

Supporting Information

**Probing the Mineral–Water Interface with Nonlinear
Optical Spectroscopy**

Ellen H. G. Backus^{+,} Jan Schaefer^{+,} and Mischa Bonn^{*}*

anie_202003085_sm_miscellaneous_information.pdf

Overview table

Material	Surface type	Chemical environment	Ref.	Method	Geometry	Result	
Silica	Fused	Ion-dependence	@pH 5.8 @pH 10 0.01-0.1 M NaCl, LiCl	Eisenthal, 1992, ^[1]	SHG (@300 nm)	EW	<ul style="list-style-type: none"> Signal decreases with increasing salt concentration Independent of cation identity
			@pH 5.7 0-0.1 M NaCl, KCl, LiCl	Chou, 2009, ^[2]	SFG (OH stretch), ssp	SA (window Backside)	<ul style="list-style-type: none"> Concentration sensitivity of the signal on the order $K^+ > Li^+ > Na^+$ Double band feature (3200 cm^{-1} and 3400 cm^{-1}) 3200 cm^{-1} band is more concentration sensitive
			@pH 6.5 0-0.12 M NaCl	Hore, 2009, ^[3]	SFG (OH stretch) ssp, sps	EW	<ul style="list-style-type: none"> 2-3 features in the band Spectral weight on the low-frequency side for ssp, on the high-frequency side for sps With increasing concentration, the overall signal, the ratio between low- and high-frequency band and the sps/ssp ratio decrease
			@pH 6 $4.8 \cdot 10^{-5}$ -4.1 M NaCl	Hore, 2011, ^[4]	SFG (OH stretch) ssp	EW	<ul style="list-style-type: none"> 4 distinct regimes of monotonically decreasing signal with increasing ion concentration: <ul style="list-style-type: none"> A: $c < 0.5\text{ mM}$: Plateau B: $0.5\text{ mM} < c < 100\text{ mM}$: Decrease C: $0.1\text{ M} < c < 1\text{ M}$: Plateau D: $c > 1\text{ M}$: Decrease

			@pH 6 10 ⁻⁴ – 0.5 M NaCl	Borguet, 2011, ^[5]	SFG (OH stretch) ssp t-resolved	EW	<ul style="list-style-type: none"> Vibrational lifetime increases with increasing ion concentration from ~200 fs at low to ~700 fs at high concentration
			@pH 10 and 6.5 0.1 mM: CsCl, RbCl, LiCl, NH ₄ Cl, KCl, NaCl 0.033 M: CaCl ₂ , MgCl ₂ , ZnCl ₂	Cremer, 2012, ^[6]	SFG (OH stretch)	SA	<ul style="list-style-type: none"> Signal intensity shows a direct Hofmeister trend from ZnCl₂ giving the weakest response to LiCl with the largest signal
			@pH 6 10 ⁻⁷ – 4 M NaCl LiCl	Backus 2017, ^[7]	SFG (OH stretch) ssp	SA	<ul style="list-style-type: none"> Under SA geometry, the signal decreases with decreasing concentration within regime A of the Hore work This results in a maximum signal around mM concentration The maximum position seems to be dependent on the cation size
			@pH 7 10 ⁻⁵ – 0.5 M NaCl (CsCl, RbCl KCl, NaBr, NaI)	Eisenthal 2018, ^[8]	SHG (@400 nm) p-in + all-out, s-in + all-out	EW	<ul style="list-style-type: none"> Qualitatively the same curve shape Shape independent of polarization combination and salt species Curve maximum varies by 20% depending on the scanning direction (low-to-high vs. high-to-low conc.)

