

## Supplementary information

### Rapid Crystallization of Amorphous Solid Water by Porosity Induction

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## Experimental section

### RAIRS Setup

The ice films were investigated using a Bruker Vertex 70 FT-IR spectrometer connected to the vacuum chamber through a ZnSe viewport. IR beam was focused on the sample through a gold-plated mirror at an incident angle of  $80 \pm 7^\circ$ . The reflected beam from the sample was refocused to an external liquid nitrogen cooled MCT (mercury cadmium telluride) detector. The IR beam path outside the vacuum chamber was purged with dry nitrogen to avoid absorption by atmospheric gases, mainly water vapor and carbon dioxide. RAIRS spectra were collected in the range of  $4000\text{--}550\text{ cm}^{-1}$  and averaged to 512 scans with a spectral resolution of  $2\text{ cm}^{-1}$ .

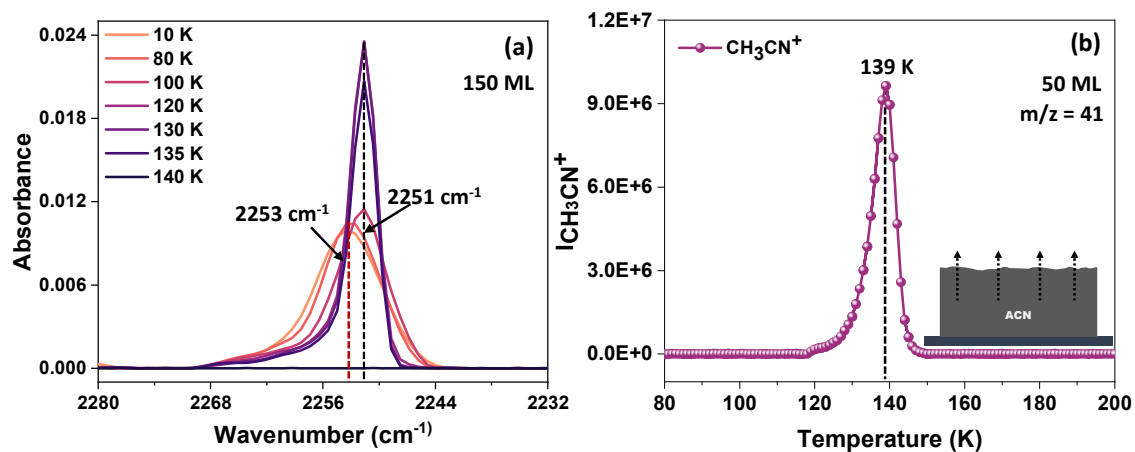
### TPD setup

TPD is a well-known technique in surface science and have been used for analysis of molecular solids. The TPD module was purchased from Extrel CMS and was attached to the chamber on a 6-inch flange through a Z-axis manipulator. The module consisted of an electron impact source, a mass analyser and a detector. The mass analyser was a quadrupole with 1 to 500 mass range and 1 amu resolution. For TPD of ACN in different compositions, as deposited ices were heated at a rate of  $10\text{ K}\cdot\text{min}^{-1}$  and suitable masses of the desorbed species ( $m/z = 41$  for  $\text{CH}_3\text{CN}^+$ ,  $m/z = 18$  for  $\text{H}_2\text{O}^+$ ) were selected by the mass spectrometer analyzer, and the intensity of the desorbed species was plotted as a function of substrate temperature.

### SIMS setup

$\text{Cs}^+$  ( $m/z$  133) is a well-known projectile for SIMS and  $\text{Cs}^+$  scattering is a good technique to characterize molecular solids. We have carried out ion collision experiments using  $\text{Cs}^+$  of 120 eV kinetic energy produced from a low-energy alkali ion gun (Kimball Physics Inc.). The scattered ions consist of  $\text{Cs}^+$  and the products arising from two other processes, such as reactive ion scattering (RIS) and low energy sputtering. RIS is a peculiar property of the alkali ions (here  $\text{Cs}^+$ ). The low energy collision of  $\text{Cs}^+$  converts the neutral adsorbate species (X) to gas phase ions ( $\text{CsX}^+$ ) by association reaction. The resulting scattered ions were analysed using a quadruple mass analyser. We have used the RIS signal intensities, corresponding to  $\text{Cs}(\text{CH}_3\text{CN})^+$  ( $m/z$  174),  $\text{Cs}(\text{H}_2\text{O})^+$  ( $m/z$  151), and  $\text{Cs}(\text{H}_2\text{O})_2^+$  ( $m/z$  169), to identify and understand the molecules appearing on the surfaces upon heating. Here, the signal intensities are directly proportional to the surface population of the molecule on the ice surfaces. The sample preparation for SIMS is the same as described in Experimental section (Main article). As prepared samples were heated at a  $5\text{ K min}^{-1}$  to the set temperatures for SIMS experiments

### Supplementary information 1:



**Fig. S1** (a) Temperature-dependent RAIRS spectra of 150 ML of pure ACN in the C≡N stretching region. ACN was deposited at 10 K and heated at a rate of 2 K min<sup>-1</sup> to the desorption temperature of ACN. ACN was found in two phases - amorphous phase (broad peak at ~ 2253 cm<sup>-1</sup>) in the window of 10-100 K, and crystalline phase (sharp peak at 2251 cm<sup>-1</sup>) above 100 K. ACN desorbed from the substrate at ~140 K. (b) Desorption of 50 ML of ACN during 10 K min<sup>-1</sup> TPD-MS experiment. Here, the intensity versus temperature of CH<sub>3</sub>CN<sup>+</sup> (m/z = 41) desorption is plotted.

