Facile Crystallization of Ice I_h via Formaldehyde Hydrate in Ultrahigh Vacuum under Cryogenic Conditions

*Jyotirmoy Ghosh,[†] Gaurav Vishwakarma,[†] Subhadip Das,[†] and Thalappil Pradeep[†,]**

[†]DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

AUTHOR INFORMATION

Corresponding Author

Corresponding author: *E-mail: pradeep@iitm.ac.in

Table of contents

Supporting Information 1:

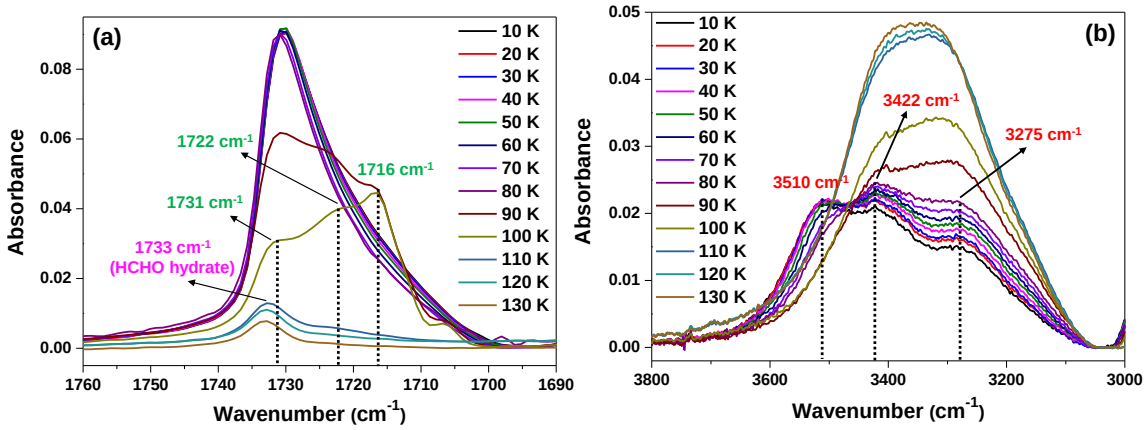

Figure S1. Temperature-dependent RAIR spectra of 300 MLs of formaldehyde:H_2O (1:1) in the (a) C=O and (b) O-H stretching regions. The mixture was co-deposited on Ru(0001) substrate at 10 K, and annealed at a rate of 2 K.min^{-1}.

Supporting Information 2:

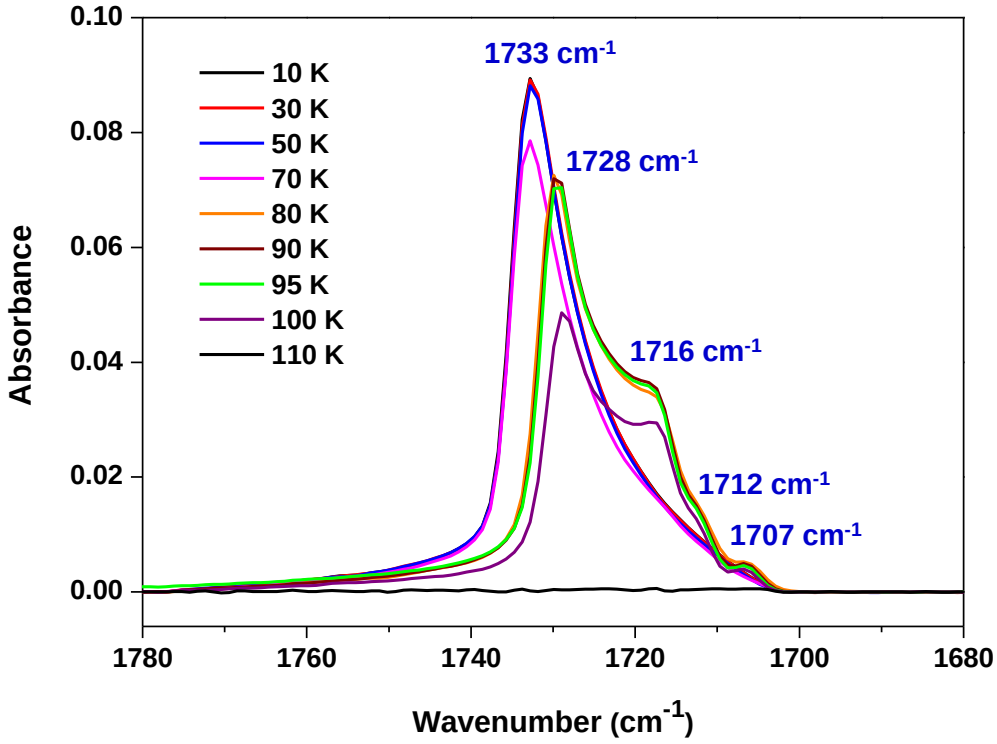

Figure S2. Temperature-dependent RAIR spectra of 150 MLs of pure formaldehyde in the C=O stretching region. The formaldehyde vapor was deposited on Ru(0001) substrate at 10 K, and annealed at a rate of 2 K.min^{-1}.

Supporting Information 3:

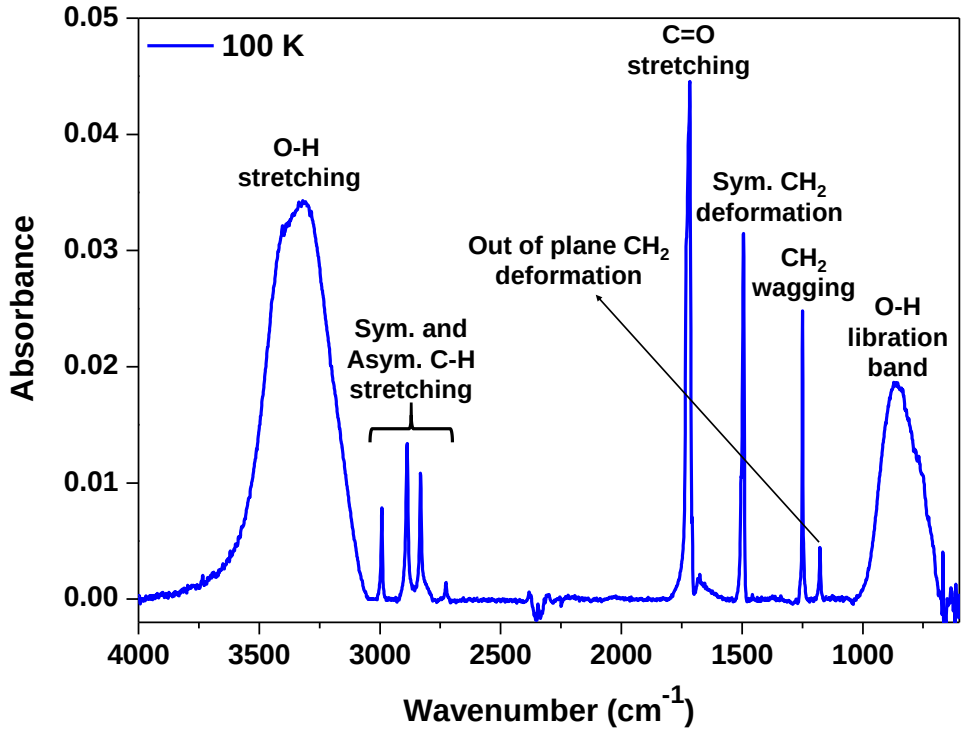

Figure S3. Full scale RAIR spectrum of 300 MLs of formaldehyde:H_2O (1:1) at 100 K.

Supporting Information 4:

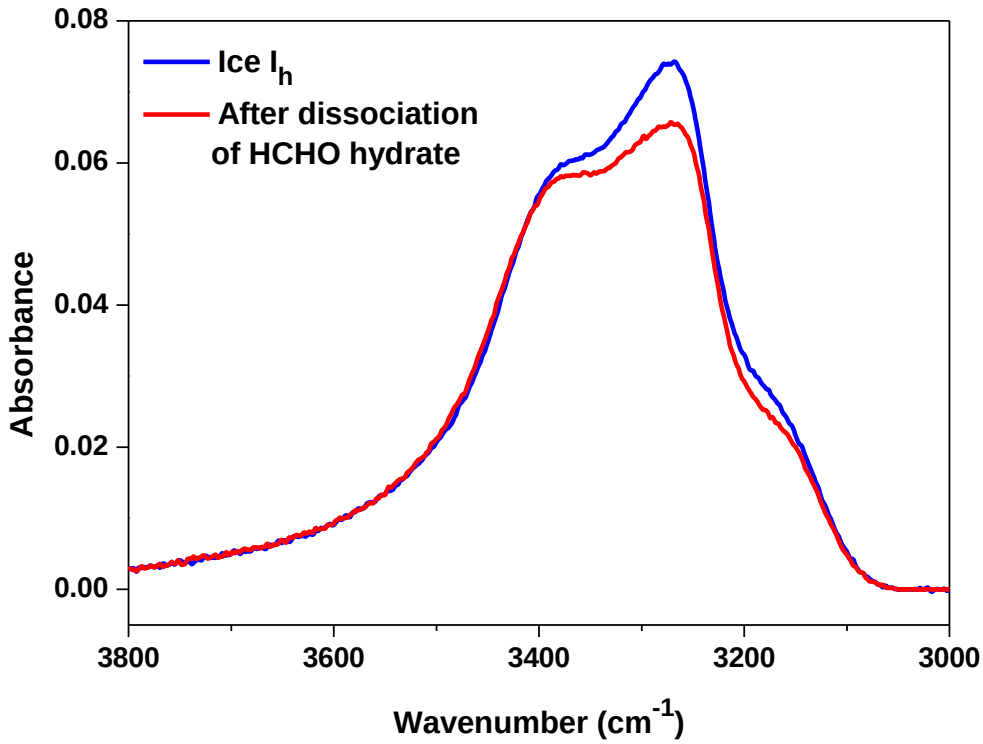

Figure S4. Comparison of O-H stretching bands of 150 MLs of solid crystalline H_2O film, which was heated to 155 K to produce ice I_h (blue trace) and the resultant ice system left after the dissociation of formaldehyde hydrate at 135 K (red trace). Both of these experiments were carried out separately. Here, the similarity of the O-H stretching bands of these two systems suggest that dissociation of formaldehyde produces nothing but ice I_h.

Supporting Information 5:

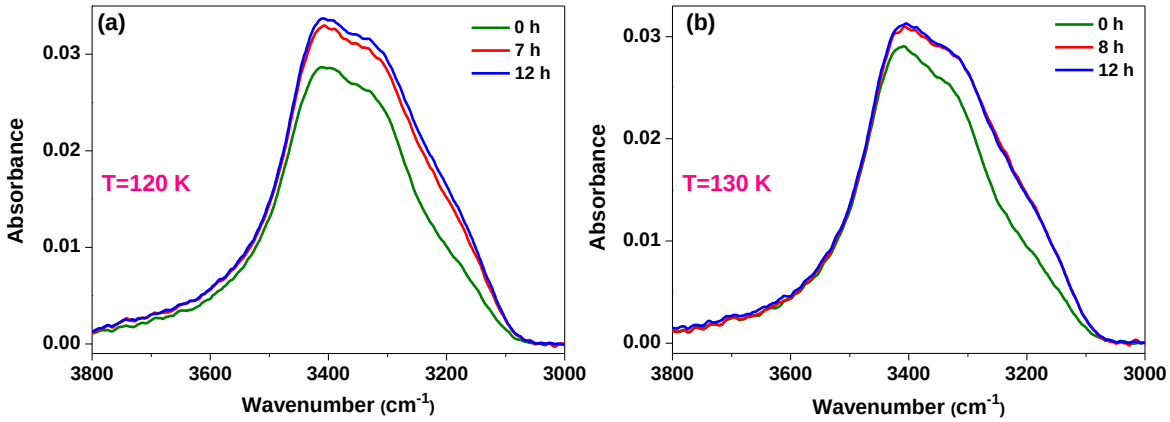

Figure S5. Time-dependent RAIR spectra of 150 MLs of solid H_2O film at (a) 120 K, and (b) at 130 K in the O-H stretching region. The water vapor was deposited at 10 K on Ru(0001) substrate. The ice films were annealed at 2 K.min^{-1} rate to the respective temperatures.

Supporting Information 6:

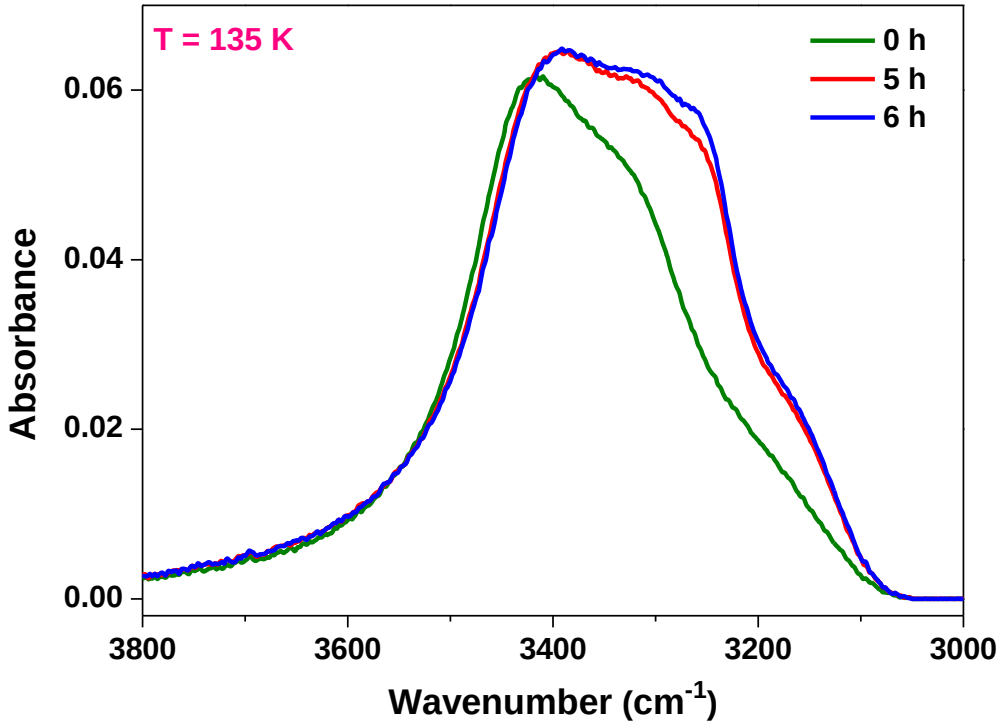

Figure S6. Time-dependent RAIR spectra of 150 MLs of solid H_2O film at 135 K in the O-H stretching region. The water vapor was deposited at 10 K on Ru(0001) substrate. The ice films were annealed at 2 $K.min^{-1}$ rate to the respective temperatures.

Supporting Information 7:

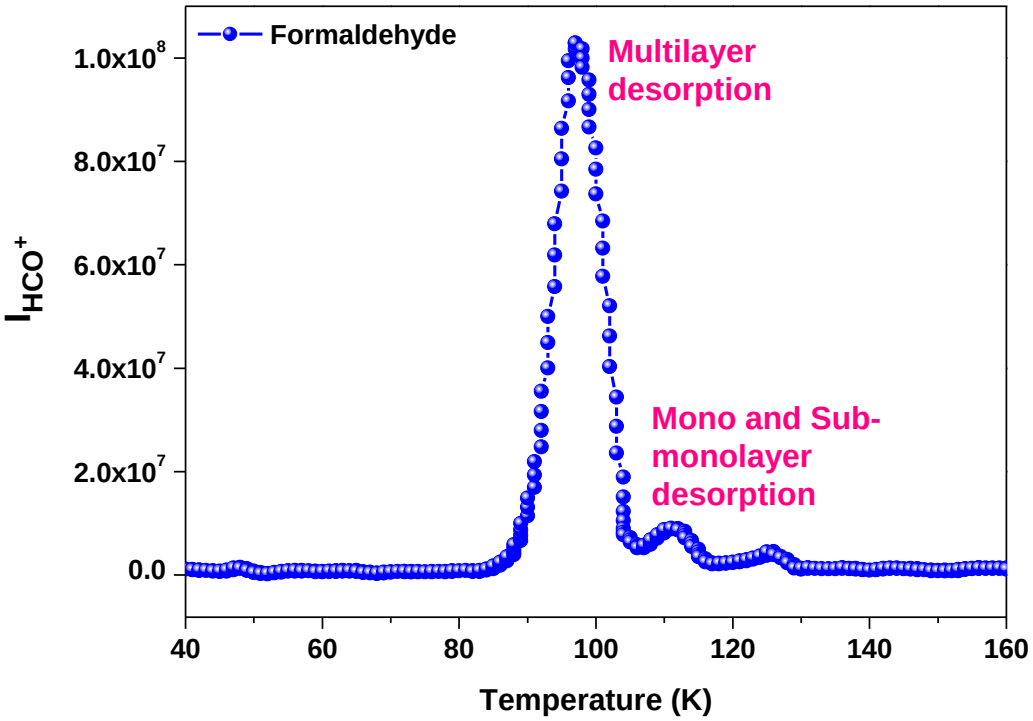

Figure S7. TPD-MS spectra of 150 MLs of pure formaldehyde. Ramping rate = 30 K.min^{-1}. Here, the intensities of HCO^+ (m/z = 29) under these conditions are plotted.

Supporting Information 8:

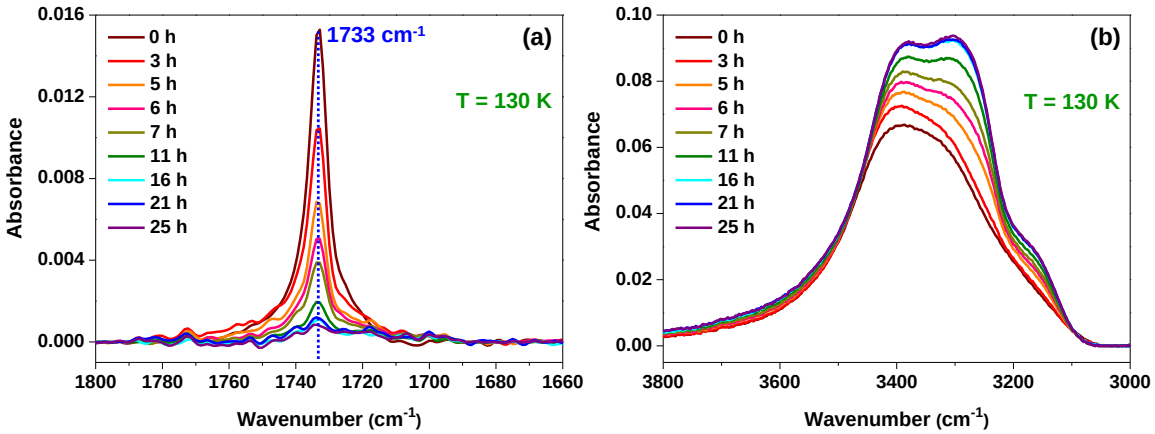

Figure S8. Time-dependent RAIR spectra of 300 MLs of formaldehyde:H_2O (1:1) at 130 K in the (a) C=O stretching region, and (b) O-H stretching region. The mixture was co-deposited on Ru(0001) substrate at 10 K, and annealed at a rate of 2 K.min^{-1} to 130 K.

Supporting Information 9:

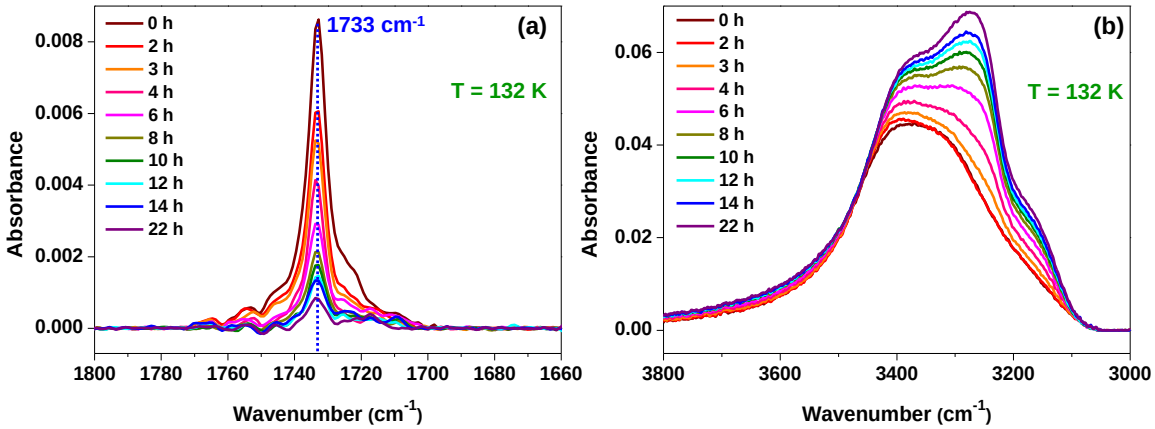

Figure S9. Time-dependent RAIR spectra of 300 MLs of formaldehyde:H_2O (1:1) at 132 K in the (a) C=O stretching region, and (b) O-H stretching region. The mixture was co-deposited on Ru(0001) substrate at 10 K, and annealed at a rate of 2 K.min^{-1} to 132 K.

Supporting Information 10:

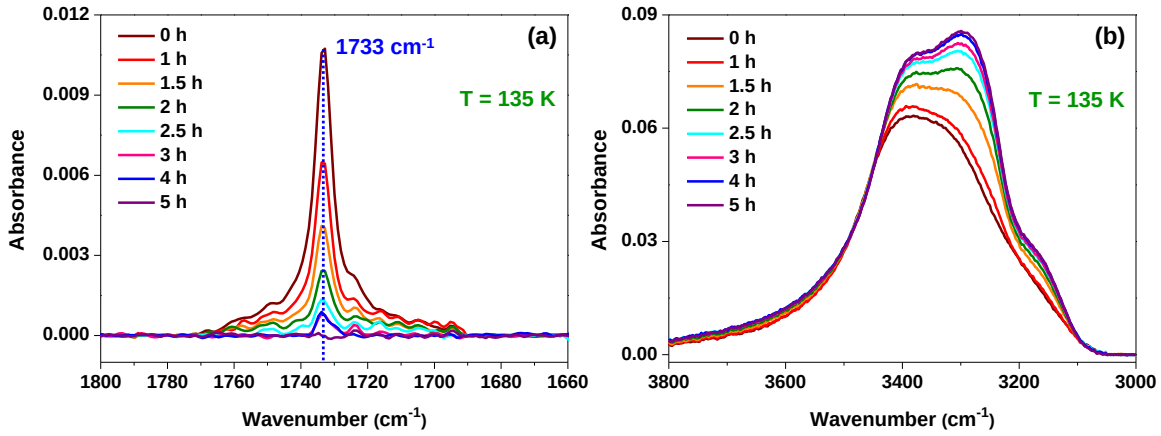

Figure S10. Time-dependent RAIR spectra of 300 MLs of formaldehyde:H_2O (1:1) at 135 K in the (a) C=O stretching region, and (b) O-H stretching region. The mixture was co-deposited on Ru(0001) substrate at 10 K, and annealed at a rate of 2 K.min^{-1} to 135 K.

Supporting Information 11:

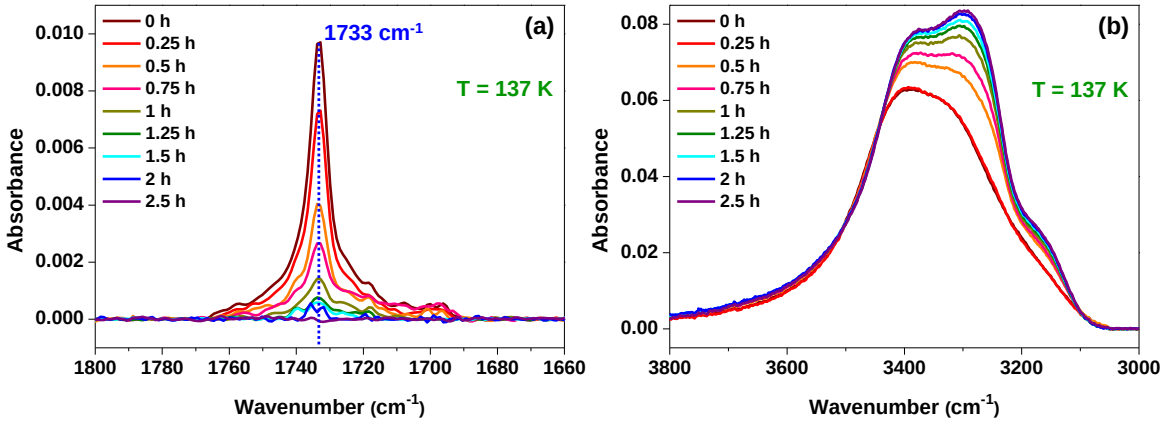

Figure S11. Time-dependent RAIR spectra of 300 MLs of formaldehyde:H_2O (1:1) at 137 K in the (a) C=O stretching region, and (b) O-H stretching region. The mixture was co-deposited on Ru(0001) substrate at 10 K, and annealed at a rate of 2 K.min^{-1} to 137 K.

Supporting Information 12:

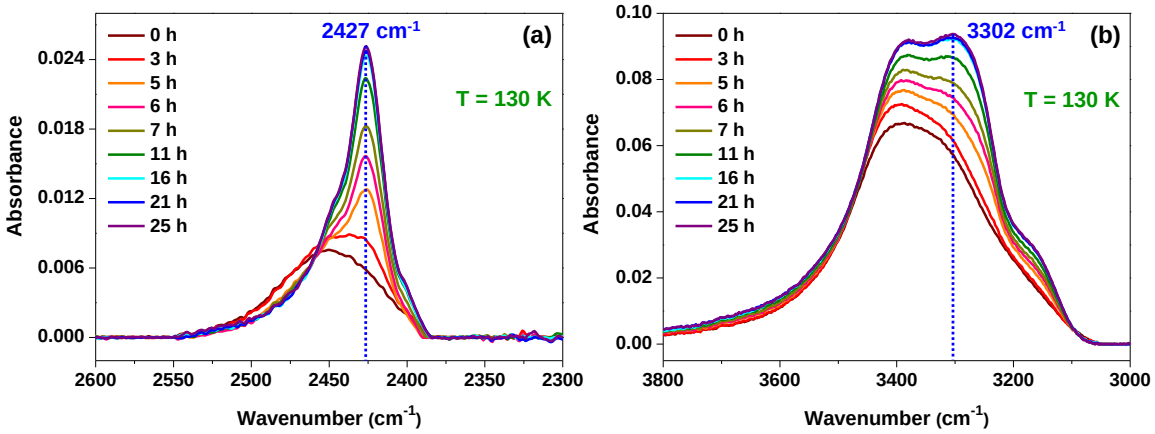

Figure S12. Time-dependent RAIR spectra of 300 MLs of formaldehyde:HDO (5% D_2O in H_2O) at 130 K in the (a) decoupled O-D stretching region, and (b) O-H stretching region. The mixture was co-deposited on Ru(0001) substrate at 10 K, and annealed at a rate of 2 K.min^{-1} to 130 K. The vertical lines at a fixed wavenumber are used to measure the absorbance changes with time, which was further utilized for calculation of crystallization fraction.

Supporting Information 13:

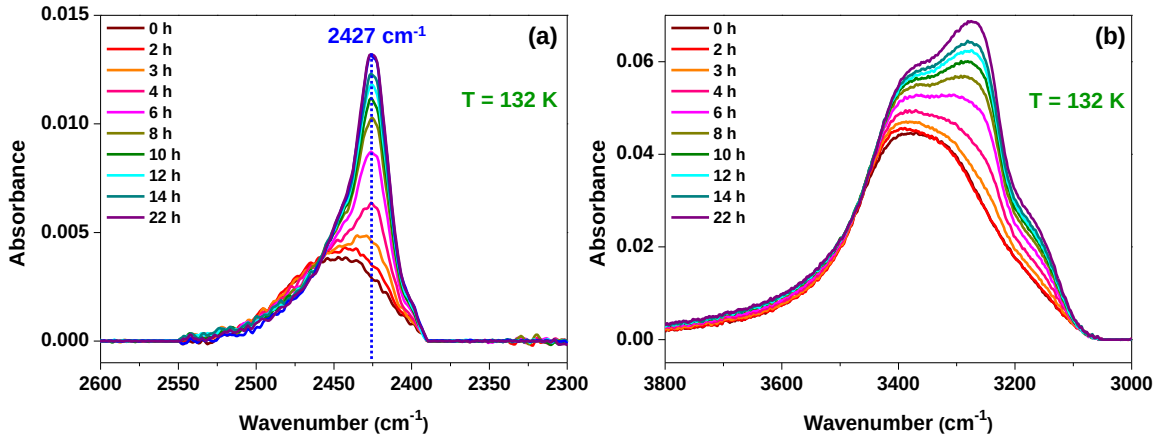

Figure S13. Time-dependent RAIR spectra of 300 MLs of formaldehyde:HDO (5% D_2O in H_2O) at 132 K in the (a) decoupled O-D stretching region, and (b) O-H stretching region.

