Pressure variation of the O–H bond length in O–H---O hydrogen bonds

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Recent neutron diffraction studies have shown that O–H bond lengths do not show the same variation under pressure as given by the well-known empirical relationship between O–H and O–H---O bond distances. In this paper, we describe a modification to include pressure effects in an earlier potential function for isolated hydrogen bonds and examine the inverse co-relation between O–H and O–H---O distances. This modification takes into account the repulsive stresses caused by other atoms which come close to the hydrogen bond on compression. However, this produces only small differences in O–H values from the unmodified ones and therefore the results indicate that there may be systematic errors present in the experimental powder neutron diffraction values of O–H distances measured under pressure.

IT is well known that at 0.1 MPa, in O–H---O hydrogen bonds, the length (r) of covalent O–H bond has an inverse relationship with hydrogen bond distance R(O---O). This correlation holds for all types of O–H and O–D bond donors and in combination with all types of O acceptors and also for cases where the hydrogen bond is not isolated, e.g. for cases where an O–H group also accepts a hydrogen bond known as co-operative hydrogen bond in chains or rings (see reference 1 and other references therein). This empirical relationship ($r = f(R)$ or $f(d(\text{H---O}))$) has been verified by calculations based on potential functions for isolated hydrogen bonds[2]. Translating the variations of O---O distance into pressure, these authors predict that O–H (or O–D) increases by 0.0025 Å/GPa near an R of 2.75 Å (e.g. in ice). However, it has been recently shown that this behaviour was not observed in neutron scattering experiments on DO_2-ice VIII under high pressure up to 10 GPa. Here the increase in O–D was much smaller[3], only 0.0004 Å/GPa. In neutron diffraction studies on $Mg(OH)_2$, Catti *et al.*[4] found that both O–H and H---O distances shorten under pressure. This led these authors to argue that it is not correct to treat the potential of a hydrogen bond as pressure independent.

The aim of this paper is to point out how a hydrogen bond in a given structure may be affected by pressure and to examine the consequent variation of the O–H bond length versus the O---O distance on compression.

Our analysis is based on the fact that under pressure other neighbouring atoms of hydrogen bonds in a given structure will come closer to it and start exerting a repulsive stress. Figure 1 illustrates this for some 'co-operative hydrogen bond' situations. Here the distances (d_h) between hydrogen atoms decrease and contribute an additional repulsive energy to the energy of an isolated hydrogen bond. At 2.05 Å the limiting value of non-bonded H---H distances at 0.1 Mpa (ref. 5), the repulsive energy is ~ 4 kJ/mole (ref. 6). To see the effect of this, we have included these non-bonded H---H interactions, as a first instance, to the modified Lippincott and Schroeder[7] type potential function for an isolated hydrogen bond. This modification by Chidambaram and Sikka[8] was for bent hydrogen bonds. This recognized the fact that O–H and H---O separations are the main parameters for describing a hydrogen bond. This has been corroborated later by many authors[9].

With the inclusion of this non-bonded H---H interaction, the hydrogen bond potential V has the following terms:

$$V = V_1 + V_2 + V_3 + V_4, \tag{1}$$

$$V_1 = D\,\{1 - \exp\,[-n(r - r_o)^2/2r]\}, \tag{2}$$

$$V_2 = -C\,D \exp\,(-n(d-r_o)^2/2Cd, \tag{3}$$

$$V_3 = A_0 \exp\,(-b_o R) - B_o/R^6, \tag{4}$$

$$V_4 = A_H \exp\,(-b_H d_H) - B_H/d_H^{\,6}. \tag{5}$$

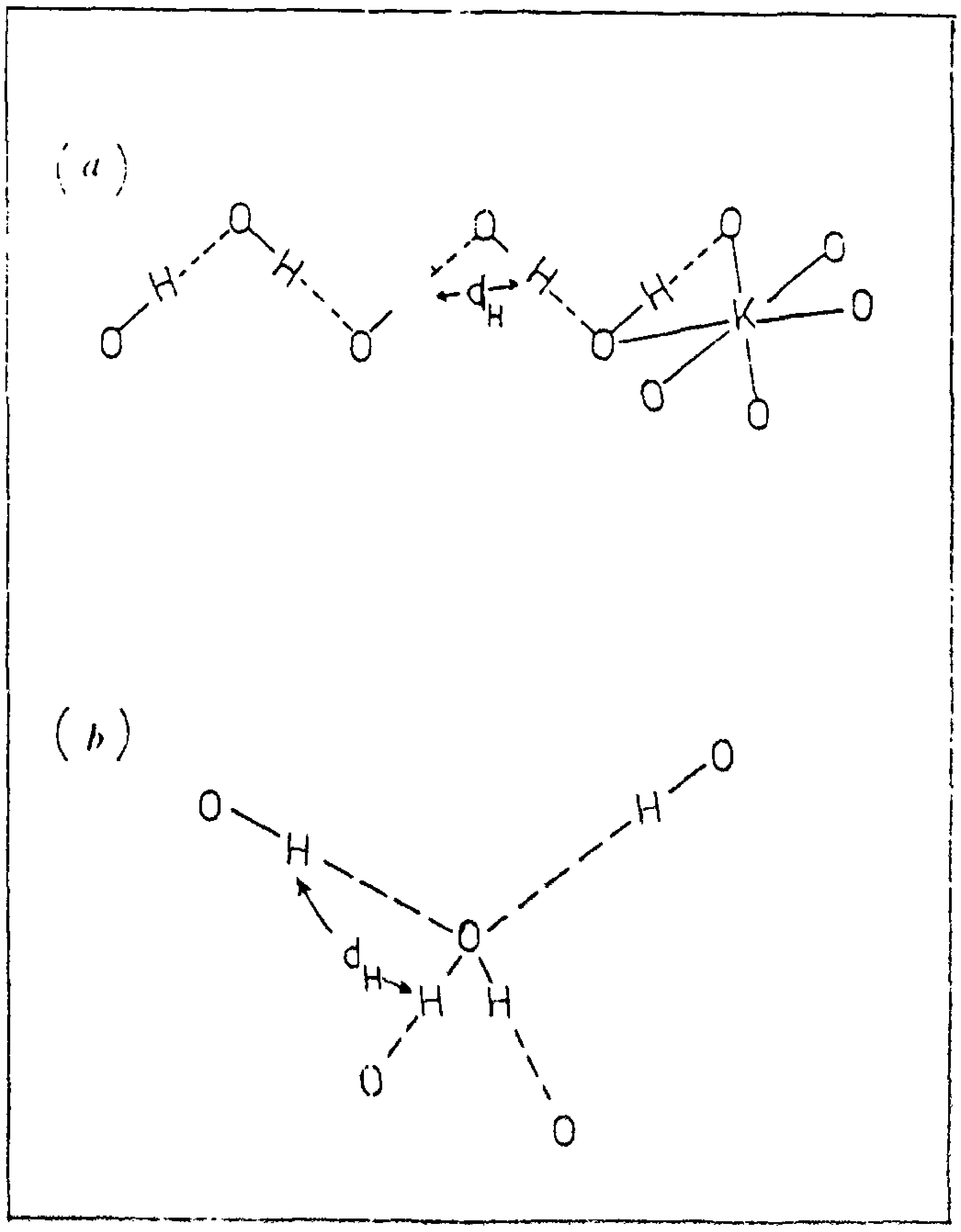

Figure 1. Some co-operative hydrogen bond situations. *a*, Hydrogen bond chains in KOH; ***b***, a tetrahedral hydrogen bonded H_2O molecule as in ice. Note the distance d_H as referred to in the text.

Here V_1 and V_2 represent the O–H and H---O interactions. The constant D is the dissociation energy of O–H bond and C is a factor which takes into account the weakness of H---O at the same separation. V_3 represents the non-bonded interaction between the acceptor and donor oxygens. V_4 is for the additional non-bonded H---H interactions. The equilibrium O–H length is determined by the condition

$$(\delta V/\delta r)_{eq} = 0. \qquad (6)$$

It may be noted that the inclusion of V_4 in equation (1) makes the potential function a specific function of the geometry of the hydrogen bond containing entity. Therefore, here, we have first done calculations for tetrahedrally coordinated oxygen atoms, which act as donors and acceptors for two hydrogen bonds each (the same situation as in ices). The values of various constants in equations (2) to (4) are as given by Chidambaram and Sikka[8]. A_H, b_H and B_H are the optimized values taken from the study by Filippini and Gavezzotti[6]. However, the results quoted below are not very sensitive to the choice of other values in literature.

