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Hydrogen Bonding in Ethanol – A High Pressure Neutron-Diffraction Study

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ABSTRACT

We have determined the high pressure structure of perdeuterated ethanol by using neutron powder diffraction in the pressure region ~ 2.5 – 4.0 GPa and compare it to that previously measured by single-crystal X-ray diffraction and the one suggested by *ab initio* structure calculations. In contrast to previous X-ray single-crystal studies, we see no evidence for a disordered proton around the hydroxyl group, but confirm the monoclinic symmetry in the measured pressure region. We also present the compression behaviour of the unit cell in this pressure range.

KEYWORDS

neutron diffraction, ethanol, molecular solids, crystal structure, high pressure, hydrogen bond

1. Introduction

High pressure provides a powerful probe for the study of polymorphic behaviour and molecular interactions. There is a strong relationship between intermolecular interactions, symmetry, molecular morphology, structure and dynamics within solid-state organic materials. Therefore, it is important to systematically perturb intermolecular distances so that the effects on the molecular structure and physical properties can be understood. It is for this reason, that extensive crystallographic and spectroscopic studies are made on hydrogen-bonded materials at high pressure [1].

Ethanol is a simple hydrogen-bonded material. It has been shown to crystallise at ambient pressure upon cooling to a temperature of ~ 156 K into a solid with monoclinic symmetry (space group P_c) and at a pressure of ~ 1.9 GPa, at ambient temperature, into a further monoclinic structure with space group $P2_1/c$ [2, 3]. The arrangement of the molecular units, and the nature of the hydrogen bonding, have been described in depth

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elsewhere [4, 5]. In brief, for the high pressure form, the ethanol molecules are shown to form linear hydrogen-bonded chains parallel to the b -axis of the unit-cell. Within each chain the molecules are co-planar and aligned parallel to each other. The methyl groups are arranged so as to link each, chain again along the b -axis, via an interlocking-like arrangement. In this work [5] the hydrogen atom positions were located by a difference synthesis method based on phases derived from the C and O positions. By using this approach, the hydrogen atoms of the methyl and methylene (CH_3 and CH_2) groups were clearly observed. However, two peaks were observed in close proximity to the O atom, indicating disorder in the hydrogen atom position within the structure.

Herein, we have revisited the crystallographic structure of ethanol at high pressure. We have performed high pressure neutron powder-diffraction measurements of perdeuterated ethanol at pressures between ~ 2.5 and 4 GPa. We see no evidence for the disordered proton of the hydroxyl group as observed previously, and hence propose a modified crystallographic structure for the high pressure polymorph of ethanol in this pressure region.

2. Experimental

High pressure time-of-flight (TOF) neutron powder-diffraction measurements were conducted on the PEARL high pressure beamline located at the ISIS Facility, Rutherford Appleton Laboratory, UK [6]. The PEARL diffractometer is a high-flux, medium-resolution instrument optimised for data collection from the Paris-Edinburgh (P-E) press [7]. The liquid perdeuterated ethanol (99% Sigma-Aldrich) was loaded into a null-scattering Ti-Zr alloy capsule gasket [8]. The loaded gasket was then sealed within a P-E press equipped with standard toroidal profile tungsten carbide (WC) anvils. In addition to the liquid sample, a lead sphere (ca. 0.8 mm in diameter) and powdered silica wool were loaded. In this standard setup, the lead acts as a suitable pressure calibration marker and the silica wool forms seeding points, which reduce the likelihood of preferred orientation in the growth of the crystallites when the sample freezes on compression. During the experiment, the unit-cell volume of the Pb calibrant, as determined by Rietveld refinement, was used to determine the pressure from a previously determined Murnaghan equation of state (EoS) [9]. The load was applied sequentially until crystallisation of the liquid occurred (33 tonnes) at which point a diffraction pattern was collected for approximately 9.5 hours. The load was then increased in 3 tonne increments up to a maximum load of 45 tonnes, and at each pressure step data were collected for ~ 6 hours. The TOF diffraction data were normalised and corrected using in-house software [10]. A beamline-developed correction for the wavelength and scattering-angle dependence of the neutron attenuation by the WC anvils and Ti-Zr gasket materials was applied to the observed pattern [6]. GSAS and EXPGUI were used for Rietveld refinement [11]. The scattering from the pressure calibrant and the anvil materials (WC and Ni binder) were accounted for by additional crystalline phases in the Rietveld refinements. A least-squares fit to the volume change with increasing pressure was used to determine the bulk modulus and was performed using the Pascal programme [12].

Table 1. Compressibilities of ethanol. The median principal compressibilities are detailed and the corresponding principal axes component X_i are also shown.

Principal axis, i	K_i (TPa $^{-1}$)	a	b	c
X_1	17.89(73)	-0.2805	0	0.9599
X_2	9.96(28)	0.0000	-1	0.0000
X_3	7.67(17)	0.8304	0.0000	0.5572

3. Results and Discussion

3.1. Behaviour upon Compression

The liquid ethanol sample was found to crystallise at an applied load of 33 tonnes. Figure 1 (left) shows the TOF diffraction pattern collected at 39 tonnes from ethanol within the WC anvils. Also shown is the subsequent results of the Rietveld refinement. Upon crystallisation at 33 tonnes determination of the pressure from the known EoS of lead gave a sample pressure of 2.48(6) GPa. Upon further compression, no change in the diffraction pattern was observed beyond that expected by compression. The diffraction patterns are shown in Figure 1 (right). Up to the pressure of 4 GPa, the sample remains in the monoclinic symmetry previously determined by X-ray single-crystal diffraction, with the space group $P2_1/c$.

Figure 2 shows the change in unit-cell volume with pressure and subsequent fit with a 2nd order Birch-Murnaghan equation of state. The determined bulk modulus (B_0) is 12.9(5) GPa with a refined value for V_0 of 283(1) Å³ (Figure 2). Often, for materials which crystallise with low symmetry, the compressibility of the unit-cell axes do not reflect the fundamental response of the material to the application of pressure. As such, a unique set of orthogonal axes (principal axes) are found that allow the response of the material to compression to be observed in a more linear manner. The principal axes and compressibilities for ethanol between 2.5 and 4 GPa have been determined and are detailed in Table 1 and Figure 2. It should be noted that the X_1 principal axis shows significantly greater compression compared to the other two axes, and is close to the crystallographic c-axis. The crystallographic axes behaviour can be seen in the SI for which all unit-cell parameters decrease linearly with pressure.

3.2. High Pressure Structure Revisited

It is well known that, by virtue of its scattering mechanism, neutron diffraction is superior in the quality of structural information it provides in comparison to that given by X-rays for materials containing low Z -atoms [13]. During the process of refinement of the current neutron data it became clear that the two-site disorder model for the hydrogen atoms of the ethanol hydroxyl group was not correct. The weighted R factor of the Rietveld refinement (indicating quality of fit) for the disordered model is 7.32 %, with free refinement of the hydrogen occupations over the two sites. Refinement of the occupancies of the two atomic sites (D11 and D12) gave a fractional occupancy ratio of 0.95:0.05. If the ratios were manually fixed to other values the quality of the fit deteriorated significantly. Performing the refinement using an ordered model, with a single deuterium at the hydroxyl site (D11), gave a weighted R factor for the fit of 2.89 % (such low values in fit parameters are expected for the backgrounds inherent in data collected with WC anvils). There were significant visual differences in the quality

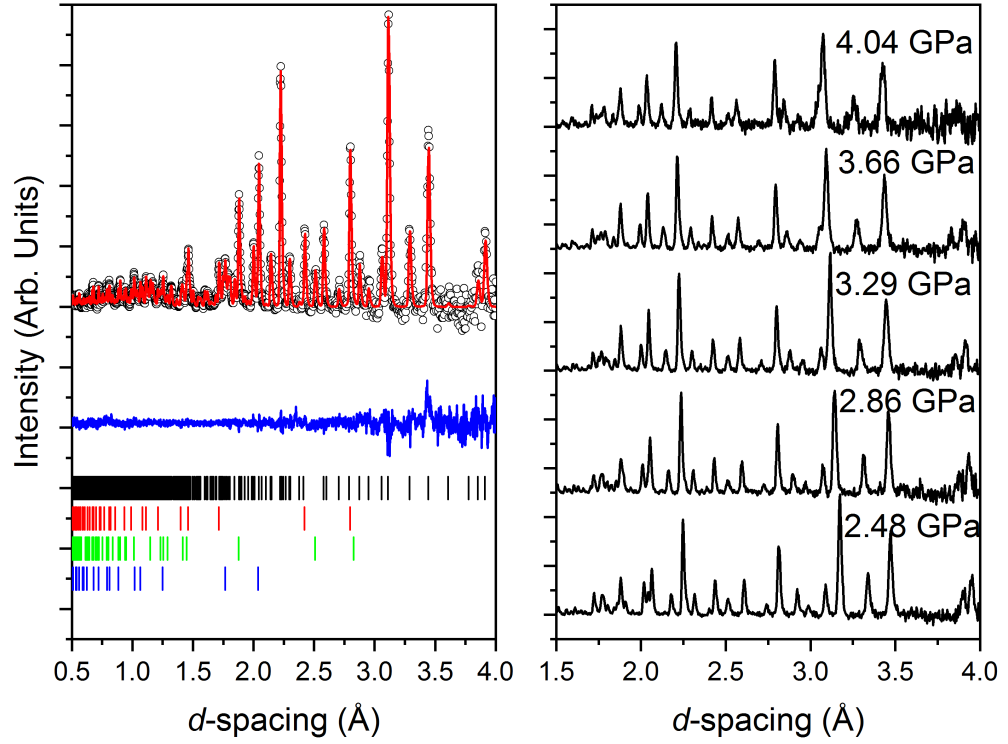


Figure 1. Neutron powder TOF diffraction of ethanol with increasing pressure. Left: Representative neutron diffraction pattern and Rietveld fit of data collected from ethanol at 3.29(4) GPa within the PE press. Experiment data are shown as open black circles, the solid red trace shows the calculated profile and the bottom blue trace shows the residual of the fit. The tick marks show the expected reflection positions for each of the phases fitted in the patterns, which are, from top to bottom, ethanol (black), Pb (red), WC (green) and Ni (blue). Right: Neutron diffraction patterns of ethanol with increasing pressure. All patterns and Rietveld fit are shown background subtracted for ease of comparison.

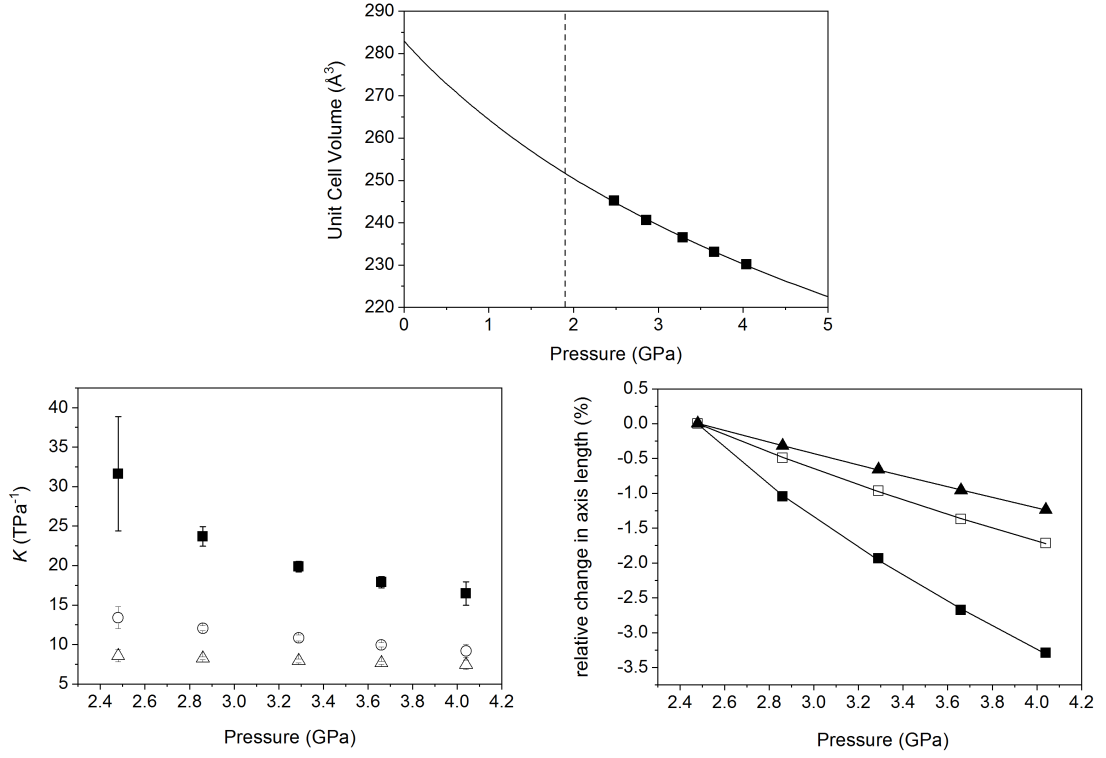


Figure 2. Compressibility of ethanol at 290 K. Top: Variation in unit-cell volume as a function of pressure. The solid line shows the determined 2^{nd} order Birch–Murnaghan equation of state (see text for more details), the dashed vertical line shows the crystallisation pressure at ~ 290 K [3]. Bottom Left: Principal linear compressibilities K_1 shown by solid squares, K_2 open circles and K_3 open triangles. Bottom Right: Relative changes in the lengths of the principal axes upon compression. X_1 shown by solid squares, X_2 open squares and X_3 solid triangles (see main text and Table 1 for further details). Error bars are shown but where they are not visible they are smaller than the symbols.

of fits between the two different models, where for the disordered model there is an overall misfit across the whole d -spacing range, but in particular for the $20\bar{2}$ reflection at ~ 3.17 Å, which is not evident in the fit for the single site model (see Figure 1). As such, we suggest that there is only a single hydrogen site for this atom within the crystallographic structure, and hence the hydrogen of the hydroxyl group is ordered. The results of the refinement for the data collected at 2.86(5) GPa are given in Table 2 and compared to those determined previously, and those calculated by *ab initio* methods [4, 5]. It should be noted that the accuracy of the determination of the deuterium positions is much improved in comparison to the hydrogens from the X-ray single crystal study.