Supporting Information 14:

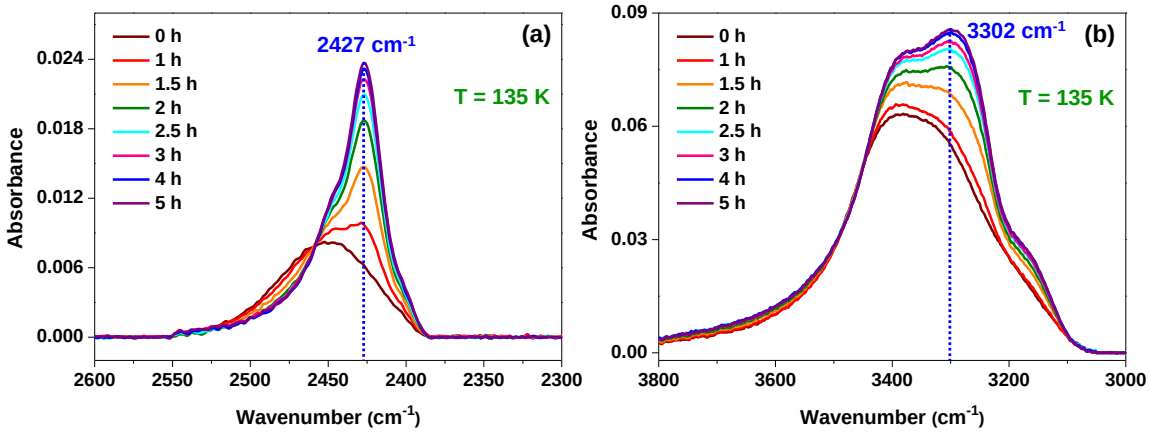

Figure S14. Time-dependent RAIR spectra of 300 MLs of formaldehyde:HDO (5% D_2O in H_2O) at 135 K in the (a) decoupled O-D stretching region, and (b) O-H stretching region.

Supporting Information 15:

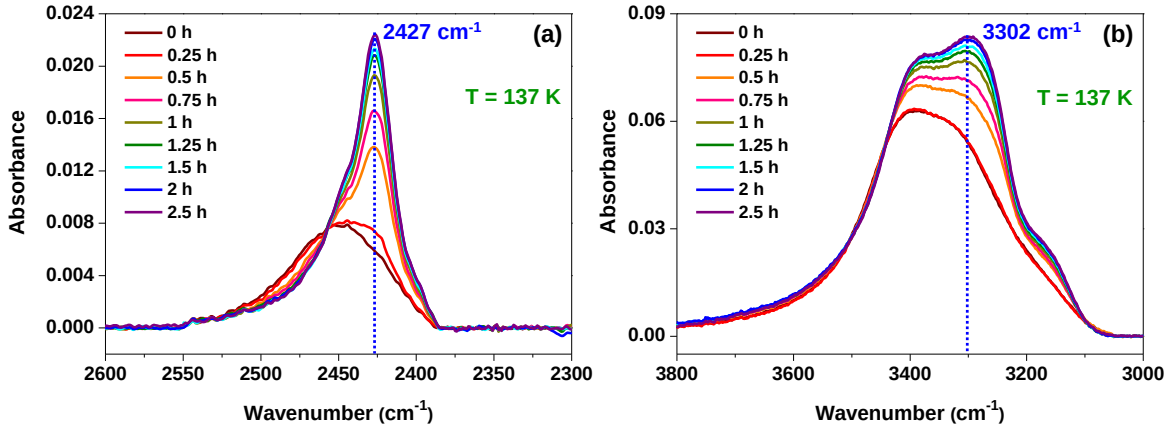

Figure S15. Time-dependent RAIR spectra of 300 MLs of formaldehyde:HDO (5% D_2O in H_2O) at 137 K in the (a) decoupled O-D stretching region, and (b) O-H stretching region.

Table S1: The parameters for crystallization of ice I_h during the dissociation of formaldehyde hydrate at different temperatures.

	Temperature (K)	*n*	Rate constant; *k* (s^{-1})
O-H stretching	130	1.65	3.07×10^{-5}
	132	1.60	3.47×10^{-5}
	135	1.59	1.52×10^{-4}
	137	1.39	3.58×10^{-4}
O-D stretching	130	1.64	3.38×10^{-5}
	132	1.52	3.94×10^{-5}
	135	1.50	1.65×10^{-4}
	137	1.34	4.01×10^{-4}