Figure 2 shows the calculated r versus R for the two cases when the V_4 term is excluded in (case I) and included from (case II) calculations. The O–H values for the co-operative case are found to be smaller on the average by 0.0005 Å. This difference is much less than the present precision (0.003 Å) of neutron diffraction experiments on D_2O ice-VIII. At R 2.6 Å (p = 24 GPa), the non-bonded H---O contacts (oxygen atoms not involved in hydrogen bond with the donor oxygen) also give repulsive contributions to the energy of the hydrogen bond. However, their effect on the O–H length was also negligible. Further, Figure 3 illustrates the calculated O–H stretching frequencies for the two cases. The very recent infra-red values of Aoki *et al.*[10] are also plotted. We have employed the equation of state of ice-VII of Hemley *et al.*[11] to convert pressure into O---O distances. There is an excellent agreement with the values evalu-

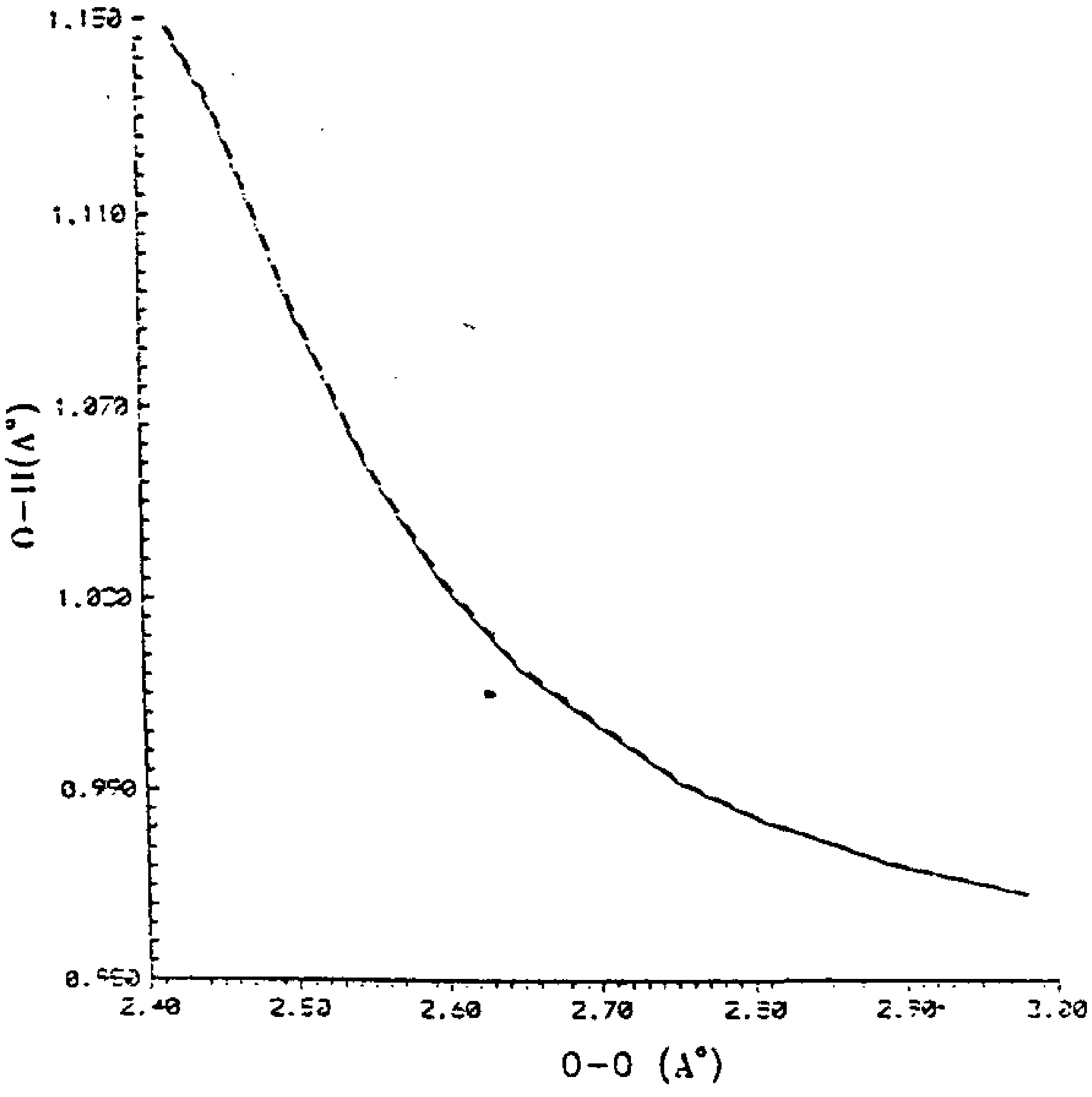

Figure 2. O–H versus O–H---O as for ice. Full curve is with H---H repulsion (equation 5) included and --- without it.

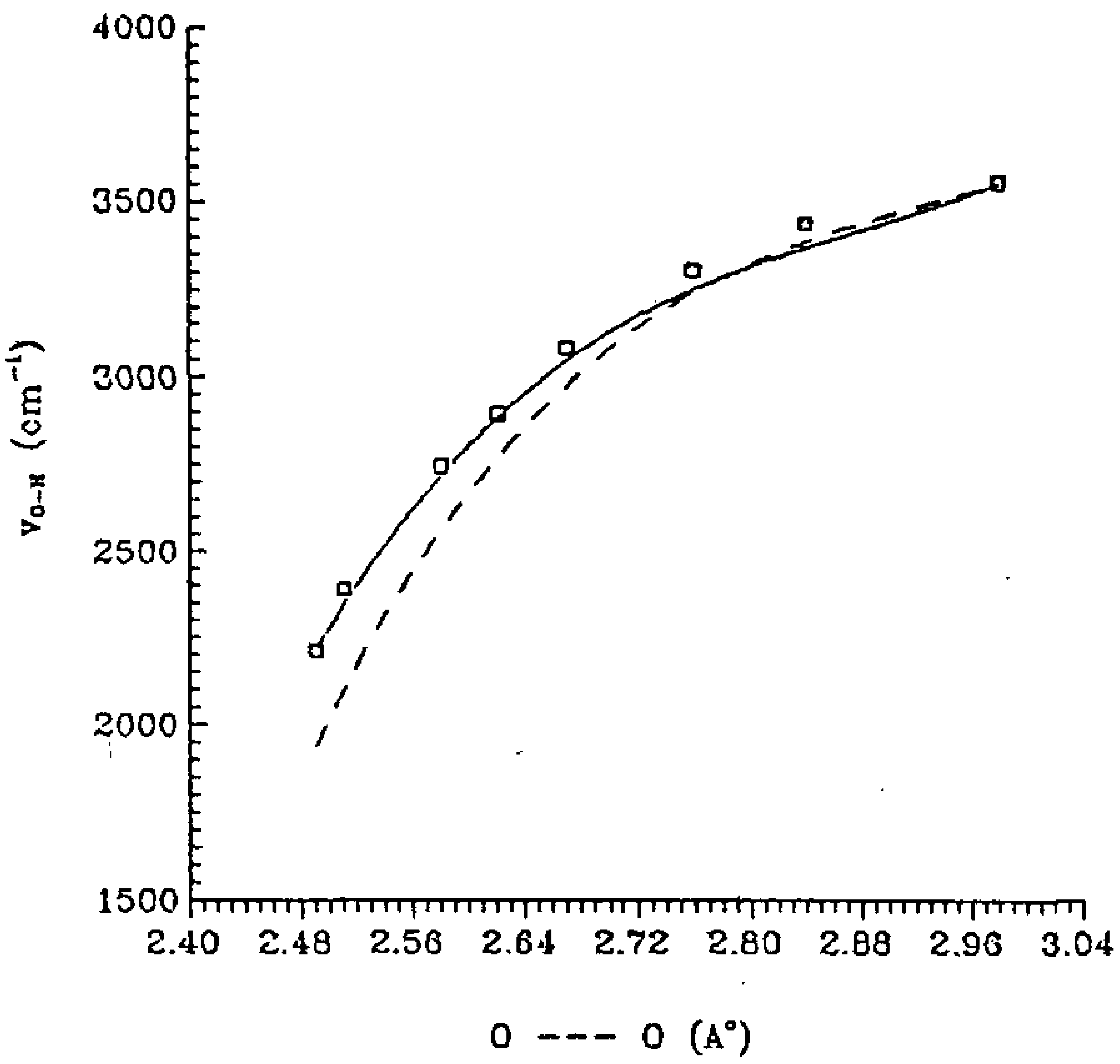

Figure 3. O–H stretching frequency ν_{OH} versus O–H---O distance for case I (-) and case II (---). The experimental data of Aoki *et al.*[10] on ice are shown as □.

Table 1. Comparison of some observed and calculated O–H distances in $M(OH)_2$ oxides⁺

	p	O---O	H---H	O---H$_{obs}$	O–H (Case I)	O–H$_{cal}$ (Case II)
$Ca(OH)_2$	0.1 MPa	3.33	2.2	0.936[b] 0.942[c] 0.950[c,d]	0.9574	0.9564
	6.3 GPa	3.12	2.06[a]	–	0.9580	0.9570
	10.7 GPa	3.00	2.00[a]	–	0.9588	0.9577
$Mg(OH)_2$	0.1 MPa	3.22	2.00	0.995[e] 0.947[c] 0.953[c,d] 0.919[f]	0.9576	0.9550
	7.8 GPa	2.94	1.85	0.912[f]	0.9595	0.9565

⁺All distances are in Å and uncorrected for thermal motion.
[a] Estimated from the data of Meade and Jeanloz[15].
[b] ref. 16.
[c] ref. 12.
[d] at 70 K for $Ca(OH)_2$ and 80 K for $Mg(OH)_2$.
[e] ref. 17.
[f] ref. 4.

ated from the 'isolated' hydrogen bond case. This means that the constants used in equation (5) overpredict the effect of other hydrogen atoms on the hydrogen bond. However, even with this, the calculated differences in O–H values for cases I and II are negligible. In $Mg(OH)_2$, the O–H bond length with H---H repulsion is shorter by 0.003 Å (see Table 1). However, the rate of increase with pressure is the same as that without repulsion (0.0002 Å/GPa). This allows us to conclude that the $r(O–H) = f(O---O)$ as given by the potential functions at 0.1 MPa continues to hold for high pressure situations within the accuracy possible in present day experiments.

How do we then reconcile with the experiments of Besson *et al.*[3] and Catti *et al.*[4]? It may be noted that these high pressure data are for a temperature of 280 K and O–H bond lengths are severely affected by thermal vibrations and their effect may be pressure dependent. Further, different correction procedures (riding model, independent model, etc.) yield different r values. This reduces the accuracy of true O–H bond length determinations to 0.01–0.02 Å even at 0.1 MPa compared to 0.003 Å precision of the present day neutron diffraction experiments (see Hamilton and Ibers[1] for a discussion). Only with low temperature data are such accuracies possible and that too using single crystals (refer Table 1 where the variation of O–H distances at 0.1 MPa may be noted). It may be argued that thermal corrections would tend to become smaller with increasing pressure as the Debye–Waller factors usually decrease under pressure. However, for the pressure ranges of the present neutron diffraction data, the thermal parameters for the hydrogen atoms do not vary drastically (e.g. see Table 3 in reference 4). Also the anharmonicity effects are again expected to be small (e.g. O–H distances for $Mg(OH)_2$ in the harmonic and anharmonic refinements at 0.1 MPa are 0.947 Å and 0.945 Å respectively[12]). Further, the experiments done with powders tend to be prone to larger errors at high pressures as preferred orientation effects make data less reliable (note the irregular behaviour of c/a ratio with pressure in the data of Besson *et al.*[3] for D_2O ice-VIII).

It may be noted that the Hartee-Fock calculations done by Besson *et al.*[3] give in ice the value of O–H bond lengths variations near to their experimental value. However, their absolute value of O–H bond lengths is near 0.95 Å, which differ from the experimental values by about 7σ. Where the calculated O–H bond length is ~ 0.95 Å, the variation produced by 0.1 MPa empirical relation is also smaller (see Table 1 and also Loveday *et al.*[13] for the variation 0.0002 Å/GPa for O–D value of 0.957 Å measured recently on NaOD-V). It is also interesting to note the observation by Ojamae *et al.*[14] that Hartee–Fock calculations do not compute well the O–H bond length for the water monomer.

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