			@pH 12 1.1 -5 M NaCl Isotopic dilution	Tahara 2018, ^[9]	SFG (OH stretch) ssp phase-resolved	SA	<ul style="list-style-type: none"> • Signal decrease with increasing ion concentration (up to 1 M), until it saturates • 2 broad main features • At low ion concentration, the 3200 cm⁻¹ feature vanishes upon isotopic dilution
			@ pH 7, pH 5.8 10 ⁻⁵ – 1 M (NaCl, NaBr, NaI and NaCl, KCl, RbCl, CsCl)	Geiger, 2019, ^[10]	SHG (@400 nm) s-in + all-out + phase resolved	EW	<ul style="list-style-type: none"> • Both, cation and anion size does not affect the curve shape and maximum position except for the plateau at high concentration which increases with decreasing ion size
			@pH 6 10 ⁻⁷ – 5*10 ⁻² M NaCl Angular dependence (40.4°-74°)	Hore and Tyrode 2019, ^[11]	SFG (OH stretch) ssp	SA, EW	<ul style="list-style-type: none"> • Well below the critical angle, the SFG signal drops below 0,1 mM salt concentration • Close to the critical angle, a plateau is observed at this regime • Results are rationalized with a model that considers 2nd and 3rd order contributions to the SFG response and an electrostatic potential beyond Debye Hückel approximation • Proposed model yields a global fit for angular dependence of the SFG signal as a function of ion concentration

			T-dependence (10°C – 75°C)	Hore 2020, ^[12]	SFG (OH stretch) ssp	EW	<ul style="list-style-type: none"> The intensity of the OH stretch band increases with increasing temperature from 10°C to 64°C and decreases from 64°C to 75°C This observation is rationalized as a convolution between increasing surface charge and decreasing contribution of aligned water molecules to the overall response
	pH-dependence	@0.5 M (NaCl) pH 2 - 14	Eisenthal 1992, ^[1]	SHG (@300 nm)	EW	<ul style="list-style-type: none"> Monotonic signal increase with increasing pH 2 turning points at pH 4.5 and pH 8.5 	
		No salt added pH 1.5 - 11	Shen 2004, ^[13]	SFG (OH stretch) ssp	SA	<ul style="list-style-type: none"> Low-frequency feature varies with pH similar to the SHG results, high-frequency feature almost insensitive to pH variation 	
		No salt added @pH 5.7	Shen 2006, ^[14]	SFG (OH stretch) ssp t-resolved	EW	<ul style="list-style-type: none"> Vibrational lifetime of OH stretch is ~300 fs (similar to bulk water) 	
		pH 2, pH 12	Borguet 2009, ^[15]	SFG (OH stretch) ssp t-resolved	EW	<ul style="list-style-type: none"> Vibrational lifetime slow at pH 2 (~570 fs) and bulk-like at pH 12 (~255 fs) 	
							<ul style="list-style-type: none">

			pH 2, pH 12 Isotopic dilution	Borguet 2010, ^[16]	SFG (OH stretch) ssp t-resolved	EW	<ul style="list-style-type: none"> • The vibrational lifetime is longer at the high-frequency feature of the band at both pH conditions • From neutral conditions towards both pH directions, the spectral weight shifts red
			@0.5 M Alkali Chlorides pH 2 - 12	Gibbs 2012, ^[17]	SHG (@275 nm) s-in+ all-out	EW	<ul style="list-style-type: none"> • Bimodal titration curve • The high pH inflection point shifts due to the presence of different salts: pH 8.3 (NaCl) to pH 10.8 (LiCl)
			@0.1 M NaCl pH 2 - 12	Borguet 2013, ^[18]	SFG (OH stretch) ssp	EW	<ul style="list-style-type: none"> • The SFG response is most sensitive to addition of 0.1 M NaCl around neutral pH and least sensitive at low and high pH

