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We have determined the crystal structure, including all atomic positions, of methanol at high pressure and room temperature by a combination of x-ray diffraction experiments and *ab initio* pseudopotential calculations. The structure has triclinic $P\bar{1}$ symmetry with six molecules per unit cell. The molecules form strained hydrogen-bonded chains in a unique sequence of molecules in a two-parallel and one-antiparallel arrangement. This complex structure reveals that at high pressures, hydrogen bonding is important relative to repulsive forces, and may explain the glass forming capabilities of this simple alcohol. [S0163-1829(98)50442-0]

The structure and dynamics of molecular solids are intimately related to the interactions of the molecules, which in turn are connected to the molecular form and symmetry. Since interactions strongly depend on intermolecular distances, high pressure is an excellent probe for molecular solids.[1] For simple molecular systems that interact through short-range repulsive forces and attractive weak van der Waals interactions, quantitative interpretation of experimental data can be obtained with models based on effective pairwise potentials. Important classes of intermolecular interactions such as hydrogen bonding, however, escape such modeling. This is exemplified by the existence of many different potential models for water, each one being optimized to a different property.[2] Recently, advances have been made in the description of dense hydrogen bonded systems by *ab initio* calculations.[3] A systematic study of hydrogen bonding is rewarding, because competition between various types of interactions causes phase transitions, including glass formation, and affects crystal nucleation.[4–7] Moreover, it has been proposed that with increasing pressure hydrogen bonding diminishes relative to the repulsive forces.[8]

To develop a systematic understanding of hydrogen bonded molecular systems at high pressure, it is vital that a homologous series of chemical compounds is studied. An important, and prototypic, series of compounds are the linear alcohols $H(CH_2)_nOH$, where the integer n denotes the chain length. With increased chain length, it is expected that the effects of hydrogen bonding are reduced. Here, we study the simplest alcohol, with $n=1$. At ambient temperature, the equilibrium freezing pressure of methanol is 3.5 GPa. In practice however, it is very easy to superpress the liquid phase. The nucleation rate of crystals rises to a maximum near 7 GPa before vanishing at 10.5 GPa.[5,6] If the liquid is compressed sufficiently rapidly beyond 10.5 GPa, crystalli-

zation never happens and the liquid becomes a pressure induced glass.[5,6] Because the crystal structure at high pressures is unknown, there is no microscopic explanation why glass formation may occur. For comparison, at ambient pressure methanol cannot be vitrified by rapid cooling of bulk liquid, but only by vapor deposition on a cold substrate (see, e.g., Ref. 9). This difficulty to vitrify at low temperatures can be rationalized by the fact that the structure of both the liquid and the two low-temperature crystal phases consist of linear chains of alternating hydrogen bonded molecules.[10,11]

In this paper we solve the high-pressure crystal structure of methanol using a combination of single-crystal diffraction and *ab initio* density-functional calculations. The structure is triclinic with $P\bar{1}$ symmetry and the hydrogen bonds appear to be strained. We propose that the low symmetry and the strained hydrogen bonds are the reasons why methanol easily vitrifies at high pressure. This observation confirms the computer simulation results of Root and Berne[12] that hydrogen bonding does not reduce with pressure, but rather increases, while the distribution of hydrogen bond angles (i.e., the strain on the hydrogen bonds) increases.

Liquid methanol was loaded and pressurized in a tungsten gasket of a Merrill-Bassett diamond-anvil cell, which had been equipped with 600 μm culet diamonds. After the nucleation of many crystallites near 7 GPa,[5] the temperature was cycled at a pressure just above the melting curve to reduce the number of crystal grains, similar to Ref. 13. Finally, a single crystal was obtained at 4.0(1) GPa, that entirely filled the gasket hole.

A set of 20 strong reflections were collected and a vector least-squares fit to their setting angles gave the triclinic unit-cell parameters to be $a=7.670(2)$ Å, $b=4.4101(13)$ Å, $c=7.199(2)$ Å, $\alpha=88.10(3)°$, $\beta=102.89(3)°$, and $\gamma=93.85(3)°$ with a volume $V=236.19(13)$ Å^3. Comparing

TABLE I. Fractional coordinates of the high-pressure methanol structure obtained from the *ab initio* calculations (second set of coordinates) and, for comparison, the coordinates of the C/O atoms obtained from the single-crystal x-ray results (first set). The standard deviations from single-crystal refinements are shown in parentheses.

	Experimental			Theoretical		
	x	y	z	x	y	z
O_1	0.7291(16)	0.5064(15)	0.8642(8)	0.7123	0.5253	0.8521
O_2	0.8562(17)	0.6658(15)	0.2022(9)	0.8836	0.6651	0.1919
O_3	0.7783(17)	0.5267(15)	0.5036(9)	0.7441	0.5255	0.4835
C_1	0.9855(23)	0.9783(22)	0.2280(13)	0.9908	0.9369	0.2362
C_2	0.6624(26)	0.2457(23)	0.4298(14)	0.6265	0.2618	0.4529
C_3	0.6061(23)	0.2567(23)	0.8853(13)	0.6173	0.2651	0.9044
H_1	-	-	-	0.8267	0.6118	0.3046
H_2	-	-	-	0.0609	0.9338	0.3880
H_3	-	-	-	0.0945	0.9520	0.1515
H_4	-	-	-	0.9129	0.1524	0.2056
H_5	-	-	-	0.7738	0.5531	0.6253
H_6	-	-	-	0.7937	0.5995	0.9766
H_7	-	-	-	0.5358	0.2541	0.5515
H_8	-	-	-	0.5408	0.2701	0.3084
H_9	-	-	-	0.6994	0.0404	0.4715
H_{10}	-	-	-	0.6190	0.2668	0.0579
H_{11}	-	-	-	0.4758	0.2583	0.8252
H_{12}	-	-	-	0.6732	0.0416	0.8738

the unit-cell volume with the equation of state for the liquid of Brown *et al.*,[14] we find that there are six molecules in the unit cell. The structure of methanol at high pressure therefore differs from the two orthorhombic structures α and β that exist at ambient pressure and low temperatures,[10] and is tentatively called γ. This contradicts a previous assertion that the high-pressure phase is similar to the lowest temperature α phase.[15]

To determine the positions of the molecules within the unit cell, intensity data were also collected for all 418 accessible reflections in the shell $\pm h$, $\pm k$, $\pm l$ for $0 \text{ Å}^{-1} < \sin \theta / \lambda < 0.36 \text{ Å}^{-1}$ and in the hemisphere $\pm h$, $\pm k$, $+l$ for $0.36 \text{ Å}^{-1} < \sin \theta / \lambda < 0.71 \text{ Å}^{-1}$. As a first step to solving the structure from the data, we used direct methods.[16] It was assumed that the space-group symmetry was $P1$ and that the unit cell contained six carbon atoms and six oxygen atoms, thereby neglecting the weakly scattering hydrogens. Although the method could determine the positions of the C and O atoms, and hence of the molecules, it was unable to discern conclusively the atomic species of individual atoms. Consequently, the resulting prototype structure was used in a series of refinements to try to discern the orientations of the molecules. The refinements were undertaken with the $P\bar{1}$ symmetry as it was apparent, from an inspection of the molecular arrangement, that the structure has a center of symmetry. As either end of the methanol molecule (CH_3 and OH) have an identical number of electrons, it is difficult to conclusively discern the relative orientations of the molecules in the crystal structure from x-ray-diffraction data. Since there are six molecules per unit cell and the cell contains an inversion center there are eight possible orientations of the molecules in the unit cell. We therefore performed the refinements for each of these possible orientations. The best

fit for the structural data ($Rw = 0.12$, $GoF = 1.67$ for 410 reflections) is presented in Table I. In a recent survey of monoalcohol crystal structures[17] only 0.4% of the structures have three or more molecules in the asymmetric unit which makes γ methanol extremely unusual.

We confirmed this refinement by performing an x-ray powder-diffraction experiment (at station 9.1 at the SRS Daresbury) on polycrystalline samples.[5,6] The diffraction patterns were ''spotty'' due to the relatively low number of crystallites, a common occurrence for powders generated directly from the liquid in a diamond-anvil cell. Consequently, the ''smoothest'' data set, taken at 6.8 GPa, was selected for refinement as this set was expected to have the most accurate intensities. The result is shown in Fig. 1 where it is apparent that the fit is excellent and all the observed peaks are accounted for. These results are in remarkable agreement with the single crystal refinement, thus confirming those results. Since the powder samples did not undergo thermal cycling, the results confirm that the single crystal was not trapped in a metastable state.

