Experiment Proposal

Experiment Number:

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Co-investigator	Dr D Bowron, Science and Technology Facilities Council, UNITED KINGDOM		
Co-investigator	Mr V DEGUIN, The Open University, UNITED KINGDOM		
Co-investigator	Dr H Fraser, The Open University, UNITED KINGDOM		
Co-investigator	Dr S Gaertner, Science and Technology Facilities Council, UNITED KINGDOM		
Co-investigator	Dr T Headen, Science and Technology Facilities Council, UNITED KINGDOM		
Co-investigator	Dr T Youngs, Science and Technology Facilities Council, UNITED KINGDOM		
Co-investigator	-		
Co-investigator	-		
Experiment Title	Evolution of porosity and structure of Amorphous Solid Water (ASW)		
Instrument	**SANS2D**	**Days Requested:** 2	
Access Route	Direct Access - Continuation	**Previous RB Number:** 1820601	
Science Areas	Physics, Chemistry		
Sponsored Grant	No	**Sponsor:** -	
Grant Title	-		
Grant Number	-	**Start Date:** - **Finish Date:** -	
EU Access?	No	**Similar Submission?** No	
Industrial Links	No		

Non-Technical Abstract

This experiment will measure the microstructure of Amorphous Solid Water (ASW), a porous material that can be formed by vapour-depositing water onto a cold plate, an excellent analogue ofthe ice found in star- and planet-forming regions of our galaxy. The thermal and temporal evolutionof this metastable condensed-matter material has major implications in the physical and chemicalrole ices play in astrophysical environments. Our previous results on ISIS NIMROD has shown that the ASW has very small-scale porosity, and hints at larger scale structure of the material; and our recent results on ISIS SANS2D showed a good overlap with these data and gave us information about aggregation and collapse of pores.This experiments aims to reproduce these results at various temperatures to elucidate how the deposition temperature modifies the pores thermal evolution.

Publications

Mitterdorfer, C , Bauer, M , Youngs, TGA , Bowron, DT , Hill, CR ,Fraser, HJ , Finney, JL , Loerting, T, PCCP (2014) 16 16013-16020

Noble JA, Fraser HJ, Pontoppidan K, Craigon AM MNRAS (2017) 467 4753

Noble JA, Fraser HJ, Aikawa Y, Pontoppidan K, Sakon I, ApJ (2013) 775 85

Hill, C.R.; Mitterdorfer, C.;Youngs T.G.A.; Bowron, D.T.; Fraser, H.J.; Loerting, T.; PRL (2016) 116 215501

Gärtner, S., Gundlach, B., Headen, T.F., Ratte, J., Oesert, J., Gorb, S.N., Youngs, T.G., Bowron, D.T., Blum, J. and Fraser, H.J.; ApJ (2017) 848 96

ISIS Sample record sheet

Principal contact	Dr P Ghesquiere
Instrument	SANS2D, 2 days, preferred contact is: Mahmoudi, N
Special requirements	to use custom bin & CCr head for ice formation / warming studies

SAMPLES

Material	D2O
Formula	D2O
Forms	Solid
Volume	100 ml
Weight	100 mg
Container / substrate	V-plate _ CCR
Storage requirements	-
Xtal details	
ALF details	ALF not required.

SAMPLE ENVIRONMENT

Equipment	Helium Cryostat, CCR
Temperature range	10-300 K
Pressure range	-
Magnetic field range	-
Special equipment	specialist CCR V plate and bin

SAFETY

Hazards	-
Hazard Details	-
Sample Sensitivity	-
Experimental Hazards	-
Sample Prep Hazards	-
Equipment Hazards	-
Prep lab needed	No
Special equip reqs	gas handling line required
Sample will be	Removed By User

Porosity in Amorphous Solid Water (ASW); influence of the deposition temperature.

