**How is the nanoscale structure of Amorphous Solid Water (ASW)**

**impacted by the presence of adsorbates?**

**Aims:- This experiment builds on a *proof of concept rapid access* result from March 2019 where we undertook preliminary tests of how the pores in meta-stable, vapour-deposited water ice, Amorphous Solid Water (ASW), were affected during its thermal evolution by the addition of an adsorbate (C2H4) to the ice surface. This proof of concept data suggests that the pore collapse in ASW is delayed by the presence of adsorbates that hinder ice restructuring, but the tests were limited by beam-off time and contamination of the V-foil by C2H4. In these new experiments we will test if surface structure, pore-sizes and shapes in meta-stable, vapour-deposited water ice, Amorphous Solid Water (ASW), are affected by the addition of an adsorbate (CO2) to the ice surface, co-deposited at 30 K with D2O, deposited post ice-growth at 30 K, and deposited pre- ice-growth at 30 K. During ice thermal evolution, we will test if it is feasible to form clathrate-hydrate type structures via ASW heating (i.e. non-pressurised-compression routes).**

**Broader Scientific Context:-** Interstellar ice, dominated by Amorphous Solid Water (ASW) is the largest molecular reservoir in the universe1,2. The porosity of ASW samples are strongly influenced by prevailing formation parameters such as the deposition temperature and the angle of incidence3,4 and ASW has huge capacity to adsorb gases5,6,7. Mostly it is assumed the meta-stable interstellar ASW loses porosity as a function of time or temperature as star-formation progresses8,9. This porosity change is astrochemically vital as it alters the total ASW surface area from ~ 2000 m2/g 3 to ~ 0.1 m2/g 10, changing the surface available for chemical catalysis, accounts for discrepancies between (observed) gas-phase and solid-state abundances of volatile interstellar molecules due to gas-trapping in the pores (most importantly of H2 and CO – the primary coolant gases in the star-formation cycle) and affects how icy grains might “stick” to form the early seeds of planets and cometary nuclei11.

A plethora of laboratory experiments and simulations have converged to conclude that structures of ASW ice grown above 77 K (often referred to as compact or c-ASW) differ in porosity from those formed below 77 K (porous or p-ASW) and both differ from cubic crystalline ice, Ic, formed on heating ASW to beyond 150 Ke.g.12-16. However, whilst conclusive experimental evidence exists that nanopores disappear as ASW is heated17,18, micro-porosity persists18. *How* this pore-collapse process happens remains a mystery, and furthermore, *except* in neutron scattering studies, porosity can only be probed indirectly – using adsorbate gases – and no-one has a clue of the extent to which adsorbate molecules impact ASW pore-evolution or ice re-structuring during (a) its growth and (b) its thermal evolution. These scenarios affect all the physical and chemical attributes of ASW that are so vital in understanding interstellar astrochemistry. *The aims of this proposal are therefore three-fold (a) to test whether an adsorbate layer either above or below the ASW impacts the thermal evolution of ASW structure and porosity (b) to test whether a mixed ice-adsorbate deposition impacts the structure and porosity of ASW during growth and thermal evolution (c) to test the extent to which ice pores change size / shape and behaviour in the presence of an adsorbate.*

Furthermore, despite strong evidence to the contrary from condensed matter physics, suggesting clathrate-hydrates can only be formed via pressurisation of water icese.g.19,20, a plethora of astronomy ice literature imply clathrate hydrates can form in interstellar and cometary ices as “polluted” ASW is warmede.g.21-24, based on observational and laboratory spectroscopic assignments to adsorbate-H2O (ice) features. Fortuitously, our proposed experiments will be able to test this highly controversial suggestion that persists in the astronomy literature, so *we also aim to prove /disprove if it is feasible to produce clathrate hydrate structures via ASW heating.*

**Broader Research Environment**: HJF’s group (2 PhDs, 1 PDRAs) are linked to Telespazio Vega, Virgin Galactic and Lockhead Martin, and STFC / RE-funded (~£1.1M) to combine observations of interstellar ices e.g.25 with laboratory studies of ice aggregation e.g.26-28 and chemical reactivity e.g.29, and molecular dynamics simulations / neutron structural studies of ASW e.g.17,18,30,31. Our ISIS work is a collaborative venture between condensed matter ice physicists, neutron diffraction experts and astrochemists, designed to improve our fundamental understanding of the material properties of ASW.

**Previous Beam-time:-** This proposal is a direct result of work conducted on NIMROD during proof of concept 1900135 where C2H4 was deposited on top of D2O ice grown at 30 K, and warmed. As shown in Fig 1, preliminary results show that depositing the adsorbate on top of ASW (1(a)) at 30 K has no discernible effect on the ice, but that as the ice is warmed the C2H4 fills the pores and delays nano-pore collapse to around 110 – 120 K in comparison to “pure” ASW (cf (1(b) and 1(c)) as well as impacting the microporosity. However these early experiments cannot ascertain if clathrates form or not (due to beam-off time occurring exactly between our isothermal 110 and 160 K data points where such effects are most likely to occur. In addition, as can be seen in Fig 1(c) we failed to anticipate pollution of our V-foil by exposure to C2H4 during flow setting, so this proof of concept experiment was further limited by our choice of adsorbate. We have therefore already replaced the V foil (for use of this experiment with SANS2D on 1920757) and propose for these experiments to use CO2.

Figure 1: ASW + C2H4 1st data

**Methodology & Analaysis:** Our previous *in situ* CCR / bin-development experiments for ASW growth and thermal evolution, 1410637, 1410542, followed by detailed experiments 1510246 and 161031818 have recently been compared with our currently ongoing ASW studies on SAN2D 1820601 / 1920757. From our NIMROD data it is clear our vapour-deposited ASW (detected after 15 minutes growth) exhibits both granularity and porosity, both of which evolve as a function of temperature17,18,30,31. We have undertaken four independent analyses of the SANS region; a ‘simple’ inflection point(s) analysis in the low Q NIMROD data (I(Q)\*Q2.5); a double Gunier-Porod (GP) fit to the low Q data; a diffuse interface model; and a lamellar pore model for the low Q data, converged to form the same picture of the nano-porosity. By applying the MAXE model (on concrete pores) we also now have pore distribution data on ASW porosity. We propose to analyse the ASW-CO2 data in commensurate formats. The GP parameters rg and s can describe the size and shape of our ASW nano-pores, showing how these vary as a function of the surface temperature during ice deposition, evolve as the ice is heated, and for ASW alone, hold a “memory” of the growth conditions, and disappear between 100 and 120 K18,30. Similar data from the GP analysis, as applied previously to 1210386 (PI Loerting) where we studied the porous properties of pre-prepared (D2O) ASW samples, held under liquid N2 conditions17,31 (as well as identifying the kinetics of the glass-transition of D2O in detail31), shows that these ASW ices retain porosity to 110 – 140 K and thermally induced pore collapse depends on how the ices were deposited. It is clear that the evolution of the pores exposed to l.N2 is different beyond 100 K to ASW ices grown in situ – suggesting adsorbates do play a role in changing ASW pore structure and evolution.

**Proposed Experiment:** Using the dedicated bin / CCR / dosing system developed previously, we will produce three ice samples. First a D2O ASW ice sample by vapour deposition on to a cold V plate over at least a 12 hour period, (approx. 0.06 g), at 30 K only. During growth we will continuously record NIMROD spectra every 15 minutes to observe the pore growth. In one sample we will then subsequently dose a 5 % sample of adsorbate on the top of the ASW (30 minutes); in the second case we will co- deposit 5 % of the adsorbate with the water-ice (12 ½ hours). In the third we will pre-deposit the adsorbate before the ASW. This overlayer / underlayer / mixture approach is common in the literature and enables us to test adsorbate diffusion into and through the ice layer. Allowing for cooling (2 hr), pressure and flow rate setting (3 hr) and a small overhead (2 hr), up to 18 hours are required for this step per sample. Fig 2. Illustrates why we choose the “layer” and “mixed” ice approach, and our choice of adsorbate. The LH panel shows H2O ice desorption (highlighted in yellow) and below (again in yellow) the desorption of C2H4 and CO2 gases “layered” on top of ASW initially at the 5 % level33. Both adsorbates become trapped in the ASW pore structure but do not form H-bonds, so are good candidate to probe the effects of ASW “pore filing”. As the RH panel of Fig. 2 shows, this trapping-desorption TPD changes with the ice-adsorbate morphology8,9 – so we will test two layered and one mixed ice. Each sample will then be heated at 0.5 K min-1, and held isothermally in 10 K steps between growth T and 190 K (1 hr per setpoint), with NIMROD spectra recording continuously every 3 minutes, to record pore collapse, glass transition, crystallisation and desorption processes. At the end the ice is fully destroyed in situ. Allowing for empty instrument, CCR, warm and cold V-plate calibration (1-2 hr each), plus contingency for the complex experimental set-up (12 hr) we request a total of 5 days on-beam beam-time (1.5 day per sample) plus 1 additional pre-beam-time set-up-day.

Figure 2: Adsorbate Strategy

**Justification:-**The fast acquisition times at NIMROD provide a unique opportunity to study how the meso-scale structure of ASW changes as a function of growth T. This requires the study of D2O samples on NIMROD to significantly lower Q, and requires *in situ* growth. Our experiments are involved and complex. Experience shows we can work 24/7 in an intensive 8 hr-on 8 hr-off shift pattern, but that for health and safety reasons this always requires a team of 4 (2+2); we therefore request funding for all 4 experimenters.

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