations [11]. Their quantitative contribution to proton dynamics is not certain [12], although it is assumed that the H hopping prevails at lower temperatures [5]. Below it is shown that a combination of H<sub>2</sub>O molecular dimensions with structural dimensions of ice *Ih* reveals new features which, when associated with the proton dynamics, afford straightforwardly an understanding of such a fundamental property of ice as its negative thermal expansion below 100 K. The discussed effects are irrespective of the mode of the ice-structure transformations; therefore, only the intermolecular H hopping is discussed in detail.

At 0.1 MPa and 273 K water crystallizes into a hexagonal polymorph of ice *Ih*, space group *P6<sub>3</sub>/mmc*, with tetrahedrally coordinated water molecules and disordered

protons [13], shown in Fig. 1. Of two symmetry-independent hydrogen bonds one lies along [00.1] on a crystal site of *D<sub>3h</sub>* symmetry (e.g., OH--O' in Fig. 1), and the other is centered on a *C<sub>2h</sub>*-symmetric position (e.g., OH--O''' and O--HO''). Two symmetry-independent O···O···O angles are both close to the tetrahedral angle [7], thus markedly more open than the H—O—H angle of the water molecule. The H—O—H angle of an isolated water molecule is 104.54236° and the O—H distance is 0.9578478 Å [14]. This geometry may only slightly change in the molecular crystal [15,16], which was confirmed by the second moment NMR studies of ice *Ih* [17]; also the D—O—D angles (D denotes deuterium) in the ordered polymorphs of heavy ice agree within experimental errors with the above angle: 105.6(11)° in ice VII [18] and 105.4(6)° in ice IX [19]. Owing to much quicker electronic than

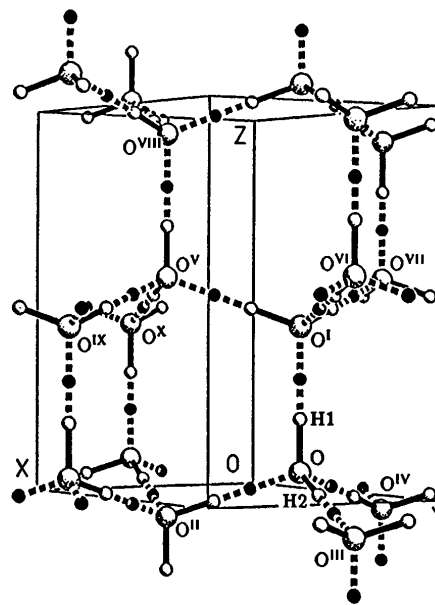


FIG. 1. Fragment of the *Ih*-ice structure viewed perpendicular to [z]. Two sets of frozen H sites are indicated by open and black circles; the covalent bonds of the former ones are drawn as full lines and their hydrogen bonds as dashed lines.

structural transformations, the H<sub>2</sub>O molecular dimensions are unlikely to be distorted by the static or dynamical disorder in the ice structures. Although precise results on the H<sub>2</sub>O geometry in the disordered structures are not available, this conclusion can be drawn by analogy to the hydrogen-bonded ferroelectric crystals of the KH<sub>2</sub>PO<sub>4</sub> type, where protons become disordered in two well resolved sites in the paraelectric phase. Precise structural data measured for such ferroelectric crystals testify to the absence of detectable geometry changes in the donor and acceptor groups when the protons become disordered [20], even though the hydrogen bonds involving *sp*<sup>2</sup> and *sp*<sup>3</sup> oxygen atoms are considerably shorter and stronger than in the H<sub>2</sub>O ices. Moreover, it was shown that the H-O distance does not change when the protons become disordered, either. Consequently, in the *Ih* structure the O—H covalent bonds cannot lie along the O···O directions, but are diverted from them by about 2.5° to satisfy the rigid H<sub>2</sub>O molecular dimensions, for the *D*<sub>3h</sub> and *C*<sub>2h</sub>-symmetric hydrogen bonds similarly. The O—H—O angles in the two hydrogen bonds are both close to 176.2° [see Eq. (1) below], and each of the  $\frac{1}{2}$  H sites indicated in Fig. 1 in fact consists of a group of three  $\frac{1}{6}$  H sites arranged in accordance with the *D*<sub>3h</sub> or *C*<sub>2h</sub> symmetries, as shown in Fig. 2. The three sites are separated by a mere 0.075 Å between themselves, the distance being far beyond the resolution of the presently available experimental methods [7].

