Structure of the α-phase of solid methanol

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The crystal structure of α-methanol at 15 K has been determined from neutron powder diffraction measurements. The structure is orthorhombic, space group $P2_12_12_1$. The molecular geometry is found to be very similar to that in the gas phase, but the methyl group no longer has ideal 3-fold symmetry. The crystal is formed by infinite hydrogen-bonded chains of molecules with adjacent chains 'pointing' in opposite directions. The O–H ... O hydrogen bonds are almost linear. No phase intermediate between the low temperature α-phase and the high temperature β-phase was found, but a new, metastable phase was discovered.

1. Introduction

Methanol (CH_3OH) is a simple organic molecule which crystallizes in at least three, and perhaps four, different phases composed of hydrogen bonded chains. As a result of its basic simplicity, methanol has been extensively studied, both experimentally and theoretically, to test theories of hydrogen bond and of chain formation.

On cooling, methanol freezes at 175·37 K and then undergoes what was originally thought to be a second-order transition [1] from a high temperature β-phase to a low temperature α-phase at 157.4 K [2]. Later measurements with a dilatometer [3] showed that there are actually two transitions, a first-order transition at 159 K and a second-order transition which occurs at 156 K. Mixtures of the α- and β-phases were observed in Raman experiments [4], which confirmed that the higher temperature transition is first-order. An amorphous phase is obtained by vapour deposition at low temperature and this phase transforms to the α-phase on warming to 130 K [5].

The structure of crystalline methanol has been investigated with X-rays [6–8]. Tauer and Lipscomb [8] described the crystal in both the α- and β-phases as consisting of parallel chains of hydrogen bonds. In the β-phase there are four molecules in an orthorhombic unit cell belonging to the space group D_{2h}^{17}–Cmcm and the zig-zag chains are parallel to the (100) face. According to the diffraction results, the carbon atoms lie in the plane of the oxygen atoms but there is strong evidence that this is only an average of two puckered structures which are expected to be closely related to the structure of the low temperature α-phase. This evidence includes: large thermal motion perpendicular to the plane of the chains [8], a dielectric constant whose value is similar to that for the liquid, and which is interpreted in terms of dipoles maintaining their orientational freedom in going from the

liquid to the β-phase [9], very narrow N.M.R. linewidths, comparable to those of the liquid, again indicating considerable motion of the molecules [10], and a Raman spectrum which consists of broad features with no splittings or fine structure as expected for a disordered structure [4].

Tauer and Lipscomb [8] obtained only low quality diffraction data for the α-phase. Their results suggested that the hydrogen bonds are puckered and that the essentials of the structure can be described in terms of a monoclinic unit cell containing two molecules in the space group C_{2h}^2–$P2_1/m$. However, the presence of some weak reflections suggested the existence of a superlattice. The detailed structure of this low temperature phase thus remained unknown. On the basis of their data there have been a number of studies of the dynamics of the hydrogen bonded chains [5, 11–14]. The thesis of Passchier [14], in particular, gives a very clear account of such studies. Obviously any future work in this area would benefit from a knowledge of the detailed structure of the α-phase. Changes in the dielectric constant [9], N.M.R. linewidths [9] and Raman linewidths [4] at the transition temperature(s) indicate that the α-phase has an ordered structure.

We present here the results of a neutron powder profile study of the α-phase of deuterated methanol. The use of a polycrystalline sample is necessitated by the inability to obtain single crystals of the α-phase. Tauer and Lipscomb [8] failed to obtain a single crystal of methanol in the α-phase even though several crystals of the β-phase were cooled through the transition(s). Since neutrons are used as the probe, the positions of the deuterium atoms can be determined. The position of the deuterium forming the chains is of particular interest since it has been suggested [14] that linearity of hydrogen bonds is the determining factor in the arrangement of the molecules.

This structural investigation complements our recent Raman and infrared [4] study of the lattice modes of methanol. Together they provide a basis for a more detailed examination of the molecular dynamics in solid methanol.