			@0.5 M Na ⁺ , K ⁺ halides pH 2 – 12	Gibbs 2013, [19]	SHG (@275 nm) s-in+ all-out	EW	<ul style="list-style-type: none"> • With increasing halide size, the titration curve gets sharper
			@0.5 M NaI pH 2 – 12		SFG (OH stretch) ppp	EW	<ul style="list-style-type: none"> • In contrast to SHG results, the SFG signal increases towards acidic and alkaline pH • At neutral pH, the Signal decrease by a factor of 30-40 when adding 0.5 M salt to pure water • This is much higher than reported by the Hore group for the ssp response and opposite to the SHG results which show a 2.5 fold increase upon adding 0.5 M salt
			@0.1 vs 0.5 M Alkali chlorides and iodides pH 2 - 12	Gibbs 2014, [20]	SHG (@275 nm) s-in+ all-out	EW	<ul style="list-style-type: none"> • Titration curve gets more similar when the concentration is reduced to 0.1 M • Curve shifts induced by different halide species are merely affected by concentration effects
			@10 mM NaCl pH 2-12	Gibbs 2015, [21]	SHG (@275 nm) p-in+ all-out	EW	<ul style="list-style-type: none"> • Titration curve shifts and shows 2 or 3 steps depending on the starting pH: From pH 2 or 7 → 2 steps From pH 12 → 3 steps
			@10 mM NaCl pH 3, 6, 10 Surface treatment: Plasma vs heat	Tyrode 2017, [22]	SFG (OH stretch) ssp, ppp, sps	EW	<ul style="list-style-type: none"> • Presence of a third (high-frequency feature) at ~ 3650 cm⁻¹, which indicates a weakly interacting OH group • This feature is enhanced for heat-treated silica

			@10 mM NaCl pH 6 Non-heated vs heated surface	Backus 2019, [23]	SFG (OH stretch) ssp, ppp static spectra vs. phase-resolved t-resolved	SA SA EW	<ul style="list-style-type: none"> The weakly interacting OH groups are oriented towards the silica surface
			@2, 4, 6, 12 M of chlorides of Na ⁺ , Li ⁺ and Mg ²⁺ , Ca ²⁺ ~neutral pH	Chou 2016, [24]	SFG (OH stretch) ssp	EW	<ul style="list-style-type: none"> At high concentration, the double band feature breaks into one low intensity, high-frequency band around 3500 cm⁻¹
			@10mM phosphate buffer pH 2.1, 5.6, 7.2 and 12.1 isotopic dilution	Tahara 2016, [25]	SFG (OH stretch) ssp phase-resolved	SA	<ul style="list-style-type: none"> At neutral pH, 3200 cm⁻¹ feature disappears indicating vibrational coupling Uncoupled spectrum still varies in shape and intensity with pH, owing to positive and negative contributions at high and low frequency, respectively The red part is negative at low pH and flips towards high pH
			@0.01, 0.05 and 0.1 M NaCl pH 2 - 12	Gibbs 2017, [26]	SFG (OH stretch) ssp vs pss	EW	<ul style="list-style-type: none"> Titration curve under pss is similar to what is known for SHG For ssp, the titration curve is non-monotonic with a minimum around neutral pH and increase towards low and high pH This trend is more pronounced at higher NaCl concentration (0.1 M)
			@0.5 M alkali chlorides pH 2 - 12	Gibbs 2017, [27]	SFG (OH stretch) ssp	EW	<ul style="list-style-type: none"> Signal intensity at neutral pH increases in the series: Cs⁺ < K⁺ < Na⁺ < Li⁺ This trend is reversed at low/high pH

			@0.5 M NaCl	Hore and Gibbs 2019, [28]	SFG (OH stretch) ssp, ppp, pss SHG (@400 nm)	EW	<ul style="list-style-type: none"> • SHG increases monotonically with increasing pH while SFG shows a minimum at around neutral pH • Conclusion: SHG is dominated by the surface potential and SFG is more sensitive to the SFG activity of sub-ensembles of differently oriented water species
			@0, 0.1, 0.5 M NaCl pH 2, 6, 12	Borguet 2020, [29]	SFG (OH stretch) ppp t-resolved	EW	<ul style="list-style-type: none"> • Acceleration of interfacial vibrational energy relaxation due to kosmotropic effect of ions driving the in-plane ordering of water at the topmost interfacial layer • Formation of local hydrophobic areas on the silica interface

