Supporting information for:

Freezing and Melting of Salt Hydrates Next to Solid Surfaces Probed by Infrared-Visible Sum Frequency Generation Spectroscopy

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Cleaning Procedure

The sapphire prisms were sonicated for 1 hr in acetone, methanol, and deionized water. This was followed by sonication for 30 min in 10–15 mM HNO_3 and then rinsing thoroughly with deionized water. This cleaning method has been used to remove surface organic residues in previous studies and has been shown to give consistent results.[S1–S4] The stainless steel components of the sample cell were also cleaned by the same method. The sapphire prisms and the water cell were blow-dried using dry nitrogen gas followed by heating in an oven at 120 $°C$.

Experimental Chamber and Cell for Cooling and Heating

Water condensation is a major issue when cooling the SFG sample cell below 0^oC, and thus, we designed a sample cell with a vacuum chamber as shown in Figure S1. The inside chamber containing the water was sealed to prevent any loss of water due to the vacuum. The temperature stage was purchased from Instec Inc. and modified in-house to hold the sapphire

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prisms. A steel dome was designed with CaF_2 window to introduce the visible and IR beams and SiO_2 window to collect the output SFG beam. The sample cell was designed with the flexibility to change the orientation of the windows to maintain the normal incidence of the input and output beams. A vacuum pressure of 8 torr was used to prevent water condensation and to maintain temperature uniformity inside the sample chamber.
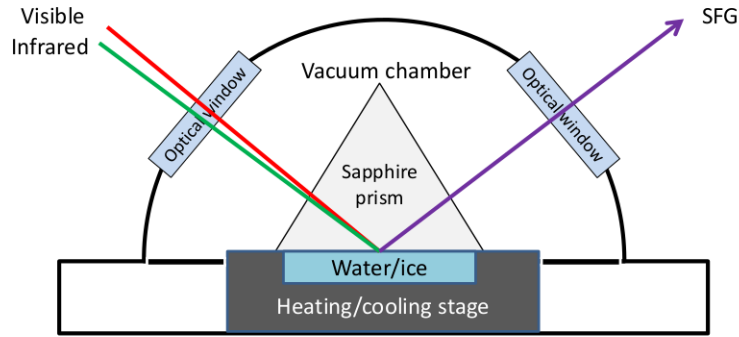

Figure S1: Diagram of the temperature stage and the sample geometry for SFG measurements.The water is sealed from one side by a sapphire prism while the other side is in contact with a heating or cooling stage purchased from Instec Inc. The top part of the temperature cell was machined to hold CaF_2 and SiO_2 optical windows for the input and the output of the laser beams. The cell was held under vacuum to prevent water condensation on the sapphire prisms and to maintain the temperature uniformity.

SFG System

The SFG experiments were conducted using a picosecond Spectra Physics laser system with tunable IR beam − 2000–3800 cm^{-1}, 1 ps pulse width, 1 kHz repetition rate and a diameter of 100–200 μm and a visible beam of 800 nm in wavelength, with a 1 ps pulse width, 1 kHz repetition rate, and a diameter of 1 mm. These two beams were overlapped

spatially and temporally on the sample. SFG signal is significantly enhanced when the IR overlaps with the resonant frequencies of the molecule being studied. A motorized, computer-controlled delay stage was used to ensure that the temporal delay was maintained while scanning IR frequencies from 2700 to 3800 cm^{-1}. The experiments were performed using sapphire prisms in total internal reflection geometry. This geometry provides an additional enhancement in the SFG signal if the incident beams are close to the critical angle.[S5] A model to calculate the SSP intensity as a function of incident angles in an internal reflection geometry has been provided in previous publication.[S6] A photomultiplier tube connected to a 0.5 m spectrometer in length was used to collect the SFG signals. All water spectra were collected at an IR incidence of 16° with respect to the face of the sapphire prism (60° angle prism). The incident angle of the visible laser beam was ∼1.5° lower than the incident angles for the tunable IR laser. The polarization combinations reported in this work are SSP (s-polarized SFG output, s-polarized visible input and p-polarized IR input) and PPP (p-polarized SFG output, p-polarized visible input and p-polarized IR input). The SSP and PPP polarizations provide complementary information and could be useful in interpreting the orientation of molecules. We have used a Lorentzian fitting function to fit our data (Equation 1).[S1] The fitting model assumes that the local field factors are not affected by the dispersion of refractive index over the scan region from 2800-3800 cm^{-1}. This effect needs to be calculated for accurate interpretation of the fit parameters obtained from this analysis.

$$I_{SFG} \propto |\chi_{NR} + \sum \frac{A_q}{\omega_{IR} - \omega_q - i\Gamma_q}|^2, \tag{1}$$