From the single-crystal and powder x-ray diffraction data a reliable model has been determined for the molecular arrangement in the structure. Since it is difficult to resolve the relative orientations of the molecules by x-ray diffraction, we have performed a series of *ab initio* pseudopotential calculations within the density-functional formalism. For a given configuration of the unit cell starting from the experimental results, above, we expand the valence electronic wave function in a basis set of plane waves up to an energy cutoff of 700 eV which converges the total energy of the system to better than 1 meV/cell. The core electrons are described using the pseudopotential approach. The Kleinman-Bylander[18] form is used for our nonlocal pseudopotentials which are

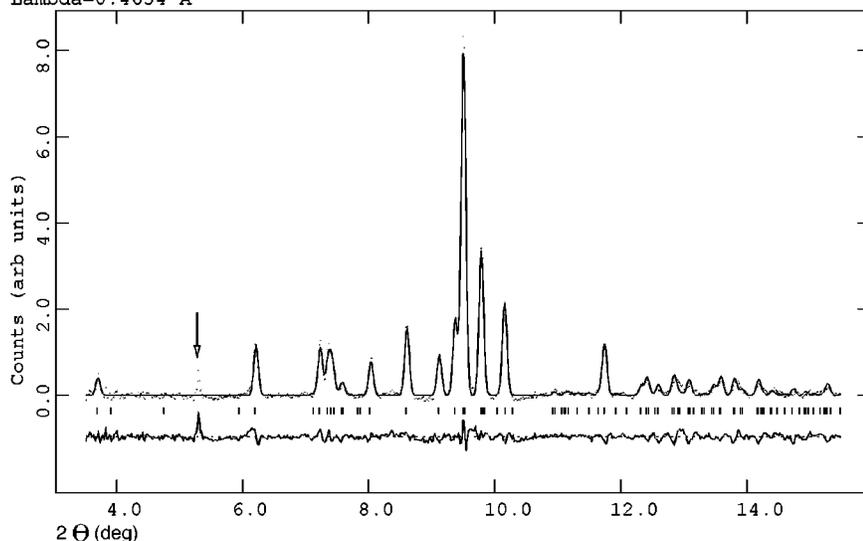Methanol at 68kbar
Lambda=0.4654 A

FIG. 1. Powder-diffraction pattern of methanol at 6.8 GPa, taken with an x-ray wavelength of 0.4654 Å (dots); background has been subtracted. The Rietveld refinement fit of the $P\bar{1}$ structure is shown by the drawn line. The tick marks indicate the positions of the reflections. The difference between the observed and calculated profiles is shown below the tick marks. The peak indicated by the arrow is due to a reflection from a diamond anvil.

generated by the Q_c tuning method of Lin *et al.*[19] The Brillouin-zone integrations are performed using a 4 k-point set which converges the total energy of the system to less than 2 meV/cell. The generalized gradient approximation[20] is used here for the exchange and correlation interactions which is generally more accurate for describing molecular systems than the conventional local-density approximation.[21] The total energy of the system is calculated using a preconditioned conjugate gradients method.[22] For each structure studied here, we fully relax all the atomic positions, using the positions of the C/O atoms determined by the single-crystal work as a starting point. For this, we calculate the forces on each atom using the Hellmann-Feynman theorem and allow the atoms to move under the influence of these forces. A conjugate gradients routine is also used to determine the minimum-energy configuration for each unit cell considered. In each case, the cell starts with $P\bar{1}$ symmetry as given from the experimental studies. However, we did not enforce this symmetry during the simulation to investigate any small symmetry breaking which may occur.

In Fig. 2 we show schematic diagrams of the eight possible configurations of the methanol structure which are experimentally almost indistinguishable along with the calculated relative total energies. We find that the configuration consisting of chains of hydrogen bonds (number 5 in the diagram) has the lowest energy, 0.44 eV/unit cell lower in energy than the closest alternative structure. The fractional coordinates from this fully relaxed structure were found to preserve the inversion center to the accuracy of the calculation. The fractional coordinates for this structure are shown in Table I where the atomic positions related by the $P\bar{1}$ symmetry have been averaged to give the final values. Comparison of the simulated carbon and oxygen fractional coordinates with those obtained by the best fit to the single-crystal experimental x-ray diffraction data shows that the agreement is extremely good and the same structural conformation is found. Although we did not constrain the symmetry of the structure in the simulation, we find that it retains $P\bar{1}$ symmetry (which included a search for pseudosymmetries) in agreement with experiment.