## Supplementary information 2:

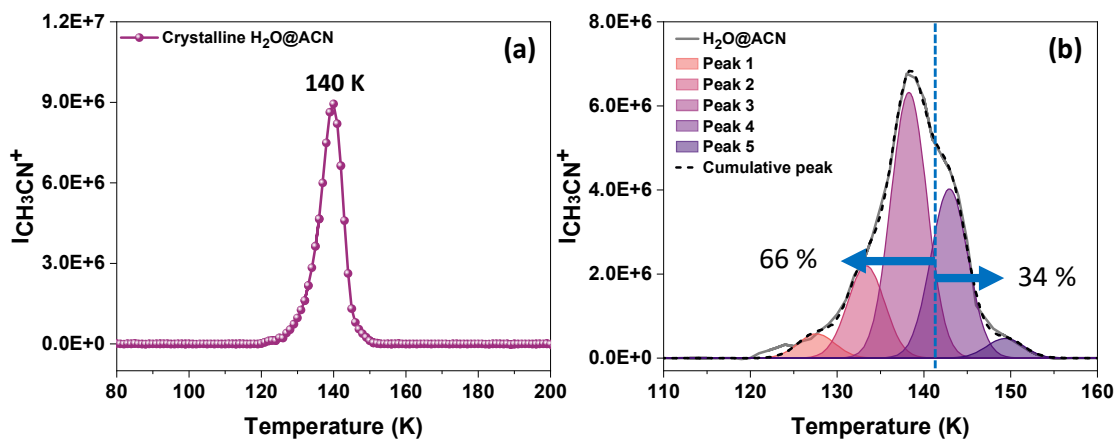
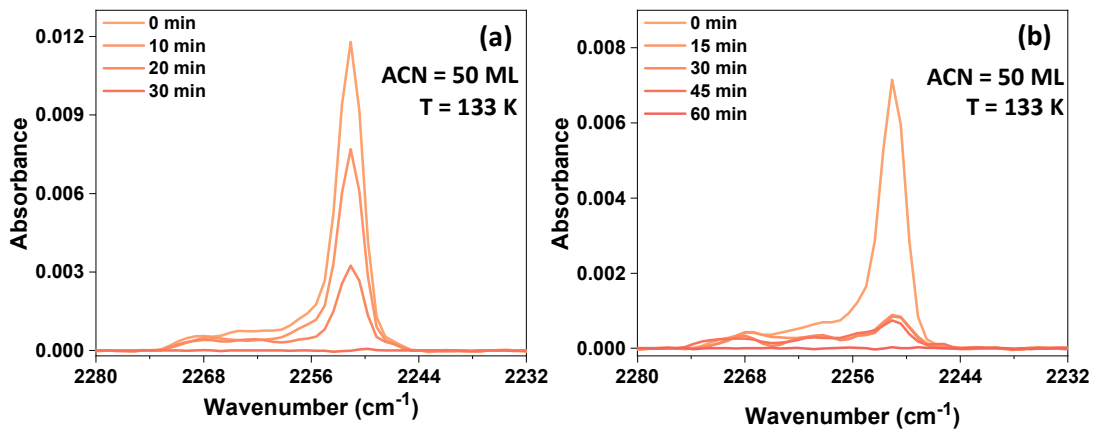


Fig. S2 (a) Desorption of 50 ML of ACN from 150 ML of crystalline H<sub>2</sub>O ice during 10 K min<sup>-1</sup> TPD-MS experiment. Here, the intensity versus temperature of CH<sub>3</sub>CN<sup>+</sup> (m/z = 41) desorption is plotted. 150 ML of crystalline H<sub>2</sub>O ice was prepared by deposition of H<sub>2</sub>O vapor on Ru(0001) at 10 K and heated to 150 K. The crystalline ice was then cooled down to 10 K and 50 ML of ACN was deposited on top of it. (b) Deconvoluted peaks of Fig. 1b (main article). It shows that about ~30% of the deposited ACN desorbs from ASW.

### Supplementary information 3:



**Fig. S3** Time-dependent RAIRS spectra of (a) ACN@ASW and (b) ASW@ACN films at 133 K in the C≡N stretching region. Ice films were prepared by vapor deposition on Ru(0001) at 10 K and heated to 133 K at a rate of 2 K min<sup>-1</sup>. The composition of films were (a) ACN(50 ML)@ASW(150 ML) and (b) ASW(150 ML)@ACN(50 ML). The peak intensity for ASW@ACN film is smaller than that of ACN@ASW film, because, when ACN was on top of ASW, a larger fraction of ACN will desorb in former case upon heating ice sample to 133 K. Also, the time required for complete ACN diffusion-desorption is nearly double in case of ASW@ACN film. The increased desorption time of ACN at 133 K is because, when ACN was on top of ASW, a fraction of ACN will diffuse into the ASW (through pores formed during ASW deposition) and will return to the surface and subsequently desorb which required an additional time.

#### Supplementary information 4:

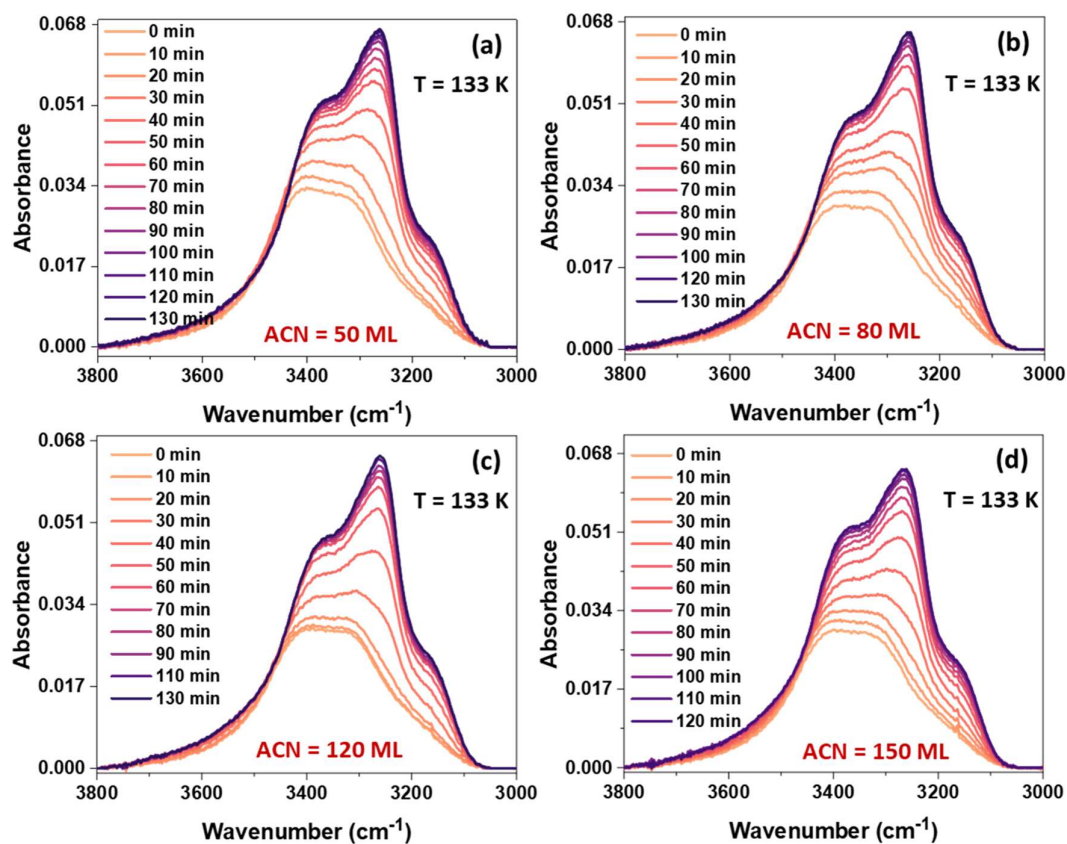


Fig. S4 Time-dependent RAIRS spectra of ACN@ASW films at 133 K in the O-H stretching region. ACN film thickness was varied from 50-150 ML while keeping ASW film thickness constant at 150 ML. Ice films were prepared by vapor deposition on Ru(0001) at 10 K and heated to 133 K at a rate of 2 K  $\text{min}^{-1}$ . The compositions of films were (a) ACN(50 ML)@ASW(150 ML), (b) ACN(80 ML)@ASW(150 ML), (c) ACN(120 ML)@ASW(150 ML) and (d) ACN(150 ML)@ASW(150 ML). The data show gradual crystallization of ASW after ACN desorption.

Supplementary information 5:

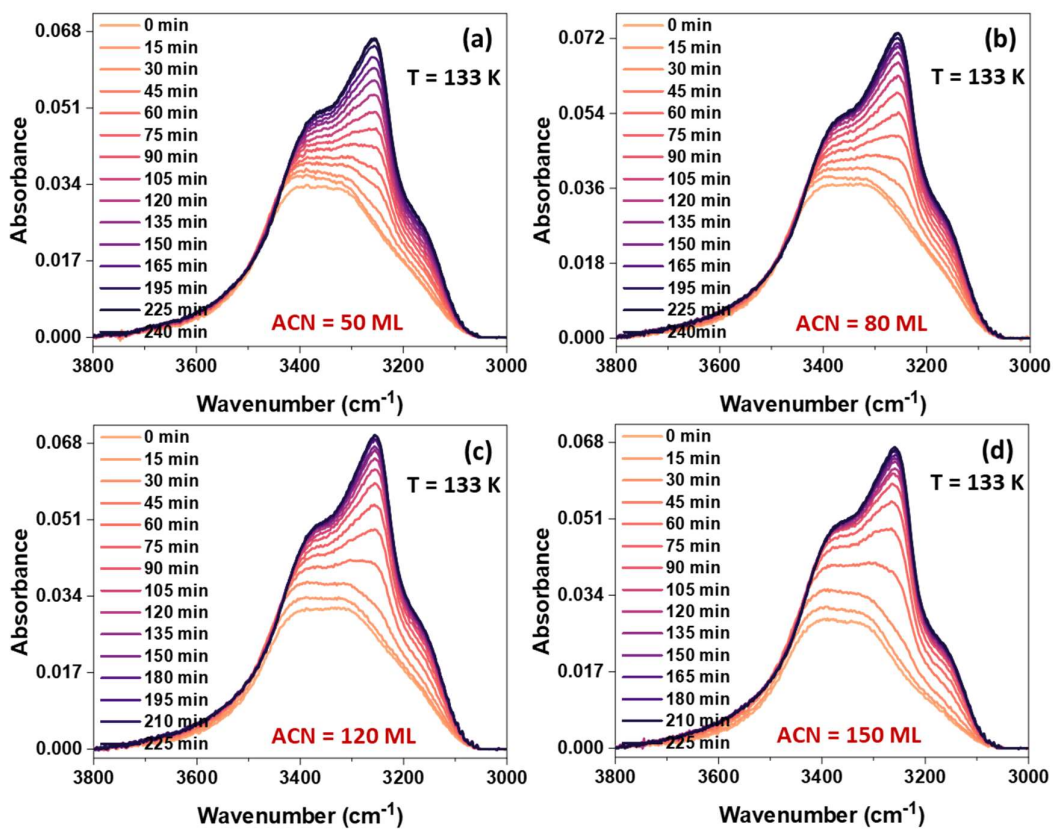
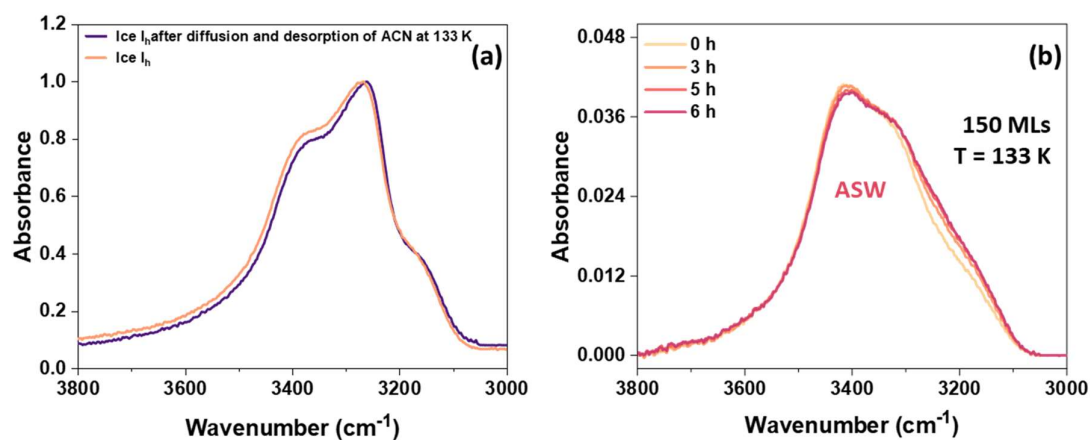


Fig. S5 Time-dependent RAIRS spectra of ASW@ACN films at 133 K in the O-H stretching region. ACN film thickness was varied from 50-150 ML while keeping the ASW film thickness constant at 150 ML. Ice films were prepared by vapor deposition on Ru(0001) at 10 K and heated to 133 K at a rate of  $2 \text{ K min}^{-1}$ . The compositions of films were (a) ASW(150 ML)@ACN(50 ML), (b) ASW(150 ML)@ACN(80 ML), (c) ASW(150 ML)@ACN(120 ML) and (d) ASW(150 ML)@ACN(150 ML). The data show gradual crystallization of ASW after ACN diffusion and desorption.

## Supplementary information 6:



**Fig. S6** (a) Normalized RAIR spectra of Ice I<sub>h</sub> obtained after diffusion and desorption of ACN from ACN@H<sub>2</sub>O film at 133 K (blue trace) and Ice I<sub>h</sub> obtained after heating the vapor-deposited solid H<sub>2</sub>O at 155 K (orange trace). Samples were prepared at 10 K and heated at a rate of 2 K.min<sup>-1</sup> to the mentioned temperatures. Both the spectrum were almost identical and confirms the formation of Ice I<sub>h</sub> after diffusion and desorption of ACN from ACN@H<sub>2</sub>O film (b) Time-dependent RAIR spectra of 150 MLs of H<sub>2</sub>O film deposited on Ru(0001) at 10 K and annealed at a rate of 2 K.min<sup>-1</sup> to 133 K, in the O-H stretching region. At 133 K, ASW was kept for several hours but remains amorphous, which confirms pure H<sub>2</sub>O could not crystallize at such low temperatures without external deriving force. This also suggests the absence of any role for Ru(0001) in ASW crystallization.



## Supplementary information 7:

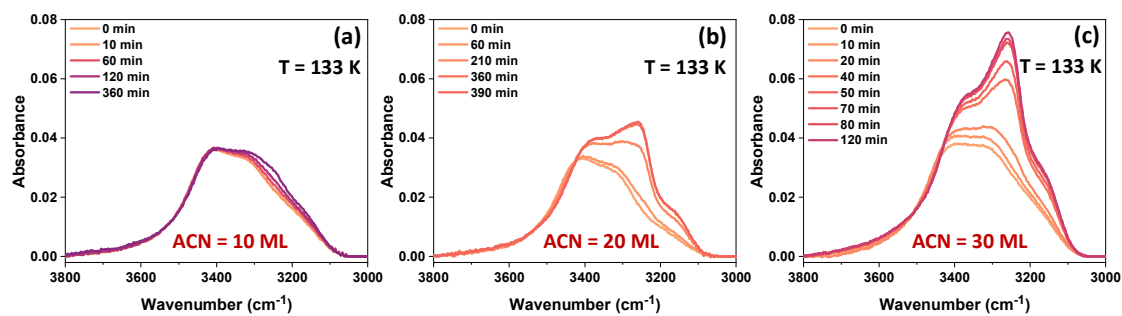


Fig. S7 Time-dependent RAIRS spectra of ACN@ASW films at 133 K in the O–H stretching region. ACN film thicknesses were varied from 10–30 ML and ASW film thicknesses were kept constant at 150 ML. Ice films were prepared by vapor deposition on Ru(0001) at 10 K and heated to 133 K at a rate of 2 K min<sup>-1</sup>. The composition of films were (a) ACN(10 ML)@ASW(150 ML), (b) ACN(20 ML)@ASW(150 ML) and (c) ACN(30 ML)@ASW(150 ML).

Supplementary information 8:

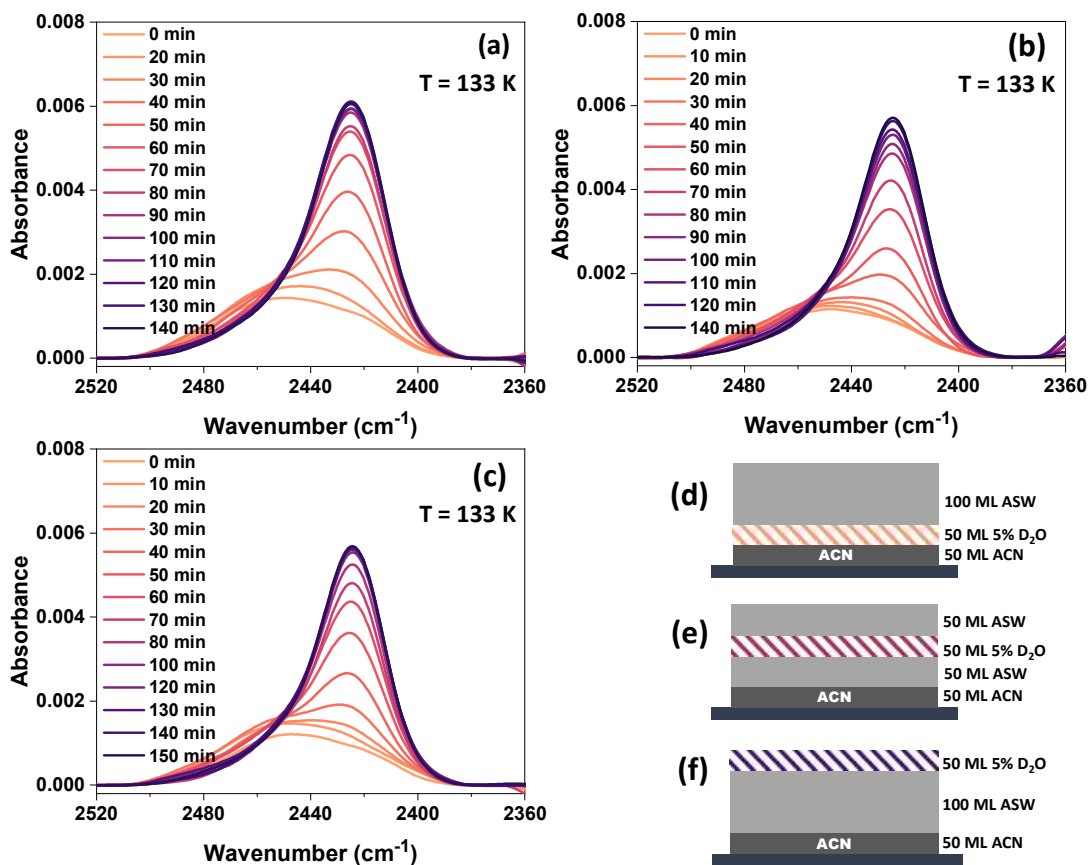


Fig. S8 Time-dependent RAIRS spectra of ACN@ASW film with HDO layer, at 133 K in the O–D stretching region. The ice films were prepared by placing a 50 ML HDO (5%  $\text{D}_2\text{O}$  in  $\text{H}_2\text{O}$ ) layer in ASW, (a) near ACN film, (b) 50 ML away from ACN layer and (c) 100 ML away from ACN layer. The film was sequentially deposited on Ru(0001) at 10 K and heated at a rate of  $2 \text{ K min}^{-1}$  to 133 K. Panels (d), (e), and (f) show the compositions of sequentially deposited ACN, ASW and HDO layers for which RAIRS spectra are given in (a), (b), and (c), respectively.

Supplementary information 9:

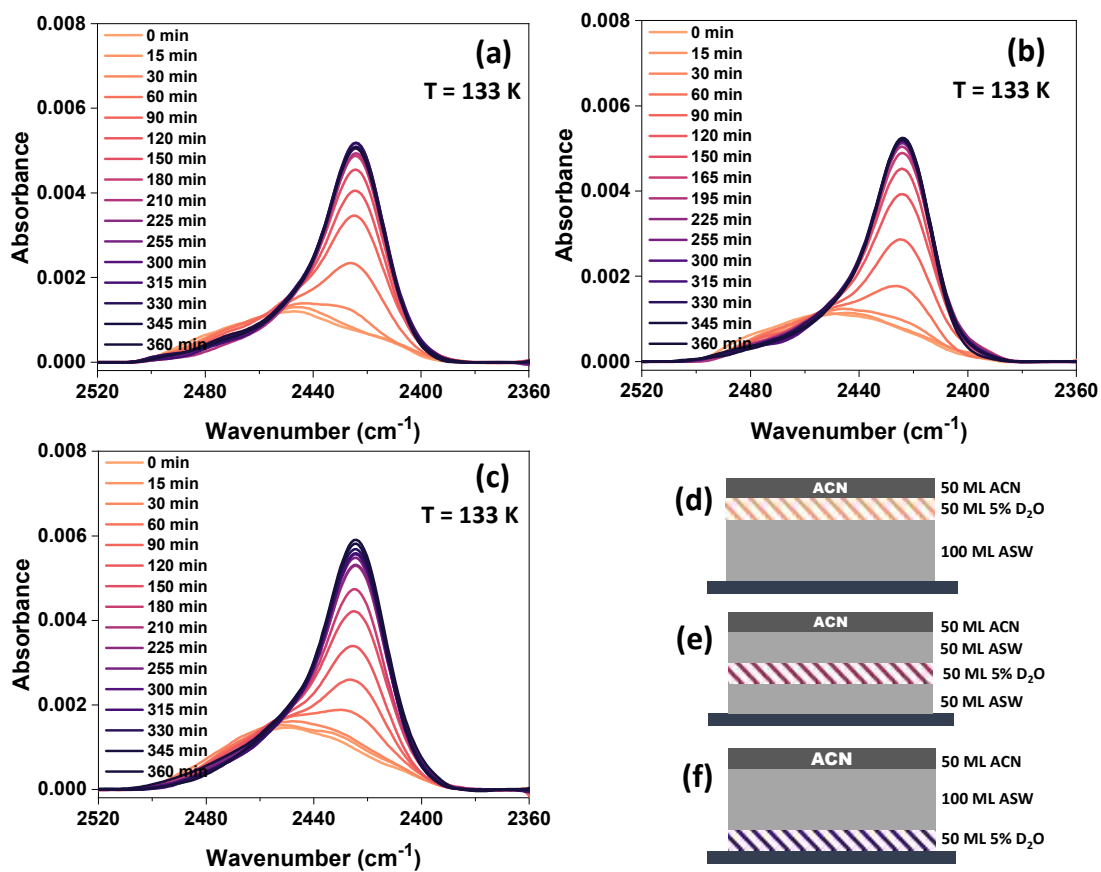


Fig. S9 Time-dependent RAIRS spectra of ASW@ACN film with HDO layer, at 133 K in the O–D stretching region. The ice films were prepared by placing a 50 ML HDO (5% D<sub>2</sub>O in H<sub>2</sub>O) layer in ASW, (a) near ACN film, (b) 50 ML away from ACN layer and (c) 100 ML away from ACN layer. The film was sequentially deposited on Ru(0001) at 10 K and heated at a rate of 2 K min<sup>-1</sup> to 133 K. Panels (d), (e), and (f) show the compositions of sequentially deposited ACN, ASW and HDO layers for which RAIRS spectra are given in (a), (b), and (c), respectively.

Supplementary information 10:

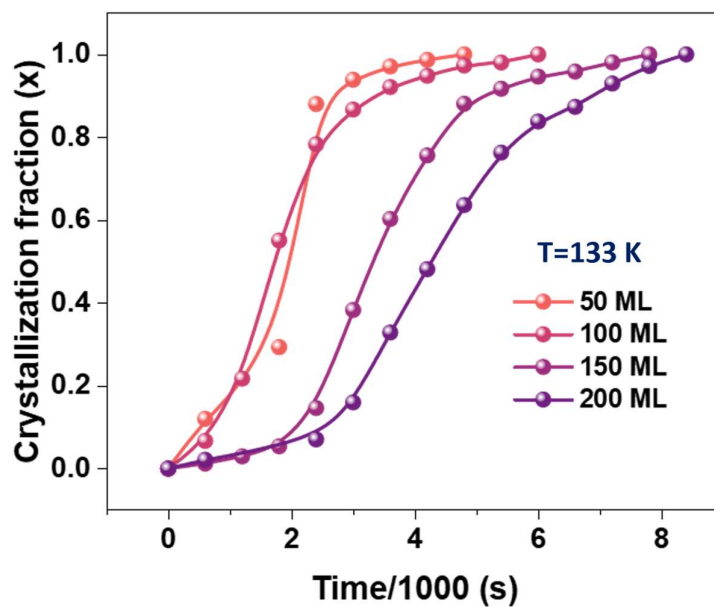


Fig. S10 The CF versus time curves for ACN@ASW films with varying ASW film thickness (50-200 ML), and keeping ACN layer thickness constant at 50 ML, obtained from isothermal RAIRS measurements at 133 K. The CF was calculated from a vertical cut at  $3260\text{ cm}^{-1}$  in the O-H stretching band of the time-dependent RAIRS spectra, shown in Fig. S10a, b, c and S5a.

### Supplementary information 11:

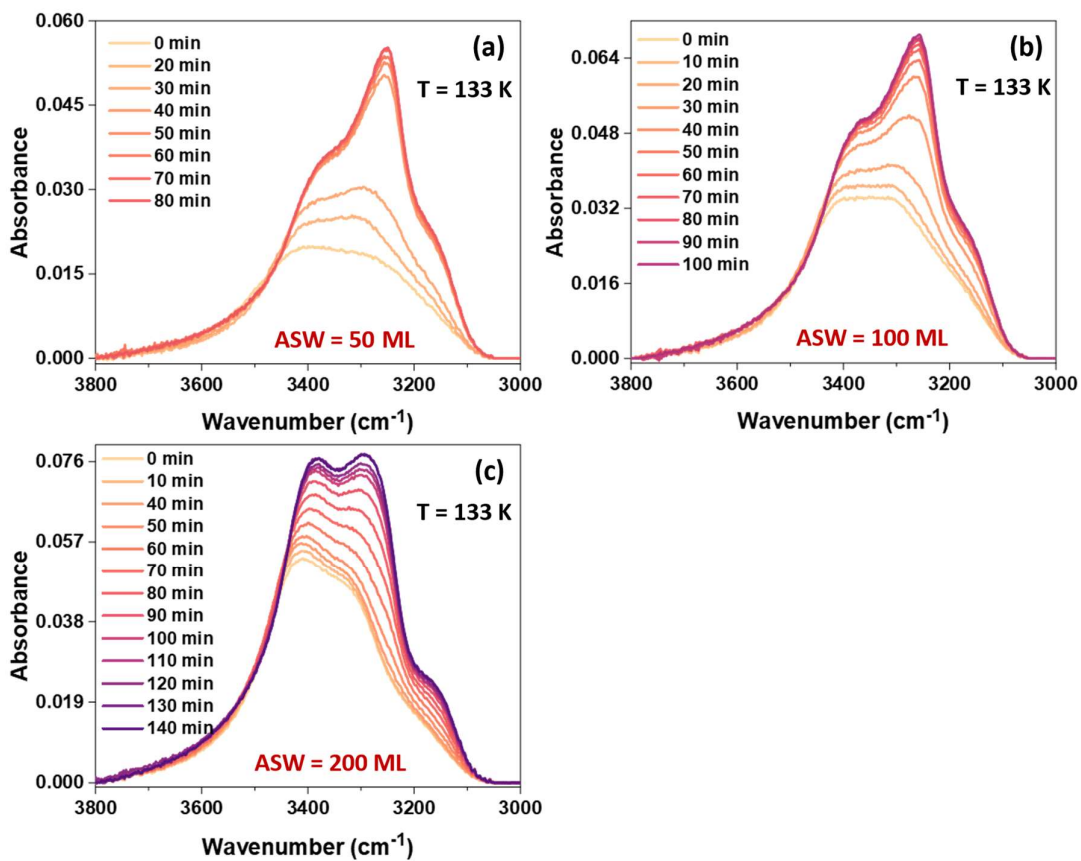


Fig. S11 Time-dependent RARS spectra of ACN@ASW films at 133 K in the O-H stretching region. ACN film thickness was kept constant, 50 ML and ASW film thickness was varied from 50-200 ML. Ice films were prepared by vapor deposition on Ru(0001) at 10 K and heated to 133 K at a rate of 2 K min<sup>-1</sup>. The composition of films are (a) ACN(50 ML)@ASW(50 ML), (b) ACN(50 ML)@ASW(100 ML), and (c) ACN(50 ML)@ASW(200 ML). The data shows that the time required for the crystallization increases with increase in ASW thickness.

Supplementary information 12:

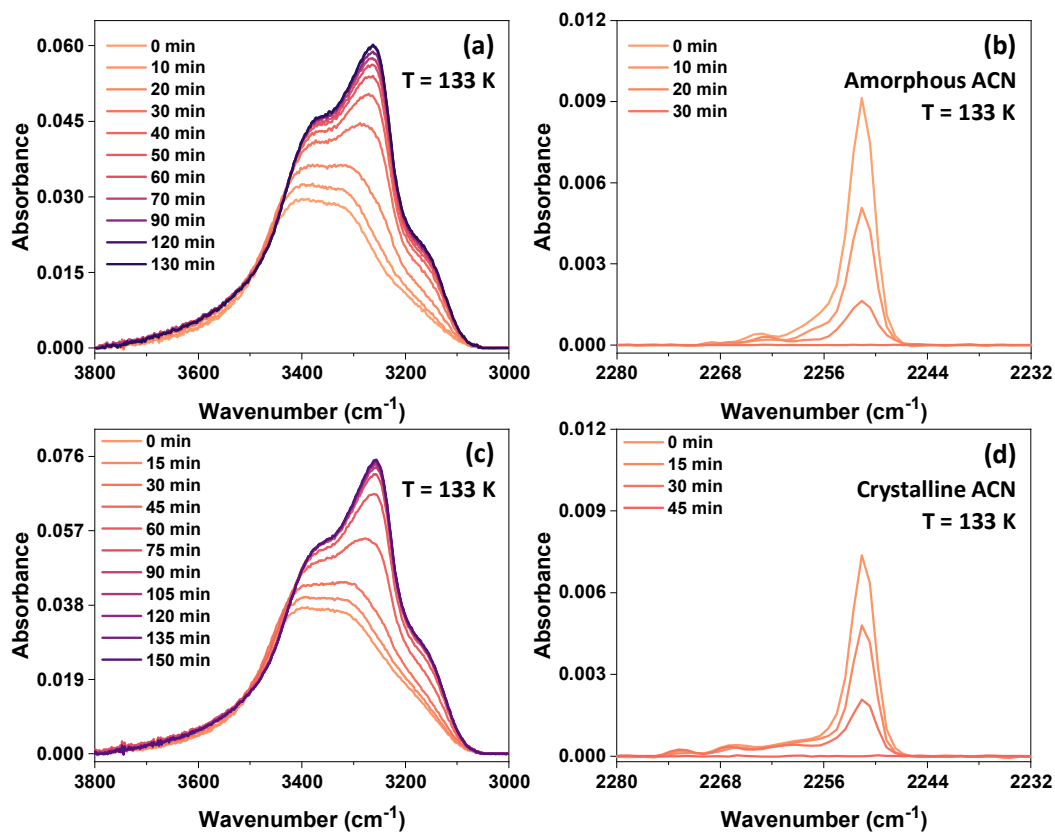


Fig. S12 (a) and (b) Time-dependent RARS spectra of ACN(50 ML)@ASW(150 ML) films at 133 K in the O-H and C≡N stretching region, respectively. Ice films were prepared by vapor deposition on Ru(0001) at 10 K and heated to 133 K at a rate of 2 K min<sup>-1</sup>. (c) and (d) Time-dependent RARS spectra of ACN(50 ML)@ASW(150 ML) films at 133 K in the O-H and C≡N stretching region, respectively. Here, first, 50 ML of ACN was deposited at 10 K and heated to 110 K, above crystallization temperature of ACN to prepare a crystalline ACN film, after that ACN film was cooled down to 10 K. Finally, H<sub>2</sub>O vapor was deposited on top of crystalline ACN film at 10 K. As prepared ice film was heated to 133 K at a rate of 2 K min<sup>-1</sup>.

Supplementary information 13:

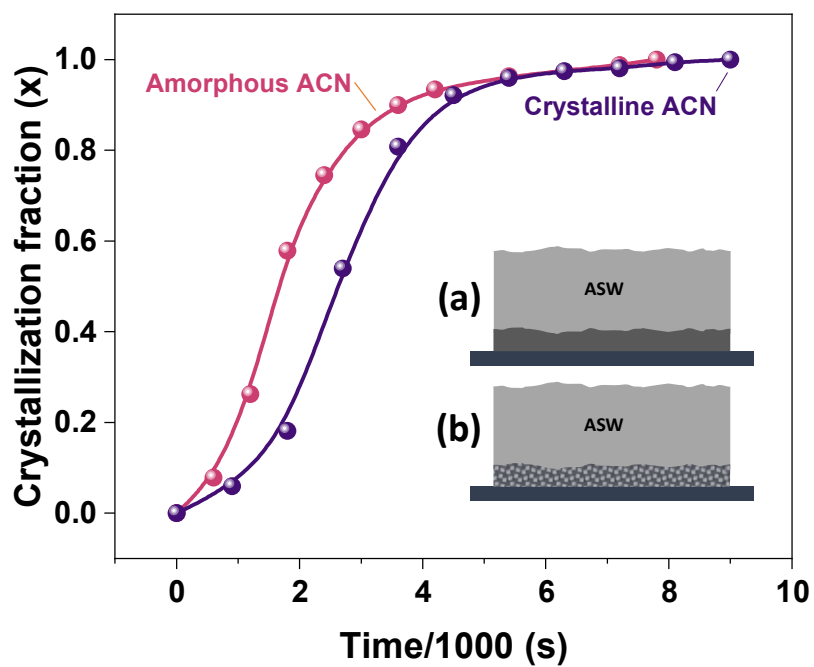


Fig. S13 CF versus time curves for ACN(50 ML)@ASW(150 ML) films with amorphous ACN film (brown curve) and crystalline ACN film (blue curve), obtained from isothermal RAIRS measurements at 133 K. The CF was calculated from a vertical cut at  $3260\text{ cm}^{-1}$  in the O-H stretching band of the time-dependent RAIRS spectra shown in Fig. S11a, c.

### Supplementary information 14:

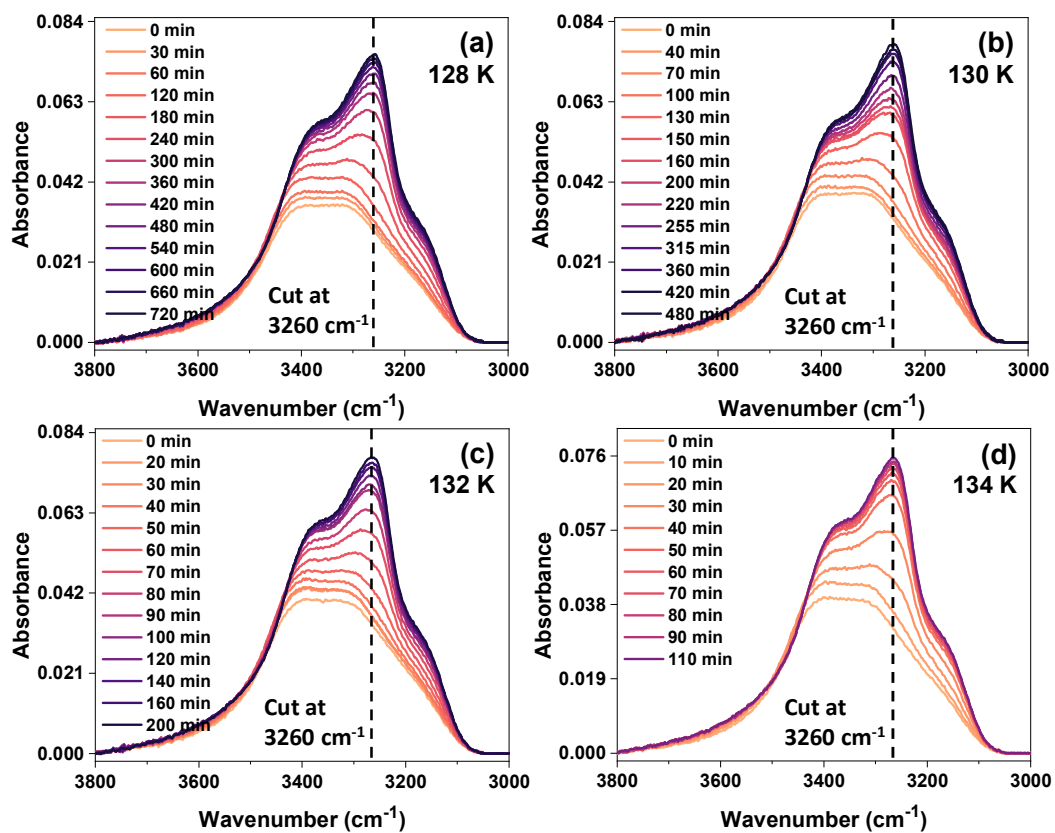


Fig. S14 Time-dependent RAIRS spectra of ACN@ASW films at (a) 128 K, (b) 130 K, (c) 132 K, and (d) 134 K in the O-H stretching region. ACN and ASW film thickness was kept constant, ACN(50 ML)@ASW(150 ML). Ice films were prepared by vapor deposition on Ru(0001) at 10 K and heated to set temperatures at a rate of  $2 \text{ K min}^{-1}$ . Vertical cut at  $3260 \text{ cm}^{-1}$  in O-H stretching band was used for the crystallization fraction evolution.



**Table S1.** The parameters of AWS crystallization at different temperatures.

	Temperature (K)	<i>n</i>	Rate constant; <i>k</i> (s <sup>-1</sup> )
O-H stretching	128	1.84	5.25×10 <sup>-05</sup>
	130	1.76	8.43×10 <sup>-05</sup>
	132	1.67	2.15×10 <sup>-04</sup>
	134	1.60	4.58×10 <sup>-04</sup>