

Bragg Institute Neutron Beam Instrument Proposal

ID P2378

Title **Structural studies of water-rich sulfuric acid hydrates**

Round **2012-2 Neutron**

Schedule

The experiment has been scheduled using the following equipment and scientists.

Equipment	Start Date	End Date	Length
Echidna	08/10/2012	11/10/2012	4

Researchers

Name	Role
Helen Maynard-Casely (Australian Synchrotron)	Principal Scientist
Helen Brand (Australian Synchrotron)	Co-proposer
Kia Wallwork (Australian Synchrotron)	Co-proposer

Proposed Research (PDF)

The next 2 pages have been uploaded as part of the proposal.

Scientific Background Crystal structures formed at the water-rich end of the sulfuric acid-water binary system are observed as seeding materials in our atmosphere [1], where they have implications for the stratospheric aerosol layer. They are also important phases in the ice shell of Jupiter's moon Europa [2] where they are likely to influence both the geomorphology of the surface and processes at depth. It has already been demonstrated that the $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ binary system exhibits a rich phase behaviour, solid phases form with $n = 1, 2, 4, 6, 5$ [3]. There is thought to exist a more water-rich hydrate which had been assumed to be an octahydrate, $\text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$. However, the existence of sulfuric acid octahydrate (SAO) has been debated in the literature in recent years with some workers suggesting that the water rich form would, in fact be, $\text{H}_2\text{SO}_4 \cdot 9.5\text{H}_2\text{O}$, a hemiennekaidecahydrate [4]. All of the known structures of sulfuric acid hydrates are dominated by hydrogen bonding and it is anticipated that variations in the hydrogen bonding networks will affect the thermal expansion, and hence energy transfer mechanisms within the icy moons and our atmosphere. A detailed neutron diffraction study has already elucidated anomalous thermal expansion behaviour in sulfuric acid tetrahydrate ($\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$) [5]. Understanding how these materials interact with the thermal environment, within icy moons and our atmosphere can only be fully modelled once the crystal structure has been well defined.

Aims of Experiment The aim of this experimental proposal is to extend and complement recent synchrotron x-ray diffraction results [6] which charted the existence of sulfuric acid octahydrate and identified a new, potentially more water rich, hydrate. The data collected in this experiment will allow for speciation of both these forms composite ions and allow for refinement of the deuterium positions. It is hoped that this will give insight into structural characteristics and thermal behaviour of the hydrogen bonding network of these hydrates.

Results of preliminary experiments As part of a recent merit experiment at the Australian Synchrotron (AS); the powder diffraction beamline was used to investigate the hydrates formed at a number of different sulfuric acid solution concentrations. From this study the existence of the sulfuric acid octahydrate was charted, its pattern indexed and lattice expansion between 80 and 200 K determined. Additionally, a new form of sulfuric acid hydrate, postulated to have a higher water-content, was discovered.

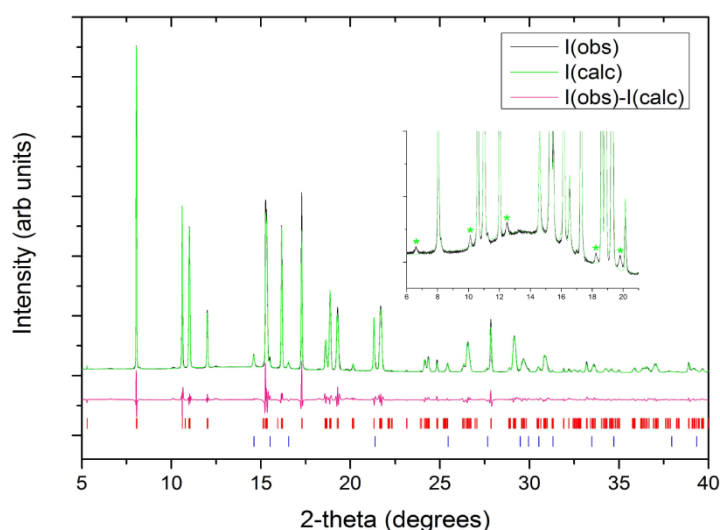


Figure 1 X-ray diffraction pattern collected at Powder diffraction, Australian Synchrotron of a mixture of sulfuric acid octahydrate (red ticks) and ice Ih (blue ticks). From these data the unit cell of SAO and positions of sulfur and oxygen atoms were found. Inset shows a region of the diffraction pattern, showing the existence of a new hydrate form (diffraction from which is marked by the green stars).

Detail of experiment Deuterated sulfuric acid solutions will be prepared in advance of data collection, loaded into a vanadium can or similar. Silica wool will be included to promote crystallisation. The solutions will be made up to represent a) the octahydrate composition and b) the “new higher hydrate”, as per the preliminary synchrotron experiments. The samples will be loaded into a pre-cooled cryostat at 6 K, to quench the solution to an amorphous material. The sample will then be warmed to 170 K and allowed to anneal for 12 hours to crystallise. A similar process was followed during the synchrotron experiments, but the time scale has been increased here to allow for the differences between the small volumes used at AS and the larger sample volumes we anticipate using on Echidna. Once annealed data will be collected at 170 K for 1 hour to ascertain the crystallinity, before the sample is cooled to 6 K. Once cooled, a data set suitable for structure solution will be collected (potentially 6 hours) before the sample is warmed in 20 K steps with a 2 hour data collection taken at each point until the sample melts at ~220 K. This path will be undertaken for the both solutions.

Reason for instrument choice To unravel the high degree of complexity within the hydrogen bonding system of these hydrates, and to speciate the component ions of these hydrogen dominated materials it is necessary use the high resolution capabilities of Echidna.

Calculation of time As outlined above, initial crystallisation and characterisation of each sample will take ~12 hours, 24 for both. The variable temperature measurements will take 32 hours per sample, a total of 64. Thus, 4 days of beamtime are requested.

References

1. Zhang, R., et al., *Physical-Chemistry of the H₂SO₄/H₂O binary system at low temperatures - stratospheric implications*. Journal of Physical Chemistry, 1993. **97**(28): p. 7351-7358.
2. Carlson, R.W., et al., *Distribution of hydrate on Europa: Further evidence for sulfuric acid hydrate*. Icarus, 2005. **177**(2): p. 461-471.
3. Bertram, A.K., D.D. Patterson, and J.J. Sloan, *Mechanisms and temperatures for the freezing of sulfuric acid aerosols measured by FTIR extinction spectroscopy*. Journal of Physical Chemistry, 1996. **100**(6): p. 2376-2383.
4. Beyer, K.D., A.R. Hansen, and M. Poston, *The search for sulfuric acid*. Journal of Physical Chemistry A, 2003. **107**(12): p. 2025-2032.
5. Fortes, A.D., et al., *Neutron powder diffraction studies of sulfuric acid hydrates. II. The structure, thermal expansion, incompressibility, and polymorphism of sulfuric acid tetrahydrate (D₂SO₄.4D₂O)*. Journal of Chemical Physics, 2008. **128**(5).
6. Maynard-Casely, H.E., K.S. Wallwork, and H.E.A. Brand. *Sulfuric acid octahydrate formation from a water rich environment: A powder diffraction study*. in *43rd Lunar and Planetary Science Conference*. 2012. Houston, TX.