2.   Experimental details

The diffraction measurements were made on the C5 triple-axis spectrometer, operated in its two-axis mode, at the NRU reactor, Chalk River. The monochromator was Si(115) and horizontal collimations of $0.44°$ and $0.40°$ were used before and after the sample respectively. A sapphire filter (5 cm long) was placed in the incident beam to reduce the flux of higher-order neutrons and to lower the background. The spectrometer was calibrated using Al powder as a standard and the neutron wavelength was determined to be $1.60129(5)\,\text{Å}$. The experimental profiles were measured by stepping the detector in $0.1°$ steps in the scattering angle, 2θ, from $10.0°$ to $116.0°$.

The deuterated methanol, CD_3OD, was supplied by MSD Isotopes and had an isotopic purity of at least 99 per cent. A polycrystalline sample was prepared by dripping the liquid into a thin-walled vanadium can immersed in liquid nitrogen. The solid methanol formed in the can was mechanically ground into a fine powder before more liquid was added. In this manner the can, measuring 7.5 cm long by 1.2 cm in diameter, was filled and then mounted on the cold tip of a closed cycle refrigerator without the temperature of the sample exceeding 90 K. The sample was annealed at 155 K to eliminate any β-phase component which may have been present. This anneal was continued (for 1.5 hrs) until the three intense peaks with

scattering angles between 27° and 30° showed no further changes. Diffraction profiles for this sample were subsequently recorded at 15 K.

As mentioned in the introduction, there is one report of an intermediate phase at temperatures near the α-β transformation [3]. To search for this phase the sample was slowly warmed to 165 K while the intense peaks were monitored. No evidence of an intermediate phase was observed. The low angle part of the β-phase powder pattern was recorded at 165 K and showed definite structure in the background which is indicative of disorder. An attempt was made to lock-in the β-phase by rapidly cooling the sample and the resulting pattern was recorded at 15 K. When the sample is held for a prolonged period at 165 K, substantial crystallite growth takes place and hence the sample is of poor quality for powder diffraction studies. Therefore short anneal times at 170 K were tried until the diffraction pattern stabilized, and then the sample was cooled rapidly to 77 K or lower. In one attempt the sample was immersed directly in liquid nitrogen.

Although warming the sample slowly through the α-β transition produced no evidence of an intermediate phase, the three intense peaks with scattering angles between 27° and 30° changed to two peaks, consistent with the β-phase structure determined with X-rays [8]. Rapid cooling of the sample from the β-phase produced a diffraction pattern with two distinct components neither of which was the β-phase. Our attempts to lock-in the β-phase at low temperatures were thus unsuccessful, but in the process we produced a metastable phase in addition to the expected α-phase. The β-phase apparently cannot be locked in by quenching to low temperature. Since crystallite growth occurs rapidly at all temperatures for which the β-phase is found, measurements to determine the detailed structure of the β-phase must be made with a data collection rate higher than that used for the present measurements. We shall report on the structure of the β-phase and of the metastable phase at a later time. Here we concentrate on the structure of the stable α-phase. Figure 1 shows the experimental profile for the sample annealed at 155 K and then cooled to 15 K.