Scientific Context Interstellar ices, dominated by ASW are the largest molecular reservoir in the universe. The porosity of ASW samples is strongly influenced by prevailing formation parameters such as the deposition temperature or the angle of incidence. Mostly, it is assumed that the meta-stable interstellar ASW loses porosity as a function of time, temperature and cosmic irradiation as star formation progresses. This porosity change is astrochemically vital as it significantly lowers the ASW surface area and modifies therefore its surface catalytic action[1]. It accounts for discrepancies between gas- and solid-phase abundances of volatiles interstellar molecules, most importantly H_2 and CO - the primary coolant gases in the star-formation cycle. The morphological changes also affect how icy grains might "stick" to form the early seeds of planets and cometary nuclei. To consolidate chemical models with observations, and extract as much understanding as possible of the synergy between gas- and solid-phase chemistry in star- and planet-forming regions, astrochemists need to understand the mechanisms of ASW pore collapse and thermal evolution.
A plethora of laboratory experiments and simulations have converged to concludes that structures of ASW ice grown above $77K$ (often referred to as compact or c-ASW) differ in porosity from those formed below $77K$ (porous or p-ASW) and both differ from cubic crystalline Ic, formed on heating ASW to beyond $150K$ [2]. However, the debate remains in the literature - as ASW is heated, do pores collapse and disappear, or do they aggregate and form larger pores, changing the granularity of an ASW sample. These different scenarios affect all physical and chemical attributes of ASW that are so vital in understanding interstellar astrochemistry. The aims of this proposal are therefore three-fold:

- *Test whether ASW pores aggregate and grow, or collapse and disappear as an ice sample is heated*
- *Identify whether pore evolution mechanisms change as a function of the initial ice state, by altering the deposition temperature and consequently the initial ice porosity*
- *Link the resultant "picture" of ASW structure back to the astronomical environments and the role of ices in solid-stat astrochemistry.*

Previous Beam-time This proposal is a direct result of work conducted on the proof of concept experiment on SANS2D, 1820601, whose results showed a very good overlap (illustrated on Figure 1) with our previous NIMROD data. Previous NIRMOD campaigns allowed us to develop a reliable experimental setup which was used during experiments 1410637, 14110542, 1510246 and 1610318, whose results are currently being prepared for publication [3]. ASW samples were successfully produced and pore collapse observed at 50 and 17K during 1410542 and 1410637 respectively, and this work formed part of Hill's PhD thesis (OU 2015). A Guinier-Porod analysis, as applied previously to 1210386 (PI Loerting)(where we studied the porous properties of pre-prepared ASW samples, held under liquid N_2 conditions as well as identifying the kinetics of the glass transition), showed the evolution of pore size, shape and density as ASW is heated[4].

