TABLE II. Initial position parameters for oxygen and deuterium atoms in ice II.

Atom	x	y	z
H(I 2)	0.154	0.204	0.992
H(I 4)	0.221	0.207	0.210
H(II 1)	0.221	0.108	0.510
H(II 3)	0.306	0.072	0.437
O_I	0.222_7	0.196_3	0.050_3
O_{II}	0.188	0.230	0.480

have been to place the deuterons along the O–O bonds even though the O–O–O bond angles are 88° and 99°. However, second-moment proton NMR measurements[10] of ice II have strongly suggested an O–D bond length near 1.01 Å and an H–O–H angle of near 105°. Also, the work of Chidambaram[14] has conclusively demonstrated that in the case of hydrogen-bonded water molecules in a variety of crystals, even though the X_1–O–X_2 angle departs significantly from the tetrahedral angle, the bonding of the water molecule in the X_1–H–O–H–X_2 configuration is such as to give rise to an H–O–H angle close to the tetrahedral angle. Accordingly, both the H(I 2)–O_I–H(I 4) and the H(II 1)–O_{II}–H(II 3) angles, following the atom-designation system used in Kamb's paper,[6] were placed at initial values of 105°.

The refined deuteron atom-positioned parameters for ice II are given in Table III. These were obtained by a least-squares computer program which minimized the quantity $\sum w(I_0-I_c)^2$, where I_0 and I_c are the observed and calculated peak intensities, respectively, and w is a weighting factor proportional to the reciprocal square of the standard deviation of I_0. The atom positions in Table III, together with the oxygen positions given in Table II, can be used to calculate the water-molecule configurations shown in Table IV.[15]

DISCUSSION

A comparison of the initial and computer-refined deuteron-atom positions given in Tables II and III,

TABLE III. Refined-position parameters for deuteron atoms in ice II.[a]

Atom	x	y	z
H(I 2)	0.151±0.003	0.200±0.002	0.983±0.006
H(I 4)	0.223±0.002	0.214±0.003	0.202±0.005
H(II 1)	0.219±0.002	0.112±0.002	0.517±0.004
H(II 3)	0.302±0.002	0.065±0.002	0.442±0.006

[a] The isotropic thermal parameter B was found to be 0.70 Å²; all atoms were constrained to have the same value.

[14] R. Chidambaram, J. Chem. Phys. 36, 2361 (1962).
[15] A. C. Larson, R. B. Roof, Jr., and D. T. Cromer, "An Integrated Series of Crystallographic Computer Programs. VII. Interatomic Distances and Angle Calculations," Los Alamos Scientific Lab. Rept. LA-3309 (1965).

respectively, shows that only small displacements of the deuterons from the initially selected values were required. The residual R was found to be 0.041, where R is defined by the ratio $\sum_i w_i |I_0-I_c|/\sum w_i I_0$. This excellent quality of the fit suggested that an additional adjustment of the oxygen positions was not warranted. Kamb's oxygen positions were obtained by an x-ray analysis[6] of single crystals of ice II and the standard deviations of the oxygen coordinates were reported to be close to 0.0010.

It is of considerable interest to observe that for the ice II lattice, evidence has been obtained which supports the existence of bent hydrogen bonds. Yet, judging from the NMR results,[10] there is no great difference in the hydrogen-bond strengths of the various ice polymorphs. The O_I–D and O_{II}–D bond distances have been shown by an analysis of the neutron-diffraction spectrum to be very close to 1.00 Å.

As pointed out in the Introduction of this paper, strong support for proton ordering has been provided in previous work on the basis of infrared, dielectric relaxation, and residual entropy considerations. To

TABLE IV. Water-molecule configurations for nonequivalent oxygens in ice II.

Molecule	Bond distances and angles	
O_I	H(I 2)–O_I	1.04±0.04 Å
	H(I 4)–O_I	0.98±0.03 Å
	H(I 2)–O_I–H(I 4)	106±3°
O_{II}	H(II 1)–O_{II}	0.98±0.03 Å
	H(II 3)–O_{II}	0.96±0.04 Å
	H(II 1)–O_{II}–H(II 3)	106±3°

these can now be added the additional fact that neutron-diffraction measurements of polycrystalline D_2O ice are in accord with a proton-ordered arrangement.

Bertie and Whalley[8] have discussed the reasons for the existence of proton order in ice II when the ices Ih and Ic, for example, do not show this preferential atom positioning. Their suggestion was that the O–O'–O angles will in general be different and the hydrogen atoms bound to an O' will seek the minimum potential-energy configuration. In view of the data obtained in the present work on atom positions, it appears that this is precisely the case. In ices Ih and Ic there is not enough difference in the various O–O–O bond angles to permit one proton orientation to be particularly favored energetically, and consequently, these are proton-disordered arrangements.

The fact that ice II was not produced by the decompression of D_2O ice V at −35°C most probably is associated with the slower rate of transformation of D_2O ice at this temperature. The description[4] of the method was outlined for H_2O ices. Typically, the phase diagram of the D_2O ices corresponds to that for the H_2O ices with the difference that at a given pressure