In equation 1, χ_{NR} describes the non-resonant contribution. A_q, Γ_q, and ω_q are the amplitude, damping constant, phase, and angular frequency of the qth vibrational resonance, respectively. Figures S2 and S3 shows the results of the fits and the fitting parameters obtained from the fits are provided in Tables S1 and S2.
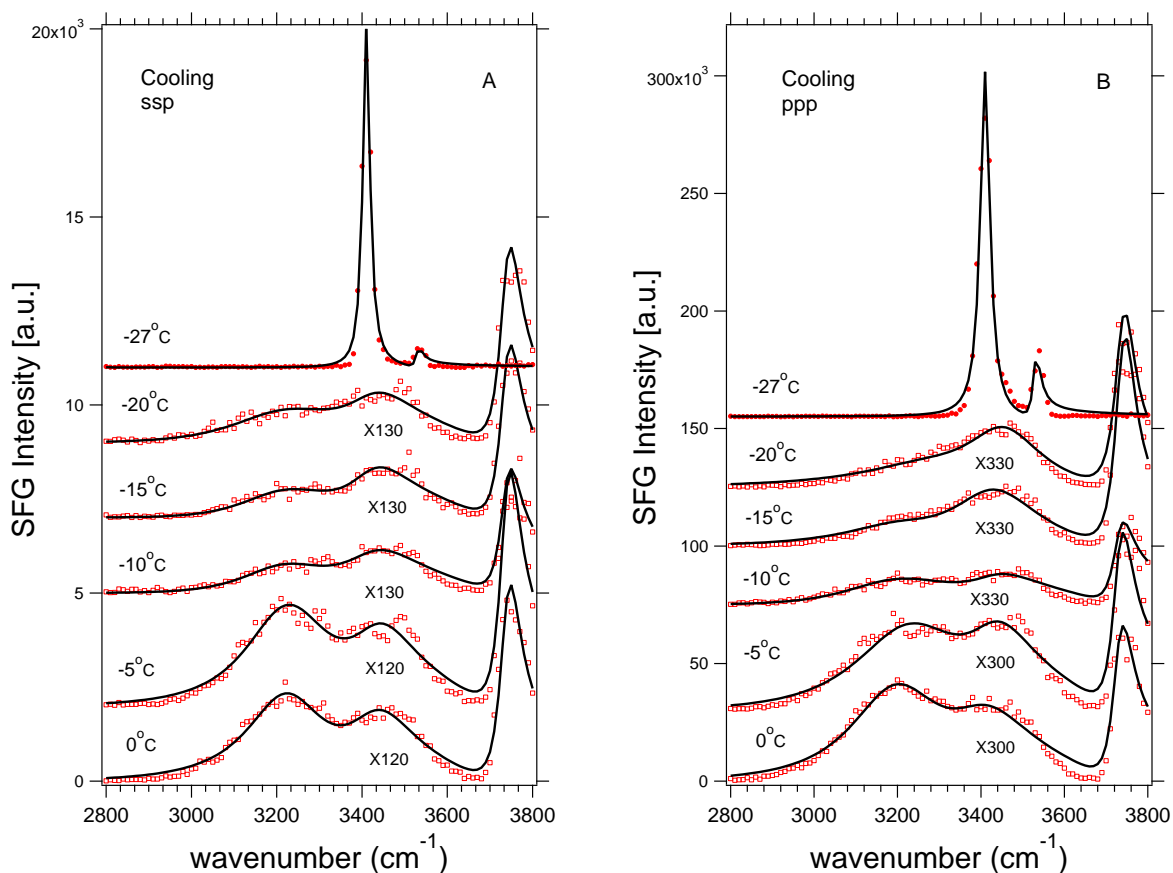
Figure S2: SFG spectra collected in SSP (A) and PPP (B) polarizations during the cooling cycle. The empty squares and filled circles correspond to temperatures where salt solution or NaCl hydrate are in contact with the sapphire substrate, respectively. The solid lines are the fits using the Lorentzian equation and the fitting results are summarized in the supporting information (Tables S1 and S2).The freezing transition temperatures for the hydrate formation are between -25°C and -30°C.

Figure S3: SFG spectra collected in SSP (A) and PPP (B) polarizations during the heating cycle. The empty squares and filled circles correspond to temperature where salt solution or NaCl hydrate are in contact with the sapphire substrate, respectively. The solid lines are the fits using the Lorentzian equation and the fitting results are summarized in the supporting information (Tables S3 and S4). The melting transition temperatures for the hydrate formation is -22°C.

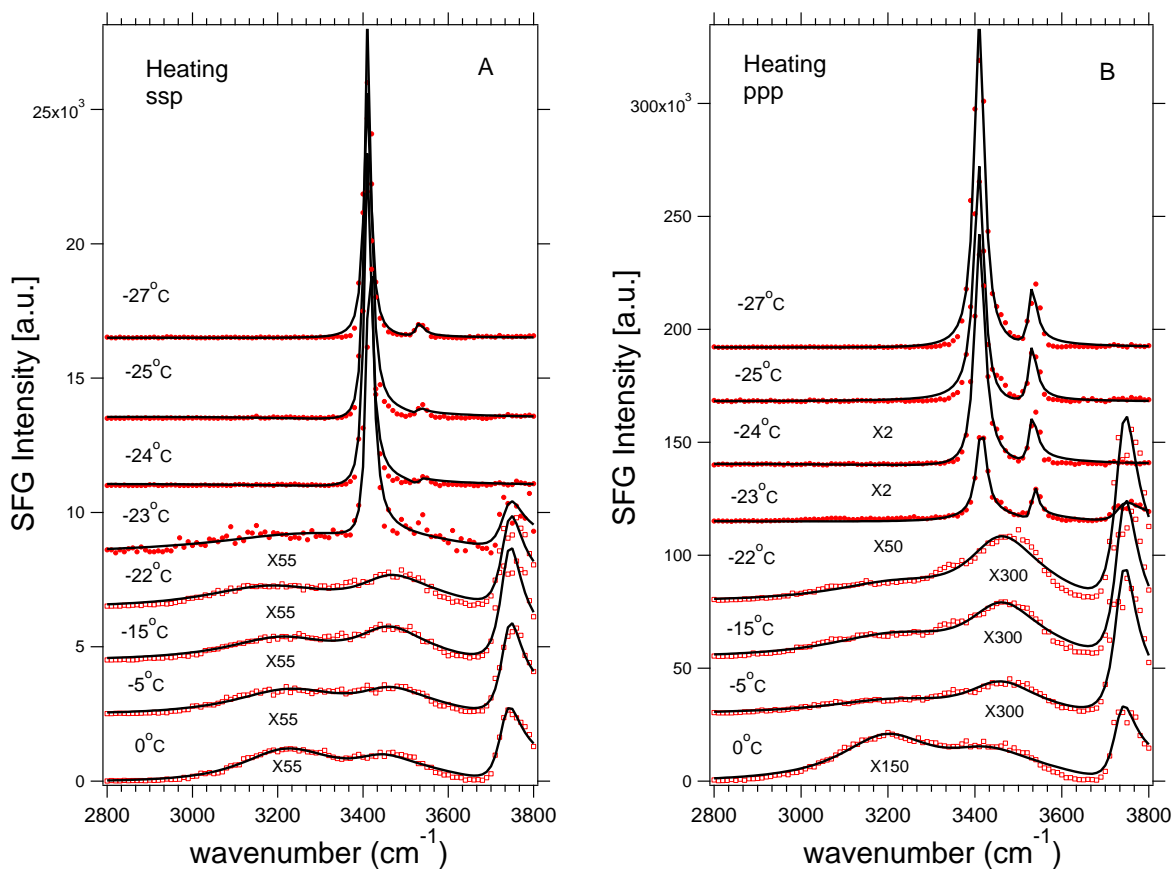Table S1: SFG spectral fitting parameters for NaCl solution and hydrate next to sapphire surface in OH region for SSP polarization in the cooling cycle

Temperature (^oC)	Peak Position (cm^{-1})	Width (cm^{-1})	Amplitude
0	3222	116	495
	3427	100	267
	3738	30	178
-5	3222	127	597
	3430	96	242
	3738	30	192
-10	3235	135	232
	3434	125	272
	3738	30	124
-15	3212	121	230
	3433	112	270
	3738	30	164
-20	3212	140	274
	3433	140	305
	3738	30	175
-27	3410	10	963
	3530	11	167

Table S2: SFG spectral fitting parameters for NaCl solution and hydrate next to sapphire surface in OH region for PPP polarization in the cooling cycle

Temperature (^oC)	Peak Position (cm^{-1})	Width (cm^{-1})	Amplitude
0	3193	140	1447
	3400	120	617
	3730	30	335
-5	3222	170	1704
	3429	100	521
	3730	30	350
-10	3212	182	581
	3440	100	679
	3730	30	262
-15	3196	160	654
	3420	130	800
	3738	30	388
-20	3278	200	644
	3450	110	749
	3738	30	380
-27	3410	14	5390
	3530	11	1369

Table S3: SFG spectral fitting parameters for NaCl solution and hydrate next to sapphire surface in OH region for SSP polarization in the heating cycle

Temperature (^oC)	Peak Position (cm^{-1})	Width (cm^{-1})	Amplitude
-27	3410	10	963
	3530	11	167
-25	3410	10	1218
	3530	11	91
-24	3410	10	1128
	3530	11	89
-23	3415	10	115
	3738	30	114
-22	3217	200	776
	3455	100	792
	3738	30	405
-15	3177	160	652
	3450	100	942
	3738	30	456
-5	3217	169	606
	3450	100	655
	3738	30	373
0	3209	143	624
	3428	90	164
	3732	31	171

Table S4: SFG spectral fitting parameters for NaCl solution and hydrate next to sapphire surface in OH region for PPP polarization in the heating cycle

Temperature (^oC)	Peak Position (cm^{-1})	Width (cm^{-1})	Amplitude
-27	3410	14	5390
	3530	11	1369
-25	3410	14	3097
	3530	11	1041
-24	3410	10	3179
	3530	11	833
-23	3415	14	324
	3534	8	97
	3738	30	295
-22	3217	200	776
	3455	100	797
	3738	30	405
-15	3217	160	652
	3450	100	942
	3738	30	456
-5	3217	200	606
	3450	100	655
	3738	30	373
0	3196	135	1391
	3410	130	700
	3732	30	337

References

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