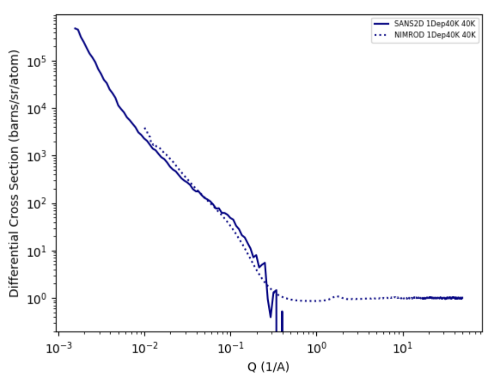

Figure 1: SANS2D and NIMROD spectra of ASW at 40K

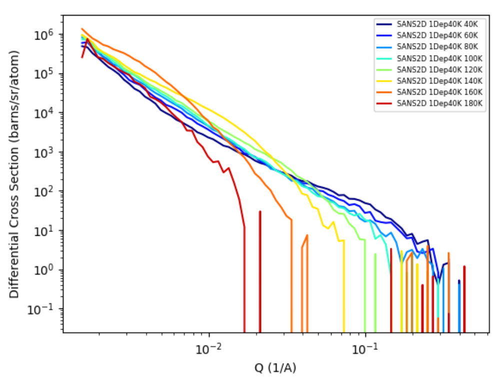

Figure 2: Thermal evolution of SANS2D spectra of ASW deposited at 40K

On the high Q region of NIMROD's data, we can confirm that our sample grows amorphous at low temperature and evolve to crystalline ices as the temperature is increased. We easily identify that our vapour-deposited ASW exhibit both granularity and porosity both of which evolve as a function of temperature. The low-Q region shows at least two bumps, both for NIMROD and SANS2D data, indicative of characteristic correlation length scales in ASW; this has been shown to be associated with the pores. The first of these bumps, centred at $Q \sim 1 - 2 * 10^{-1} Å^{-1}$, associated to nanopores is mainly present at low temperature and disappears as the ice is heated as can be seen on the figure 2. The second bump, centred at $Q \sim 1 - 2 * 10^{-2} Å^{-1}$ show an increase until T reaches $100K$ where the main shape of the curve starts increasing in convexity and peaking to larger length scales as T increases. Good reproductibility was observed for our two SANS2D deposition at 40 K and these data have recently be analysed and confronted with the NIMROD data for the same deposition temperature, with the MAXE software [5] to extract from the low-Q region a pore size distribution as shown on the figure 3 below. This latest results clearly show a good agreement between NIMROD and SANS2D data at low T but that at high T, SANS2D is able to see the larger pore sizes and improves therefore our understanding of the pore collapse process at high temperatures [6]. These very promising data confirmed the interest of SANS2D Q-range to study the pore evolution and now require a secondary study of the impact of deposition temperature, as our previous NIMROD investigations revealed crucial variation of ice micro-structure when this parameter is explored.

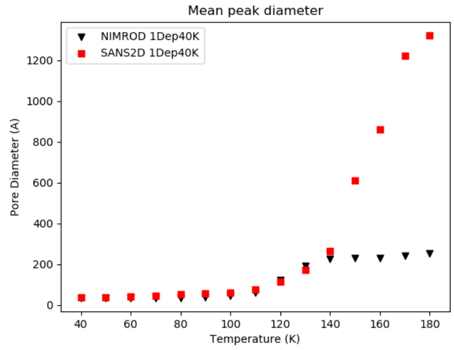

Figure 3: Mean pore sizes for an ASW sample deposited at 40K seen by SANS2D and NIMROD

Proposed Experiment and beamtime justification SANS2D is ideally suited to studying internal structure and spatial arrangements of materials; we will be able to probe the ASW structure in the dimension range of 10's to 100's nm. We therefore propose to use the 12-m SANS2D detector setup with Q spanning $0.3 - 0.001 Å^{-1}$.

Our previous proposal on SANS2D (RB1920757) has been accepted and is scheduled on the beginning of the 20/1 cycle. This previous beamtime will be used to study the deposition and annealing procedure of three ASW samples deposited at 60, 80 and 100K respectively. We propose in this application to extend the previous beamtime by two extra days to allow for the deposition and annealing of two supplementary samples at 20 and 120K, respectively, in order to explore the limits of the temperature range relevant for astronomical purposes. This will therefore provide us with a complete set of data exploring the deposition temperatures parameter on data points we previously recorded with NIMROD.

Using the dedicated bin/CCR/dosing system developped previously for these studies, we will produce two D_2O ASW ice samples by vapour deposition onto a cold Vanadium plate over a 12 hour period, (approx. 0.6g). The bin/CCR combination has been used successfully on SANS2D: it "fits" the sample area and gives a background scattering from the V-plate low enough that our ice can be observed. During deposition we will continuously record spectra every 15 minutes to observe the pore growth. The samples will then be heated at 0.5 $K.min^{-1}$, and held isothermally in 10 K steps between growth T and 190 K (1 hour per setpoint), with spectra recording continuously every 3 minutes. At the end, the ice is fully destroyed (1hr) in situ before recooling the plate (3hr) and restarting the next sample (2hr). Considering that the calibrations will have already been done before the first run already, we request a total of 2 days beamtime [18 hr ($120K$ sample) + 6 hr (reset) + 23 hr ($20K$ sample)]. Our diffuse interface/lamellar pore model and the MAXE software will be used to extract pore parameter data from the SANS2D spectra, both during growth and thermal evolution; we anticipate rapid publication of the results, in combination with our earlier NIMROD and SANS2D data.

Working Team and setup Moreover, our previous SANS2D experiment showed that our CCR setup for ASW vapour deposition can reliably generate ASW samples and that it gives us complementary information to our previous NIMROD's results. Experience shows we can work 24/7 in an intensive 8hr-on 8hr-off shift pattern, but that for health and safety reason, this always requires a team of 4; we therefore request funding for all 4 experimenters. As it is the continuation of our previously accepted beamtime RB1920757, we specifically ask that this extra beamtime is scheduled in the direct following of the previous one so that the experimental setup can be kept and used in a row.

References

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