Introduction: The water - methanol system is of great importance in biological and industrial chemistry [1] (particularly the oil industry where it is used as a clathrate inhibitor in pipelines), and is also of interest to cosmochemists studying ice grain reactions in the interstellar medium and the source of carbon in comets and other primitive solar nebula materials [2]. Moreover, methanol may be an important constituent of aqueous cryovolcanic solutions (along with ammonia) on the icy moons of our solar system [3]. In the methanol-water system there exists a single binary compound, methanol monohydrate (CH\textsubscript{3}OH.H\textsubscript{2}O), and in the methanol-ammonia system there exists a mono-ammoniate (CH\textsubscript{3}OH.NH\textsubscript{3}) and a hemi-ammoniate (CH\textsubscript{3}OH.½NH\textsubscript{3}). X-ray powder diffraction has been used previously [4,5] to determine that methanol monohydrate is tetragonal (\(a = 4.660(1)\), \(c = 13.813(5)\) at 80 K), but the structure remains unknown and nothing is known at all regarding the ammoniates.

We proposed to collect powder neutron diffraction patterns from all three compounds suitable for ab initio structure determination. Having been awarded two of the three days required, we decided to focus solely on methanol monohydrate.

Sample preparation: A solution of 1:1 molar stoichiometry was prepared from deuterated methanol and heavy water at room temperature. The solution was flash frozen to a glass in a liquid-N\textsubscript{2} cooled steel and heavy water at room temperature. The solution was stoichiometry was prepared from deuterated methanol monohydrate.

Three days required, we decided to focus solely on structure determination. Having been awarded two of the patterns from all three compounds suitable for ab initio ammoniates.

Results: The structure of deuterated methanol monohydrate was solved by ab initio methods, using the FOX software package, and refined to Rp = 2.35 % in GSAS. The crystal is orthorhombic, space-group Cmc\textsubscript{2}1 (\(Z = 4\)) with unit cell dimensions \(a = 4.649100(24)\) \(\text{Å}, \ b = 14.084637(67)\) \(\text{Å}, \ c = 4.693577(10)\) \(\text{Å}, \ V = 307.340(2)\) \(\text{Å}^3\) at 160 K and \(a = 4.66319(6)\) \(\text{Å}, \ b = 13.61287(22)\) \(\text{Å}, \ c = 4.637841(26)\) \(\text{Å}, \ V = 294.408(4)\) \(\text{Å}^3\) at 4.2 K. The structure consists of water - water chains, linked by an ordered hydrogen bond, extending along the c-axis, which cross link methanol - water chains with disordered hydrogen bonds along the a-axis. These perpendicularly oriented water - water and methanol - water chains form sheets which are stacked parallel to the b-axis and which interact only through weaker contacts between the methyl hydrogens and hydroxyl oxygens of neighboring sheets. Details of the structure solution are presented elsewhere [6].

Data collected between 4.2 K and 160 K (twice on warming and once on cooling) yield the thermal expansivity of methanol monohydrate. The volume thermal expansion coefficient, \(\alpha_V\), is positive and normally behaved at all temperatures although it is very large, being \(527 \times 10^{-6} \text{K}^{-1}\) at 160 K - almost six times larger than ice Ih at the same temperature. The greater part of this expansion occurs along the axis perpendicular to the H-bonded sheets.

References: