Supplementary information

Desorption-induced Evolution of Cubic and Hexagonal Ices in Ultrahigh Vacuum and Cryogenic Temperatures

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Supplementary Information 1A:

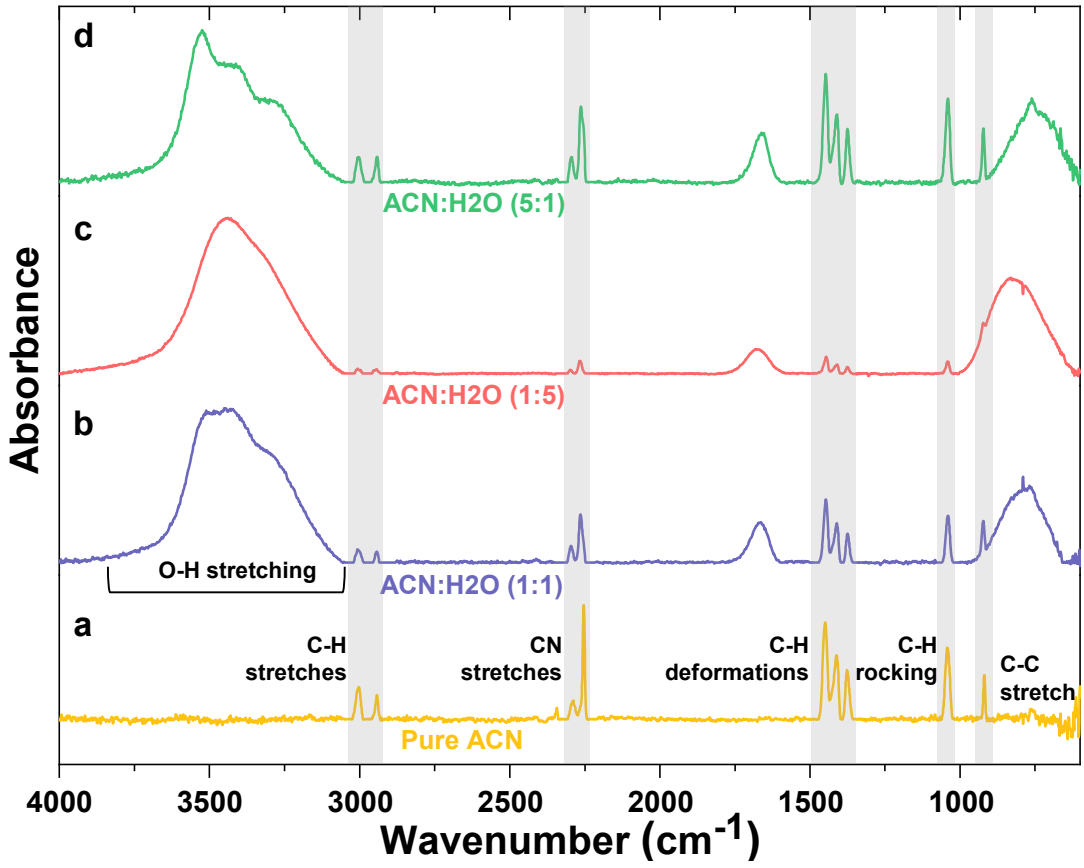

Fig. S1A RAIR spectra of (a)150 MLs of ACN, (b) 300 MLs of 1:1 ACN:H_2O, (c) 300 MLs of 1:5 ACN:H_2O, (d) 300 MLs of 5:1 ACN:H_2O at 10 K.

Supplementary Information 1B:

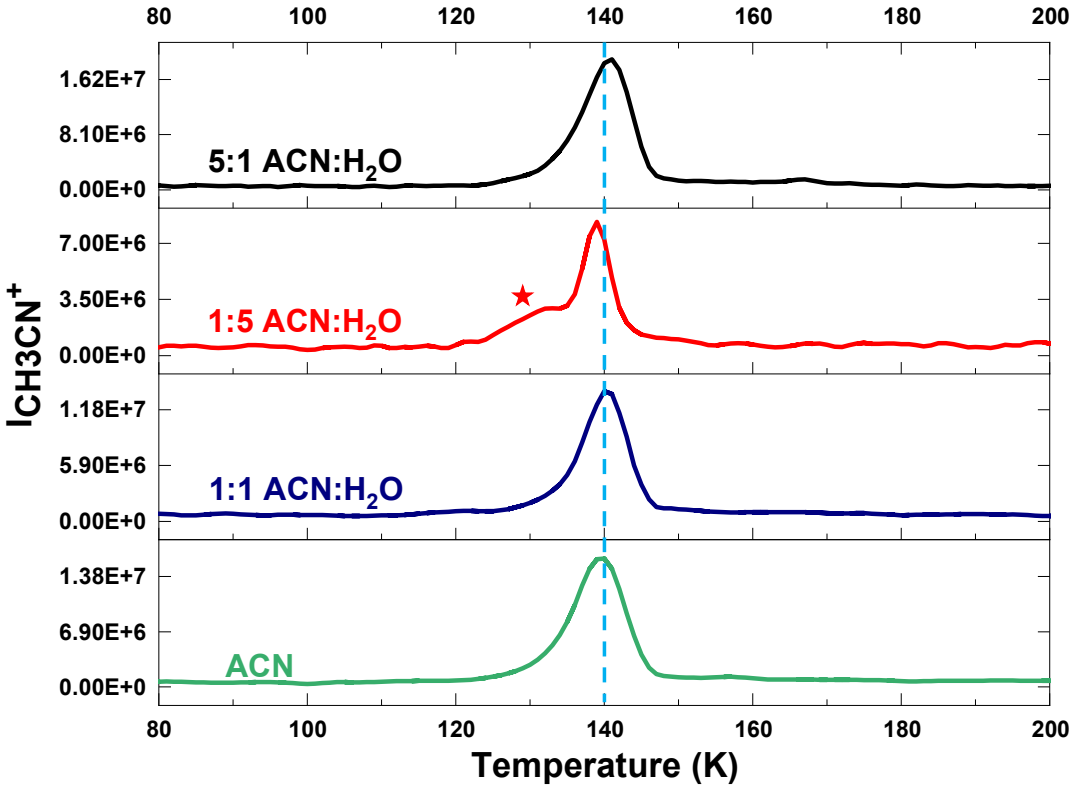

Fig. S2B TPD-MS spectra of 150 MLs of pure ACN (green), 300 MLs of 1:1 ACN:H_2O (blue), 300 MLs of 1:5 ACN:H_2O (red), and 300 MLs of 5:1 ACN:H_2O (black). Ramping rate = 10 K.min^{-1}. Here, the intensities of CH_3CN^+ (m/z = 41) under these conditions are plotted. The marked desorption (*) hump is due to the restricted ACN desorption from 1:5 ACN:H_2O film during annealing.

Supplementary information 2:

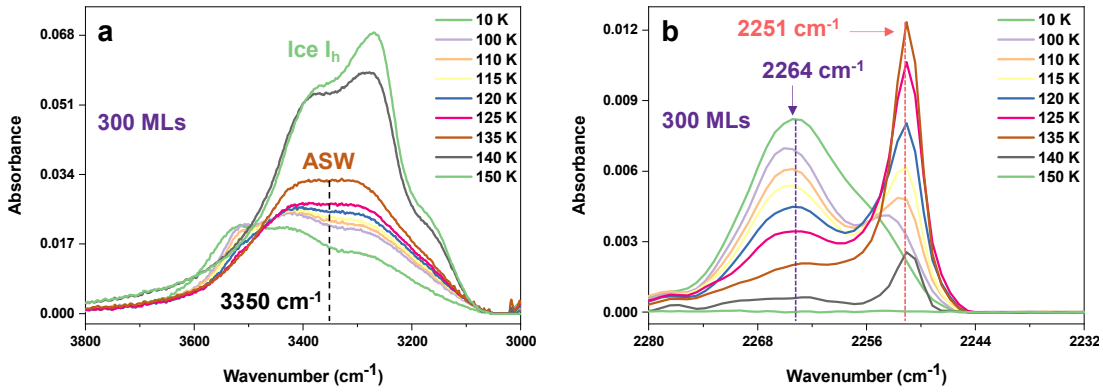

Figure S3 Temperature-dependent RAIR spectra of 300 MLs of 1:1 ACN:H_2O film co-deposited on Ru(0001) at 10 K and heated at a rate of 5 K min^{-1}. (a) O-H stretching region (b) C≡N stretching region.

Supplementary information 3:

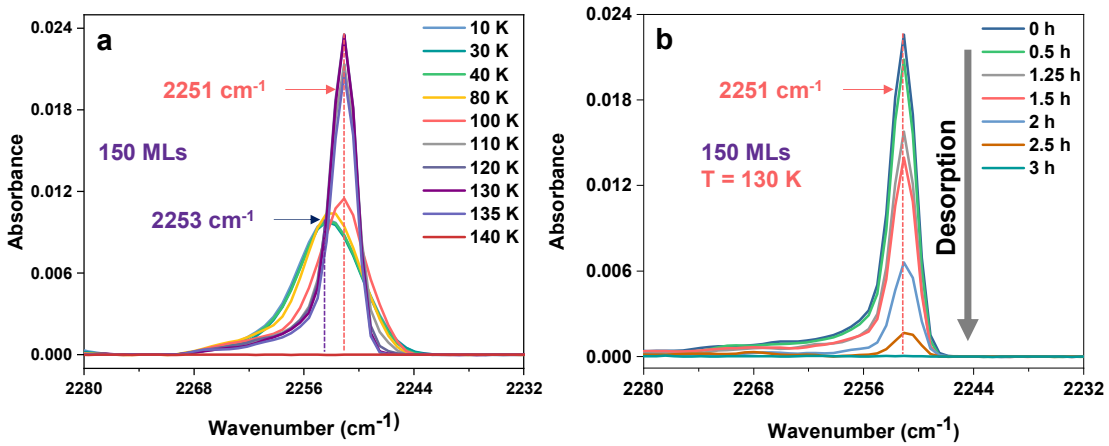

Fig. S4 RAIR spectra of 150 MLs of pure ACN in the C≡N stretching region. (a) Temperature-dependent spectra taken after ACN deposited at 10 K and heated at a rate of 5 K min^{-1} to the desorption temperature of ACN. ACN was found in two phases, where a low temperature amorphous phase (broad peak at ~ 2253 cm^{-1}) converted into crystalline phase (sharp peak at 2251 cm^{-1}) after 100 K.[1,2] (b) Isothermal time-dependent spectra at 130 K. The ACN vapour was deposited at 10 K and heated at a rate of 5 K min^{-1} to and kept at 130 K. ACN desorbed from substrate within 3 h.

Supplementary Information 4:

(a) Hexagonal Ice

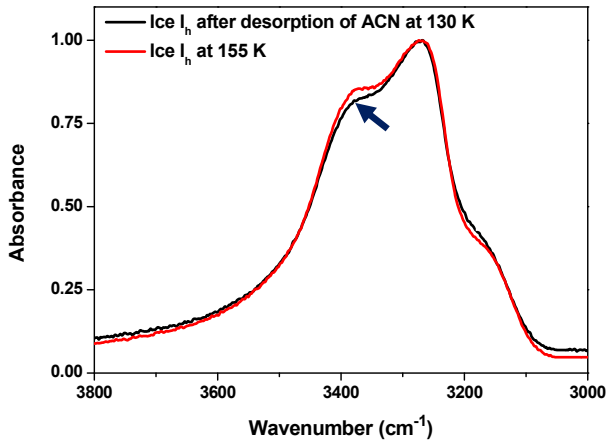

Fig. S5a RAIR spectra of Ice I_h obtained after desorption of ACN from 300 MLs of 1:1 ACN:H_2O film at 130 K (black trace) and Ice I_h obtained after heating 150 MLs of pure solid H_2O at 155 K (red trace) in the O-H stretching region. The spectra were normalized by the integral intensity of the absorbance. ACN:H_2O (1:1) film of 300 MLs and pure H_2O film of 150 MLs were prepared by depositing at 10 K and heating at a rate of 5 K min^{-1} to the mentioned temperatures. Both the spectrum were almost identical and confirms the formation of Ice I_h after desorption of ACN from 1:1 ACN:H_2O film.

(b) Cubic Ice

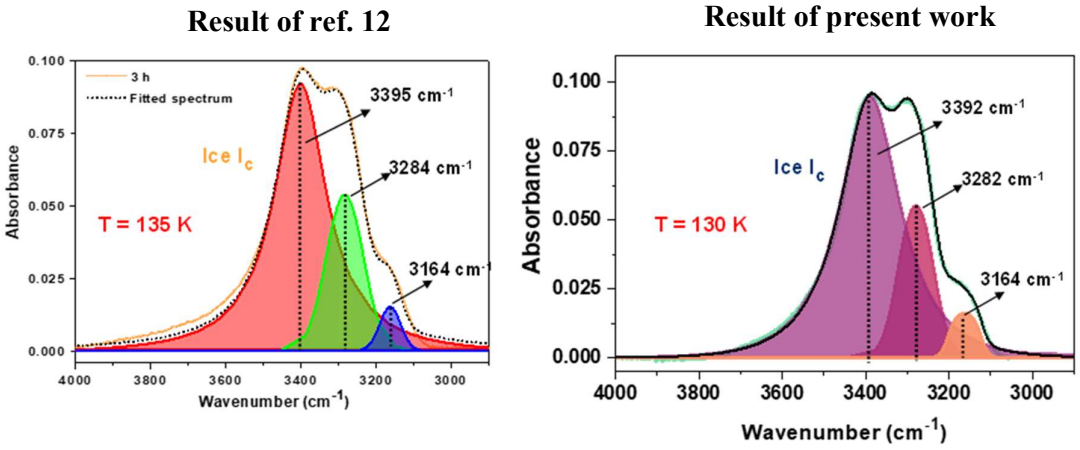

Fig. S4b The deconvoluted features of IR data of ref. 12 (J. Phys. Chem. Lett. vol. 11 (2020) p. 26) and the current work. In ref. 12, Ice I_c via acetone hydrate was prepared by annealing a co-deposited ~300 MLs acetone:H_2O (1:1) film to 135 K and maintaining it there in UHV for 3 h.

Supplementary Information 5:

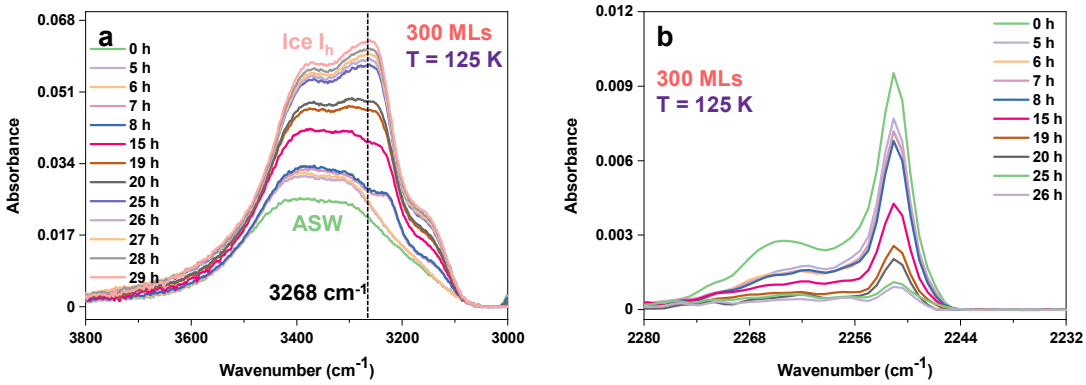

Fig. S6 Isothermal time-dependent RAIR spectra of 300 MLs of 1:1 ACN:H_2O film at 125 K in the (a) O-H stretching region and, (b) C≡N stretching region. Mixed film was prepared by vapour deposition on Ru(0001) at 10 K and heated to 125 K at a rate of 5 K min^{-1}.

Supplementary Information 6:

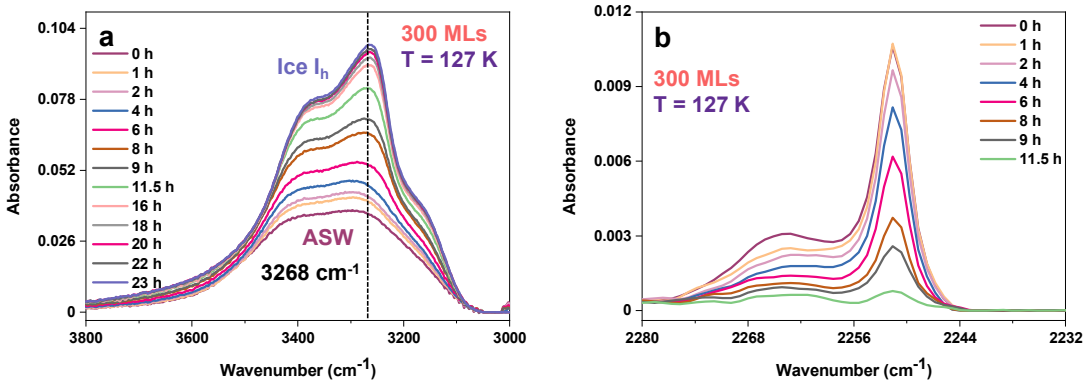

Fig. S7 Isothermal time-dependent RAIR spectra of 300 MLs of 1:1 ACN:H_2O film at 127 K in the (a) O-H stretching region and, (b) C≡N stretching region. Mixed film was prepared by vapour deposition on Ru(0001) at 10 K and heated to 127 K at a rate of 5 K min^{-1}.

Supplementary Information 7:

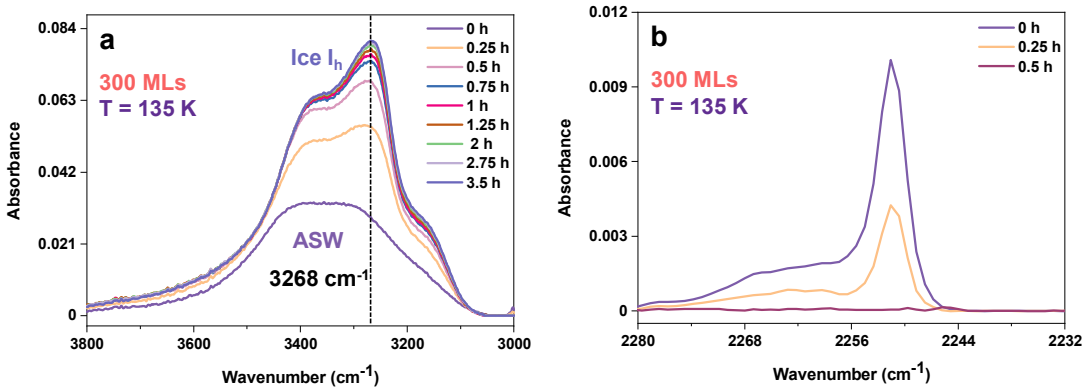

Fig. S8 Isothermal time-dependent RAIR spectra of 300 MLs of 1:1 ACN:H_2O film at 135 K in the (a) O-H stretching region and, (b) C≡N stretching region. Mixed film was prepared by vapour deposition on Ru(0001) at 10 K and heated to 135 K at a rate of 5 K min^{-1}.

Supplementary Information 8:

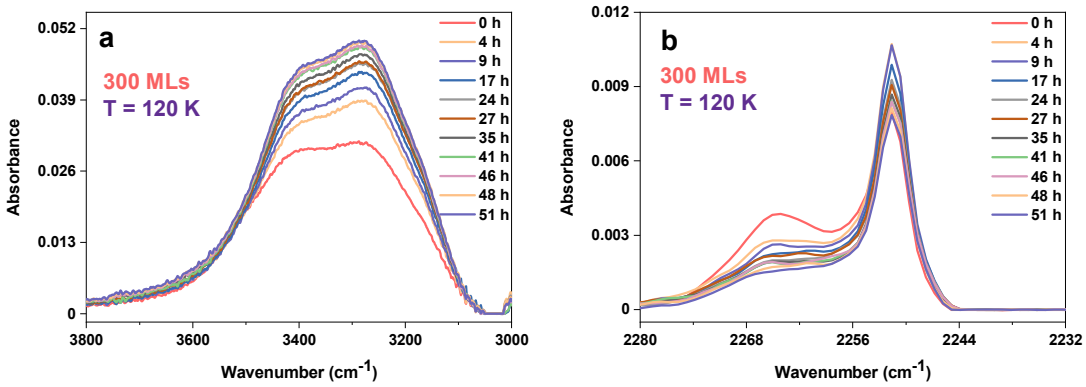

Fig. S9 Isothermal time-dependent RAIR spectra of 300 MLs of 1:1 ACN:H_2O film at 120 K in the (a) O-H stretching region and, (b) C≡N stretching region. Mixed film was prepared by vapour deposition on Ru(0001) at 10 K and heated to 120 K at a rate of 5 K min^{-1}.

Supplementary Information 9:

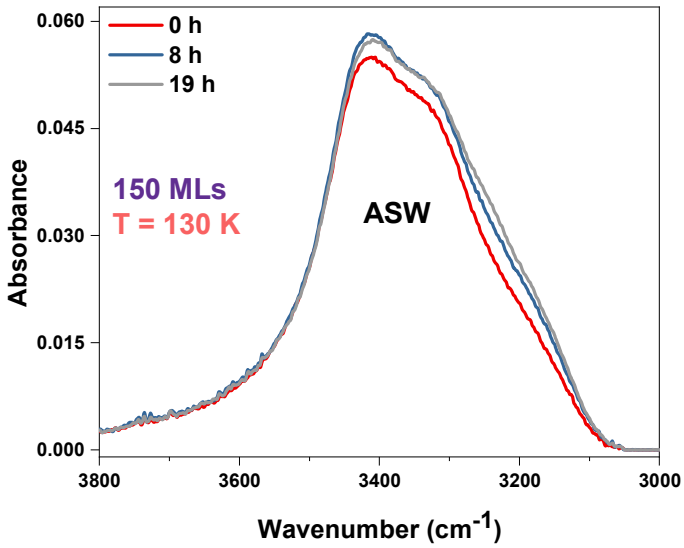

Fig. S10 Isothermal time-dependent RAIR spectra of 150 MLs of H_2O film at 130 K in the O-H stretching region. Thin film was prepared by vapour deposition on Ru(0001) at 10 K and heated to 130 K at a rate of 5 K min^{-1}.

Supplementary Information 10:

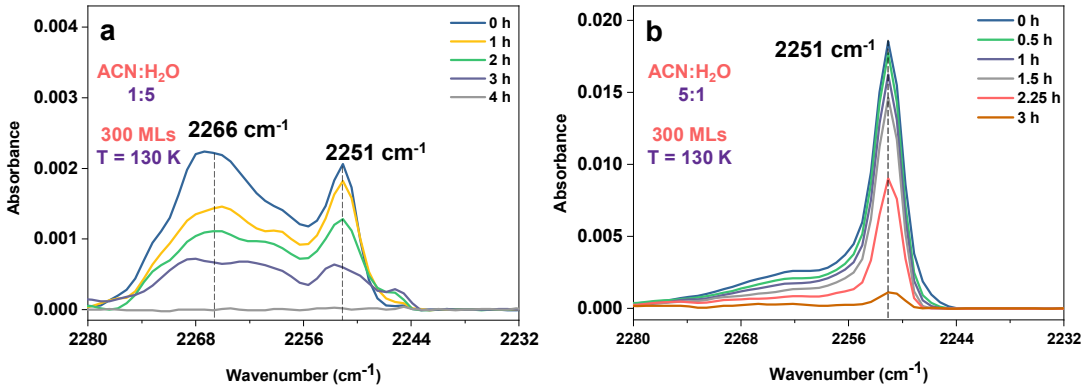

Fig. S11 (a) Isothermal time-dependent RAIR spectra of 300 MLs of 1:5 ACN:H_2O film at 130 K in the C≡N stretching region. (b) Isothermal time-dependent RAIR spectra of 300 MLs of 5:1 ACN:H_2O film at 130 K in the C≡N stretching region. Mixed film was prepared by vapour deposition on Ru(0001) at 10 K and heated to 130 K at a rate of 5 K min^{-1}.

Supplementary Information 11:

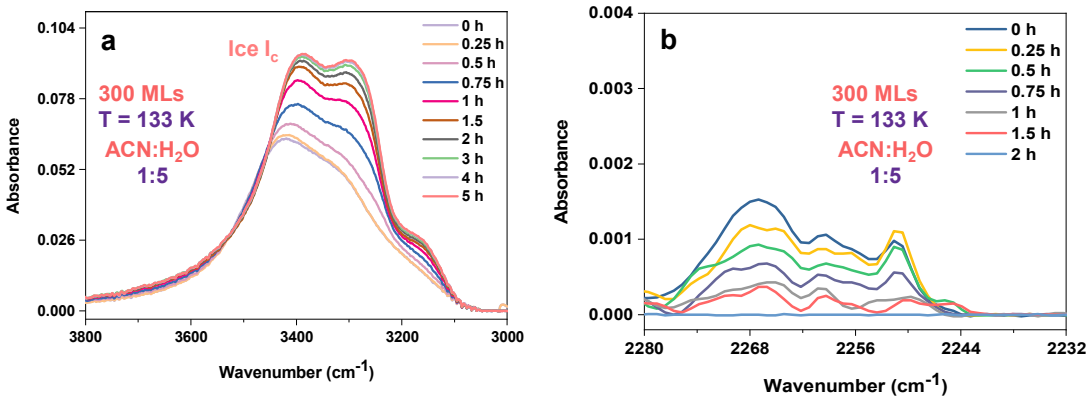

Fig. S12 Isothermal time-dependent RAIR spectra of 300 MLs of 1:5 ACN:H_2O film at 133 K in the (a) O-H stretching region and, (b) C≡N stretching region. Mixed film was prepared by vapour deposition on Ru(0001) at 10 K and heated to 133 K at a rate of 5 K min^{-1}.

Supplementary Information 12:

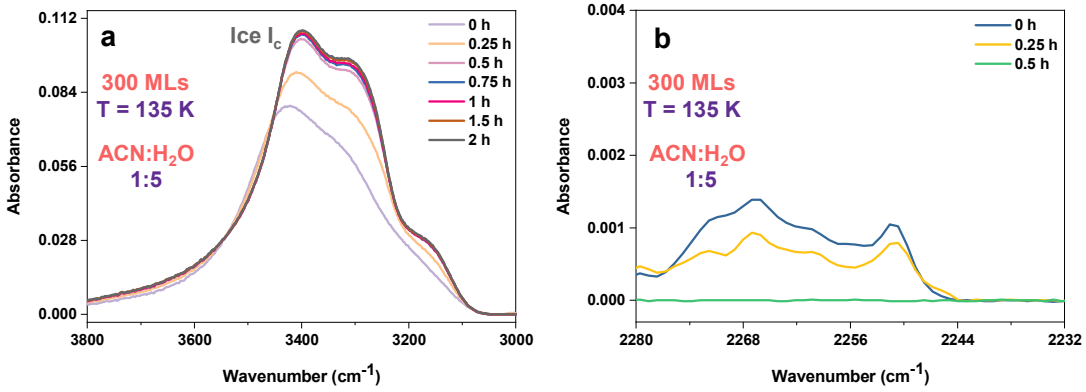

Fig. S13 Isothermal time-dependent RAIR spectra of 300 MLs of 1:5 ACN:H_2O film at 135 K in the (a) O-H stretching region and. (b) C≡N stretching region. Mixed film was prepared by vapour deposition on Ru(0001) at 10 K and heated to 135 K at a rate of 5 K min^{-1}.