Dimensions of a static hydrogen bond can be obtained from the interdependence of the molecular and crystal dimensions:

$$\eta_H = 180^\circ - \mu_a - \mu_d, \quad (1)$$

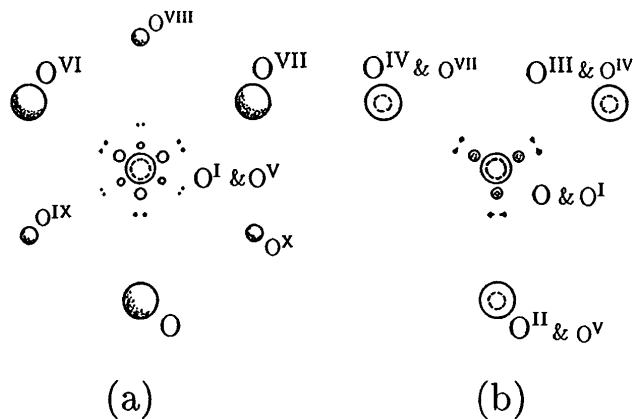


FIG. 2. Schematic drawing of the time-averaged distribution of the H sites (small circles) in the *C*<sub>2h</sub>-symmetric (a) and *D*<sub>3h</sub>-symmetric (b) hydrogen bonds viewed along O<sup>I</sup>···O<sup>V</sup> and O···O<sup>I</sup> directions (compare Fig. 1), respectively. The small circles are the H sites located below the midpoint of the bonds; slightly larger are the circles indicating the H sites above the midpoint. The small and larger dots indicate the virtual H sites, described in the text, below and above the hydrogen-bond midpoint, respectively.

where  $\eta_H$  is the O—H—O' angle characterizing the hydrogen bond,  $\mu_d$  is the H—O···O' angle, and  $\mu_a$  the H—O'···O angle:

$$\mu_d = (\eta_t - \eta_d)/2, \quad (2)$$

$$\mu_a = \sin^{-1}[(d_d/d_a) \sin \mu_d]; \quad (3)$$

$\eta_t$  is the O···O···O angle,  $\eta_d$  is the H—O—H angle and  $d_d$  the O—H covalent bond length, and  $d_a$  is the H—O distance:

$$d_a = \sqrt{d_d^2 + r^2 - 2d_d r \cos \mu_d}, \quad (4)$$

where  $r$  is the O···O distance between the oxygens of hydrogen-bonded water molecules. For the H<sub>2</sub>O *Ih* ice at 60 K [7] and the theoretically determined molecular dimensions  $d_d$  and  $\eta_d$  [14],  $\eta_H$ ,  $\mu_a$ , and  $d_a$  are 176.21°, 2.47°, and 1.7915 Å, respectively.

The interplay between the molecular and crystal dimensions in ice also affects the process of proton transfer between the hydrogen-bonded water molecules. This is illustrated in Fig. 3, showing an ice-structure fragment (compare Fig. 1) undergoing a transformation: atom H transfers from O<sup>I</sup> to O, which in accordance with Pauling's ice rule is accompanied by H transfers in the neighboring hydrogen bonds: atom H<sup>VII</sup> moves to O<sup>I</sup>, and H<sup>IV</sup> moves from O to O<sup>IV</sup>. The rigid molecular geometry implies that each H transfer can be considered to proceed in two steps. In the first step the protons transfer between