The full structure, including the positions of the hydrogen atoms, is shown in Fig. 3. It can be seen that the molecules form infinite linear hydrogen-bonded chains, consistent with the formation of one hydrogen bond for each molecule, and they are orthogonally aligned to the chains in a pseudohexagonal arrangement. Within each chain the molecules are sequenced so that two neighboring molecules are aligned parallel to one another, forming a hydrogen-bonded pair (molecule $P1$ and $P2$), while the third (molecule $A1$) is aligned antiparallel and correspondingly shifted by its own length to form a hydrogen bond between each pair. This arrangement of the molecules, along with the very large variation in the O-H$\cdots$O bond angles, is unique to the range of chain conformations (alternating chain, ring, helix, and dimer) in the monoalcohols observed at ambient pressure.[17] The C-O bond lengths show very little variation and are 1.415 Å, 1.404 Å, and 1.411 Å for the $P1$, $P2$, and $A1$ molecules, respectively. As expected, these bond lengths are smaller than those for the gas phase, 1.42 Å, and are compa-
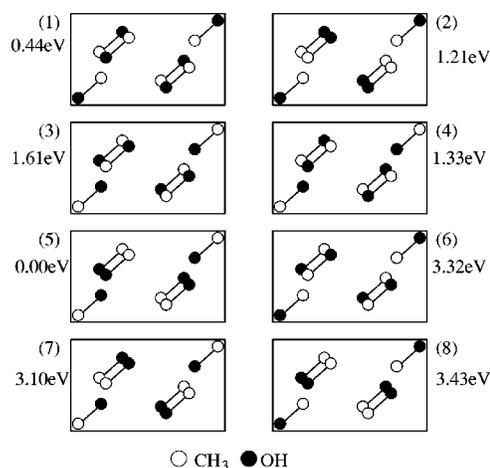

FIG. 2. Schematic diagrams of the candidate structures obtained from the diffraction experiments. The projections (in the ab plane of the unit cell) show the positions of the C/O atoms. Their relative energies per unit cell found from the *ab initio* calculations are also shown. The structure with the lowest energy (number 5) has chains of hydrogen bonds, and is shown in more detail in Fig. 3.

rable with the low-temperature crystalline α phase, 1.407(6) Å at 15 K.[10] The C-H distances of the methyl groups also show little variation, differing at most by 0.04 Å from their average value of 1.11 Å, as do the average H-C-H bond angles, which differ on average by 0.7° from their mean value of 107.7°. The average C-H distance compares favorably with the average C-D distance of 1.09 Å and 1.07 Å for the gas phase and α phase, respectively, while the average H-C-H bond angle is slightly smaller than those of the gas and crystalline phases, 108.6° and 109.4°.[10] In contrast to the intramolecular bonds the intermolecular hydrogen bonds are extremely irregular: the O-H distances vary between 1.005 and 1.033 Å and the H···O distances between 1.571 and 1.796 Å. Similarly, the O-H···O bond angles range from 150.9 to 178.2°. This contrasts markedly with the α-phase structure where the O-H distances are equal by symmetry and the hydrogen bond favors a collinear geometry. The irregularity of the hydrogen-bond chain in the high-pressure phase does not, however, appear to affect the intramolecular C-O-H bond angles as these differ by at most 1.2° from their average of 105.9° (only slightly smaller than the 108.5° and 110.2° for the gas and α phases, respectively).

Although the structure of the methanol molecules themselves appear to be altered slightly in the high-pressure phase, the unique irregularity of the hydrogen-bond chain suggests that the crystal structure is under some strain. As the low-temperature α phase has linear chains, where pairs of molecules linked by hydrogen bonds are antiparallel with one another, and forms a regular relatively high-symmetry structure, the molecules bonding in the parallel arrangement of the high-pressure phase exhibit the most pronounced differences between the structures and would appear to offer a major contribution to the strain. Combined with the low symmetry of the structure, this may explain why methanol is difficult to crystallize at high pressure and so readily forms a glass.[5,6] This assertion is also consistent with the behavior of ethanol ($n=2$) at high pressures: Recent experiments[23] re-
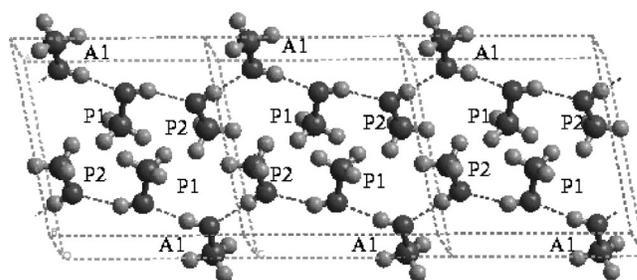

FIG. 3. The structure of methanol at 4.0 GPa as found from the x-ray-diffraction experiments and the *ab initio* computer simulations. Three neighboring unit cells are shown which depict the hydrogen bonded chains (two per unit cell) related by $P\bar{1}$ symmetry.

veal that it forms the alternating molecular arrangement as in the low-pressure forms of the monoalcohols,[17] while it does not vitrify.

To assess the influence of the hydrogen bonds on γ methanol it is instructive to compare it to similar molecular systems. Both methane and ethane freeze into plastic crystalline phases, i.e., the orientations of the molecules are disordered, before undergoing transitions to fully ordered phases.[24] This is also the case with the polar molecule carbon monoxide (CO),[25] which implies that the ordering of methanol is not caused by its polar character. We conclude that even at high pressure, the hydrogen bonds of methanol are strong enough to freeze it into an orientationally ordered phase.

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