Supplementary Information 13:

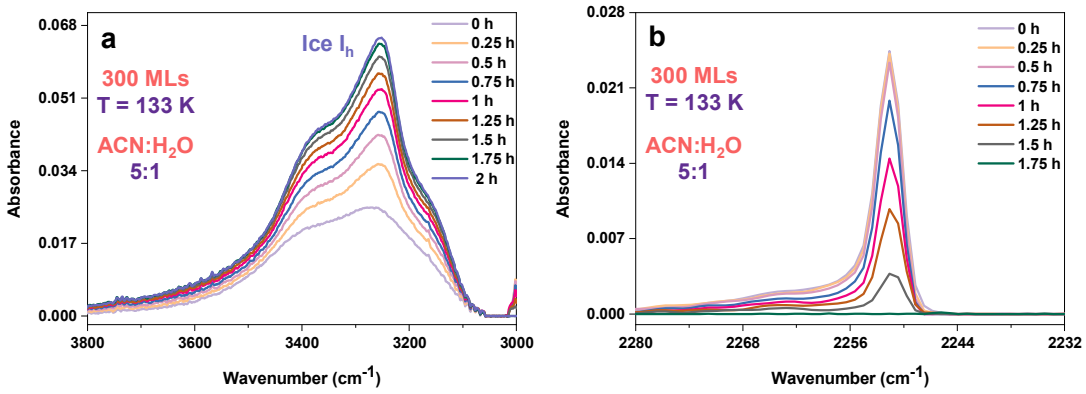

Fig. S14 Isothermal time-dependent RAIR spectra of 300 MLs of 5:1 ACN:H_2O film at 133 K in the (a) O-H stretching region and, (b) C≡N stretching region. Mixed film was prepared by vapour deposition on Ru(0001) at 10 K and heated to 133 K at a rate of 5 K min^{-1}.

Supplementary Information 14:

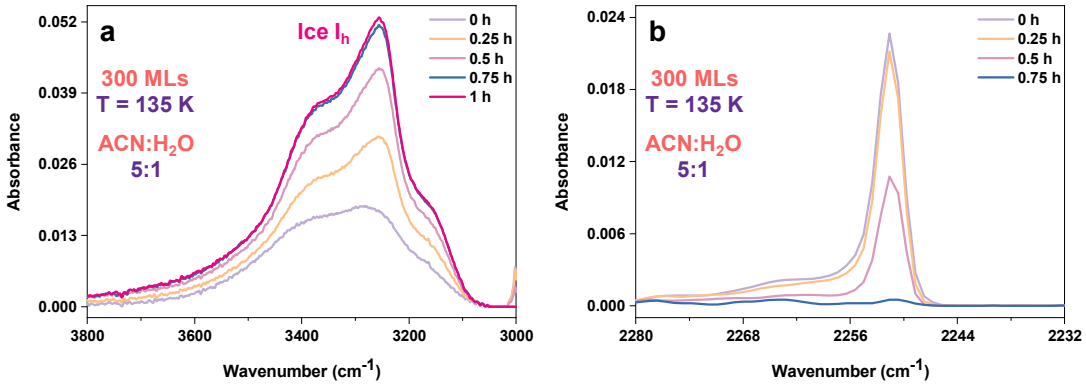

Fig. S15 Isothermal time-dependent RAIR spectra of 300 MLs of 5:1 ACN:H_2O film at 135 K in the (a) O-H stretching region and, (b) C≡N stretching region. Mixed film was prepared by vapour deposition on Ru(0001) at 10 K and heated to 135 K at a rate of 5 K min^{-1}.

Table S1 The parameters for crystallization of Ice I_h during the desorption of ACN from ice films at different temperatures.

	Temperature (K)	*n*	Rate constant; *k* (s^{-1})
O-H stretching	**125**	**1.80**	**1.39×10^{-05}**
	127	**1.75**	**2.66×10^{-05}**
	130	**1.63**	**9.60×10^{-05}**
	135	**0.91**	**8.05×10^{-04}**

References:

(1) Tizek, H.; Grothe, H.; Knözinger, E. Gas-Phase Deposition of Acetonitrile: An Attempt to Understand Ostwald's Step Rule on a Molecular Basis. *Chem. Phys. Lett.* **2004**, *383* (1–2), 129–133.

(2) Hudson, R. L.; Moore, M. H. Reactions of Nitriles in Ices Relevant to Titan, Comets, and the Interstellar Medium: Formation of Cyanate Ion, Ketenimines, and Isonitriles. *Icarus* **2004**, *172* (2), 466–478.