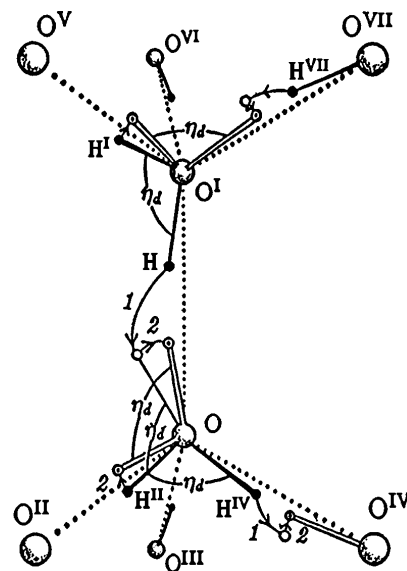


FIG. 3. Fragment of the *Ih* structure depicted in Fig. 1, showing schematically the process of H transfer. The initial stable sites of the H atoms are presented with full small circles and their bonds to the O atoms with solid lines. The virtual H sites immediately after transfer are shown with open circles, and are indicated with arrows 1. The stable H sites after the  $\varrho$  readjustments, indicated by arrows 2, are marked as open circles with dots inside, and their H—O bonds as open lines.

oxygen atoms, as indicated by arrows 1 in Fig. 3. Instantaneously after the transfers, so formed water molecule  $H^{IV}OH$  is unfavorably oriented with respect to the neighboring water molecules. To assume an energetically favored orientation, the molecule must readjust its orientation in the way indicated by arrows 2 in Fig. 3 (compare the H sites shown in Fig. 2). In the discussion below the H sites immediately after the H transfer, before the molecular reorientation, will be referred to as virtual H sites, the H sites after the molecular reorientation will be referred to as the stable ones, and the orientation adjustments will be called  $\varrho$  adjustments. The virtual H sites, marked near each stable H site in Fig. 2, are split due to two possible sites of the H atom leaving the water molecule ( $H^{IV}$  in Fig. 3). The  $O \cdots O$  distances corresponding to the stable and virtual H sites,  $r$  and  $r^v$ , are described by the formula

$$r = \sqrt{d_d^2 + d_a^2 - 2d_d d_a \cos \eta_H}, \quad (5)$$

$$r^v = \sqrt{d_d^2 + d_a^2 - 2d_d d_a \cos \eta_H^v}, \quad (6)$$

respectively; where

$$\eta_H^v = 180^\circ - \mu_d - \varrho - \sin^{-1}[(d_d/d_a) \sin(\mu_d + \varrho)]. \quad (7)$$

The  $\varrho$ -adjustment angle is approximately equal to  $\sqrt{3} \mu_d$ , i.e.,  $4.28^\circ$ .

In the ice structure the  $\varrho$  adjustments superimpose with other modes of vibrations of considerable amplitudes [12]. As the  $\varrho$  adjustments are inherent parts of any H-site changes, the effect of the  $\varrho$  adjustments on the structural dimensions depends on the time required by the  $\varrho$  adjustments to complete,  $\tau_\varrho$ , compared to the mean residence time  $\tau_H$  of an H atom in a given position. Assessed from the O-H-O bending-force constant [21],  $\tau_\varrho$  equals  $1.3 \times 10^{-13}$  s. The estimates of  $\tau_H$  in ice are  $10^{-13}$  s [22], while the relaxation time of the rotational diffusion measured for the overcooled water at 253 K is  $2 \times 10^{-12}$  s [23]. Thus, in the dynamically disordered *Ih* structure  $\tau_\varrho$  is comparable to, or somewhat shorter than  $\tau_H$ , and a substantial number of the molecules are in a stage of the  $\varrho$  adjustments. This influences the average  $O \cdots O$  distances, which becomes shorter than  $r$  owing to some contribution of  $r^v$ , and may be regarded as a time weighted average of  $r$  and  $r^v$ . This contribution of  $r^v$  disappears for the structure with proton motions frozen out.