Table 3 gives details of selected bond lengths and compares them to those determined previously by single-crystal X-ray diffraction and the *ab initio* structure calculations. There is a marked improvement in the agreement between the hydrogen bond lengths determined by neutron diffraction and those calculated for the previous *ab initio* study [4] than those determined by X-ray single-crystal diffraction [5]. However, not surprisingly, the previous single-crystal X-ray study gives a better determination of the atomic positions within the C and O framework, but subtle differences between values as a result of deuteration can also not be ruled out. Upon compression, the O–D and O \cdots D bond lengths show the expected linear behavior in the pressure range measured, whilst the C–O and C–D bond lengths show no measurable change in value upon compression.

4. Conclusions

We have revised the crystallographic structure of ethanol at high pressure. By using high pressure neutron diffraction we have shown that there is only one deuterium site around the oxygen atom and hence its position is ordered, and not disordered, as previously suggested by single-crystal X-ray diffraction [5]. This result is in agreement with *ab initio* modelling [4].

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Table 2. Atomic coordinates of ethanol at 2.86(5) GPa (this study), those from the previous X-ray single-crystal diffraction study at 2.75 GPa [5] and the *ab initio* calculations [4]. Note that for the current and theoretical study the H12 atom is not observed/predicted.

Atom	Current			X-ray			<i>Ab initio</i>		
	x	y	z	x	y	z	x	y	z
O1	0.9388(16)	0.2838(25)	0.1592(14)	0.9344(5)	0.2950(10)	0.1622(6)	0.9429	0.2763	0.1750
D(H)11	0.9667(19)	0.4752(24)	0.2083(19)	0.952(5)	0.462(9)	0.188(8)	0.9872	0.4627	0.2312
H12	-	-	-	0.933(11)	0.18(3)	0.239(15)	-	-	-
C2	0.7470(16)	0.2863(21)	-0.0008(15)	0.7515(8)	0.2786(13)	0.0015(8)	0.7691	0.3003	0.0076
D(H)21	0.6488(14)	0.3738(24)	0.0396(14)	0.660(2)	0.363(3)	0.034(3)	0.6631	0.4124	0.0456
D(H)22	0.7597(13)	0.3948(24)	-0.1283(14)	0.755(2)	0.372(3)	0.113(3)	0.7877	0.4222	0.1103
C3	0.7053(19)	-0.0259(25)	-0.0547(17)	0.6995(7)	0.0200(12)	0.0541(8)	0.6950	0.0142	0.0704
D(H)31	0.6904(13)	-0.1414(27)	0.0623(15)	0.695(6)	0.112(4)	0.058(3)	0.6629	0.1058	0.0385
D(H)32	0.8136(18)	-0.1035(28)	-0.0937(17)	0.793(4)	0.103(4)	0.088(5)	0.7995	0.1006	0.1067
D(H)33	0.5767(20)	-0.041(4)	-0.1729(22)	0.579(3)	0.029(3)	0.163(4)	0.5575	0.0344	0.2112

Table 3. Selected bond lengths (in Å) of ethanol at 2.86(5) GPa (this study), those from the previous X-ray single-crystal diffraction study at 2.75 GPa [5] and the *ab initio* calculations [4]. Note that for the current and theoretical study the H12 atom is not observed/predicted, and hence some bond lengths are not determined.

Bond	Neutron	X-ray Single Crystal	<i>Ab initio</i>
O1...H11	1.752(12)	2.06(4)	1.626
O1-H11	0.977(12)	0.82(4)	0.970
O1...H12	-	1.92(5)	-
O1-H12	-	0.80(5)	-
C2-O1	1.411(11)	1.408(7)	1.336
C2-C3	1.548(10)	1.487(8)	1.484
C2-H21	1.010(13)	0.936(18)	1.101
C2-H22	1.114(12)	0.967(18)	1.097
C3-H31	1.071(13)	0.944(18)	1.091
C3-H32	1.054(15)	0.937(18)	1.091
C3-H33	1.003(15)	0.931(18)	1.087

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