3. Analysis of the α-phase

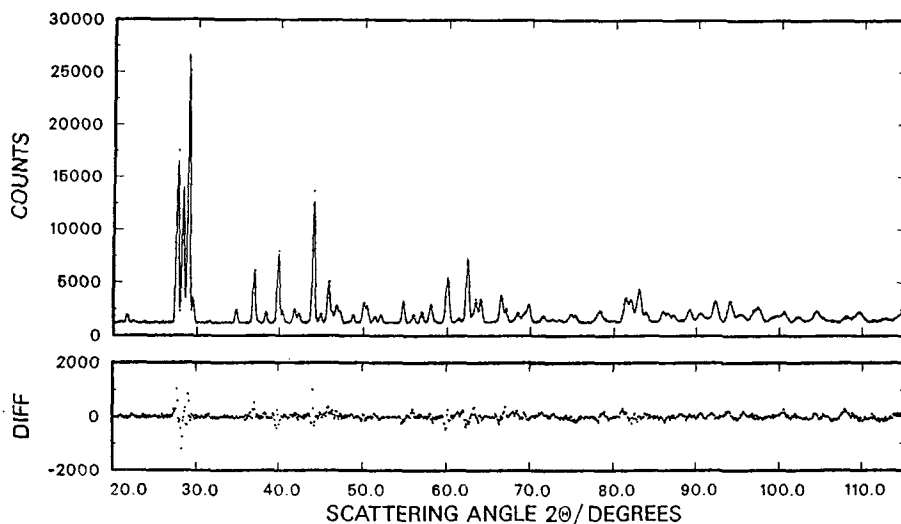The powder diffraction profiles were analysed by means of the program EDINP

Figure 1. Comparison of the observed and fitted profiles for deuterated α-methanol at 15 K.

[15], a modification of the Rietveld analysis [16] in which molecular orientations and bond lengths can be constrained during the initial refinement cycles. The shapes of the Debye–Scherrer peaks were well described by gaussian profiles with the full width at half height, Γ, given by $\Gamma^2 = U \tan^2 \theta + V \tan \theta + W$ where 2θ is the scattering angle. Initial values for the constants, U, V and W were derived from the calibration results but the values were subsequently adjusted as part of the profile refinement.

The neutron powder profile was indexed on a trial-and-error basis by looking for Pythagorean relations among the lattice spacings determined from the low angle peaks. Systematic absences were used to identify the space group but the absences were sufficiently ambiguous that the final trial space group was found as a result of testing a number of possibilities. The geometry of the molecule was fixed in the gas phase configuration [17, 18] and the orientation and position of the molecule were varied as allowed by the trial space group. Once it was established that the space group was D_2^4–$P2_12_12_1$, then the three positional coordinates and isotropic temperature factors for each atom were allowed to vary. In addition to these 24 parameters, the scale factor, sloping background (background $= a + b \cdot 2\theta$), the effective zero of the scattering angle 2θ, the lattice parameters and peak shape parameters (U, V, W) were allowed to vary for a total of 34 variables. Anisotropic temperature factors were not included because this would have increased the number of adjustable parameters by an unreasonable amount (from 34 to 64 variables). Isotropic temperature factors were corrected for absorption by an amount $\Delta B = 0.27 \, \text{Å}^2$ [19].

The structural parameters determined from the refinement are given in the table. The quality of the fit is specified by the values of R_p and R_{wp} where

$$R_p = \sum_i \left| y_i^{\text{calc}} - y_i^{\text{obs}} \right| \bigg/ \sum_i y_i^{\text{obs}},$$

$$R_{wp} = \left[\sum_i w_i (y_i^{\text{calc}} - y_i^{\text{obs}})^2 \bigg/ \sum_i w_i (y_i^{\text{obs}})^2 \right]^{1/2}$$

while the statistically expected value of R_{wp}, R_{exp}, is defined as

$$R_{\text{exp}} = \left[(N - P) \bigg/ \sum_i w_i (y_i^{\text{obs}})^2 \right]^{1/2}.$$

Here $y_i^{\text{obs}}(y_i^{\text{calc}})$ is the observed (calculated) intensity at scattering angle $2\theta_i$, $w_i(\equiv 1/y_i^{\text{obs}})$ is the weight assigned to y_i^{obs}, N is the number of data points and P the number of adjustable parameters. It is evident from the values of these parameters that the proposed crystal structure is a very good fit to the experimental data.

4. Molecular geometry in the α-phase

The geometries of the molecule in the gas phase [17, 18] and the solid α-phase are compared in figure 2. Errors listed in the table and figure 2 are the errors derived from the least-squares errors in the positional parameters as determined by the fitting program. They should be multiplied by a factor of approximately three to give a more realistic estimate of errors (see the discussion of errors in [20]). With these error limits in mind, the only significant differences in the molecular geometry in the solid phase compared to that in the gas phase are an increase in the OD_1

The structural parameters of α-methanol at 15 K.

		x	y	z	B
$R_{exp}/\%$		2·2			
$R_p/\%$		3·9			
$R_{wp}/\%$		4·8			
Lattice parameters/Å	a	4·8728(2)			
	b	4·6411(2)			
	c	8·8671(4)			
Unit cell volume $V/\text{Å}^3$		200·53(3)			
Atomic position coordinates, isotropic thermal parameter, $B/\text{Å}^2$					
	C	0·1847(8)	0·5074(15)	0·1055(4)	1·03(7)
	O	0·4450(8)	0·4750(13)	0·1721(4)	0·48(8)
	D_1	0·4940(12)	0·6533(10)	0·2316(6)	2·01(9)
	D_2	0·1504(12)	0·3126(16)	0·0397(7)	2·42(15)
	D_3	0·0289(8)	0·5217(11)	0·1882(5)	2·35(9)
	D_4	0·1837(11)	0·6828(16)	0·0275(7)	2·59(14)
Bond lengths/Å	O–C	1·407(6)			
	$O–D_1$	1·010(7)			
	$C–D_2$	1·089(9)			
	$C–D_3$	1·058(6)			
	$C–D_4$	1·068(9)			
Bond angles/deg.	$D_1–O–C$	110·2(6)			
	$D_2–C–D_3$	108·3(6)			
	$D_2–C–D_4$	106·6(6)			
	$D_3–C–D_4$	113·4(6)			

(OH_1) bond length, presumably as a result of the hydrogen bonding, and a distortion away from the ideal 3-fold symmetry of the methyl group.

5. Crystal structure

The crystal structure of α-methanol is made up of infinite hydrogen bonded chains, as expected. Adjacent chains have molecules related by a two-old screw axes

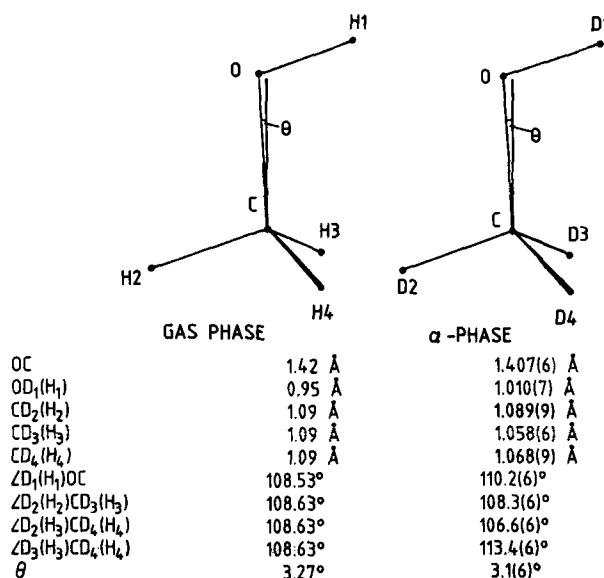|	GAS PHASE	α -PHASE
OC	1.42 Å	1.407(6) Å
$OD_1(H_1)$	0.95 Å	1.010(7) Å
$CD_2(H_2)$	1.09 Å	1.089(9) Å
$CD_3(H_3)$	1.09 Å	1.058(6) Å
$CD_4(H_4)$	1.09 Å	1.068(9) Å
$\angle D_1(H_1)OC$	108.53°	110.2(6)°
$\angle D_2(H_2)CD_3(H_3)$	108.63°	108.3(6)°
$\angle D_2(H_3)CD_4(H_4)$	108.63°	106.6(6)°
$\angle D_3(H_3)CD_4(H_4)$	108.63°	113.4(6)°
θ	3.27°	3.1(6)°

Figure 2. Geometry of the methanol molecule in the gas and solid phases.

so the chains 'point' in opposite directions as shown in figure 3 (a). The hydrogen bond favours a collinear geometry of the participating oxygen and hydrogen atoms [21, 22] and this is likely the dominant factor in determining the molecular arrangement within the chains. In previous discussions of the chain structure the oxygen atoms were taken to define a plane and the chains were puckered as a result of the C–O bonds being tilted out of this plane [5, 8, 13, 14]. This approach can still be used with the individual chains and the puckering angle is calculated to be $\phi = 43.5$ (see figure 3 (b)) which is to be compared with the value $37.5°$ calculated from Tauer and Lipscomb's proposed structure [8] and the value $43°$ determined by Pellegrini *et al.* [13] from a packing energy calculation.

The view down the chain axis, as shown in figure 3 (b), is much less symmetric than the equivalent view given by Tauer and Lipscomb [8] (their figure 7). The C–O bonds in adjacent chains, instead of being almost parallel, make an angle of approximately $50°$ to each other. This suggests that the lower transition observed by Staveley and Hogg [3] involves the puckering of the individual chains so that there
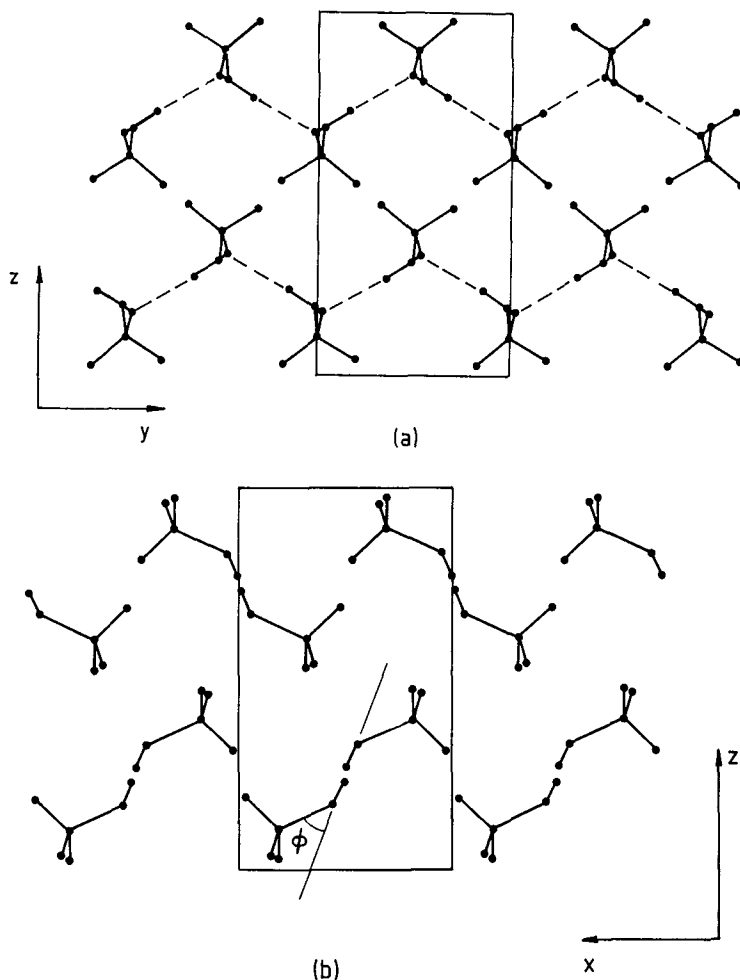

Figure 3. Crystal structure of α-methanol showing the hydrogen bonding and the projection of the unit cell. (a) view down the a-axis, (b) view down the b-axis.

is a change from puckered chains to chains which are, at least on average, planar as the temperature is increased, i.e. the angle ϕ in figure 3 (*b*) has the value $+\phi$ or $-\phi$ to give an average of zero. The upper transition would then involve a reorientation of the planar chains so that they are parallel to each other as found in the β-phase [8]. Changes at the lower transition could be subtle enough that there is no observable change in the intense diffraction peaks which we monitored in our search for evidence of a double transition.

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