The residual entropy of ice was connected with proton disorder by Pauling [24], and the thermal equilibration observed about 100 K was associated with freezing of the H motion [25]. More recent reinvestigations indicated that the relaxation heat capacity anomaly about 100 K for  $H_2O$ , and 115 K for  $D_2O$  ices is connected with the very initial stage of the freezing process [26], which takes place at considerably lower temperatures [27]. The theoretically postulated ambient-pressure orthorhombic phases of ice, ferroelectric of space group  $Cmc2_1$  or antiferroelectric

$Pna2_1$  [28], have not been confirmed, and the ice transformation is considered as a glassy one [27]. Diffraction studies below 100 K provide space-averaged positions of the atoms [7]. However, in annealed KOH-doped ice *Ih* a phase transition to the ferroelectric structure was observed at 72 K [29], in accordance with theoretical predictions [30,31]. The H motion halting coincides with the long-known anomalous thermal expansion of ice *Ih* [32], which levels up about 100 K and becomes negative below 80 K [33].

Dimensions of the two symmetry-independent hydrogen bonds in *Ih* at 60 K are identical within the experimental errors, and remain identical at 123 and 223 K [7]; also the changes in  $O \cdots O$  distances,  $\Delta r$ , are similar. The changes in the unit-cell dimensions of ice *Ih* depend directly on  $\Delta r$ :

$$\Delta a = 2\Delta r_a \sin(\eta_t/2), \quad (8)$$

$$\Delta c = 2\Delta r_c - 2\Delta r_a \cos \eta_t, \quad (9)$$

where  $\Delta a$  and  $\Delta c$  are the changes in unit-cell dimensions  $a$  and  $c$ , and  $\Delta r_a$  and  $\Delta r_c$  are changes in two symmetry-independent hydrogen bonds:  $O \cdots O''$  and  $O \cdots O'$  (Fig. 1), respectively. According to Ref. [33]  $\Delta a$  is 0.00106(8) and  $\Delta c$  is 0.0012(3) Å, when ice *Ih* is cooled from 80 to 70 K. The corresponding shortenings of the  $O \cdots O$  distances [Eqs. (8) and (9)] are  $\Delta r_a = 0.00065$  Å, and  $\Delta r_c = 0.00082$  Å. These magnitudes compared with the maximum shortening of the  $O \cdots O$  distance,  $r - r^v$  [Eqs. (5) and (6)] of 0.0088 Å, allow the mean residence time of H atoms,  $\tau_H$ , in ice *Ih* at 80 K to be assessed as of about  $10^{-12}$  s, the value being in agreement with the experimental results cited above [22,23].

In conclusion, the model of rigid water molecules accounts for the lengthening of the  $O \cdots O$  distances of hydrogen bonds, and hence the negative thermal expansion of the structure, when the H hopping is halted at about 80 K. The coupling between the H transfers and molecular reorientations is intrinsic to all aggregates of  $H_2O$  molecules, where angles H—O—H do not ideally match the  $O \cdots O \cdots O$  angles. This type of coupling is present in all supramolecules of  $H_2O$  on disordering of protons, and in all transformable structures with bistable hydrogen bonds: substances like  $NH_3$ ,  $H_2S$ , or  $HCl$ , nonsolvate and inclusion compounds or biopolymers, e.g., see [4,34,35]. In particular, it can be predicted that the cubic polymorph *Ic* of ice will also exhibit a negative thermal expansion at about 80 K, although no such an experimental evidence is presently available. In the diamond-type *Ic* structure all hydrogen bonds are centered on the crystal sites of  $D_{3d}$  symmetry, but they are nearly identical with the  $C_{2h}$ -symmetric hydrogen bonds of ice *Ih* [see Figs. 1 and 2(a)] [36]. The results presented here also indicate that the structural mechanism of the anomalous expansion of ices is more complex than that of

the much smaller in magnitude similar effect of negative thermal expansion in tetrahedrally bonded structures of Si, Ge, InSb, GaAs, ZnSe, or ZnS [37], connected with the transversal acoustic phonons [38].

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