		Chemistry	@0.01 – 0.5 M alkali halides pH titration	Geiger 2008, [30]	SHG (@300 nm) p-in + all-out	EW	<ul style="list-style-type: none"> • SHG response (as reporter of the surface conditions) lags bulk pH changes both, spatially and temporally • Delay time increases with ion concentration (up to ~4.5 h) and with polarizability of the halide
	@0.01 M NaCl Effect of flow		Bonn 2014, [31]	SFG (OH stretch) ssp	EW	<ul style="list-style-type: none"> • At neutral pH, flow drops the SFG signal • Recovery time with flow-off about 0.5 h • At low and high pH, flow does not have an effect on the SFG response 	
	@10 ⁻⁷ to 3 M NaCl, pH~6.5 Equilibration		Bonn 2018, [32]	SFG (OH stretch) ssp	SA	<ul style="list-style-type: none"> • Within roughly a day, the SFG response of pure water rises to an equilibrated level • This level corresponds to addition of 5*10⁻⁴ – 10⁻² M of salt (NaCl) • Upon flow, the signal drops again 	

	α-Quartz	pH-dependence	pH 1.5 – 12.3 0.1, 0.5 M NaCl	Shen 1994, [33]	SFG (OH stretch) ssp, ppp, pss, sps	SA	<ul style="list-style-type: none"> • Double feature (3200, 3450 cm⁻¹) with different relative and absolute intensity depending on pH, ion concentration and polarization combination • From low to high pH (without salt), the absolute intensity decreases first and increases when passing pH 5.6
			No salt added pH 1.5 - 11	Shen 2004, [13]	SFG (OH stretch) ssp	SA	<ul style="list-style-type: none"> • With increasing pH, the signal increases monotonically • Compared to fused silica, the high-frequency band is more pronounced
			No salt added pH 1.5 - 11	Shen 2005, [34]	SFG (OH stretch) ssp phase-resolved	SA	<ul style="list-style-type: none"> • The absolute spectrum is composed of two positive high frequency and one negative low-frequency feature • The negative feature decreases with increasing pH • The positive features increase with increasing pH

Alumina	Sapphire		No salt added pH 3 – 12 dehydrated vs. hydrated surface	Pink 1999, ^[35]	SFG (OH stretch) ppp	EW	<ul style="list-style-type: none"> • 3 featured OH stretch band • Overall response enhanced by a factor of ~6 if the surface is hydrated • At the isoelectric point (pH 8) the signal is lowest and increases towards lower and higher pH with changing relative sign
			T-dependent	Leisner 2015, ^[36]	SHG (@400 nm)	EW	<ul style="list-style-type: none"> • Small decrease in SHG signal upon cooling down till the phase transition • At phase transition stepwise large decrease in SHG intensity upon freezing
	Corundum		@ 1-100 mM of NaCl, NaNO ₃ , NaClO ₄ pH 2 - 12	Eggelston 2001, ^[37]	SHG (@520 nm)	EW	<ul style="list-style-type: none"> • Point of zero charge is between pH 5 and 6
	Corundum (0001) vs. (1102)		@ 1, 10 and 100 mM of NaNO ₃ pH 4 – 7.5 @pH 6.7, 4 1 – 100 mM	Eisenthal 2005, ^[38]	SHG (@400 nm) p-in + p-out	SA	<ul style="list-style-type: none"> • Titration curves indicate pzc at pH 4.1 ± 0.4 for (0001) and pH 5.2 ± 0.4 for (1102) • With increasing ion concentration, the signal decreases above the pzc and increases below the pzc
	Corundum (001)		pH 2.7 – 12	Fanghänel 2008, ^[39]	SFG (OH stretch) ssp, ppp	EW	<ul style="list-style-type: none"> • Above 3400 cm⁻¹ 4 doubly coordinated (Al₂OH) surface OH species • Below 3400 cm⁻¹ at pH 12 two broad resonances due to water molecules oriented with the H to the surface

	Corundum (1 $\bar{1}$ 02)	pH 2.7 – 10.5	Waychunas 2011, ^[40]	SFG (OH stretch) ssp, sps + phase resolved	SA	<ul style="list-style-type: none"> • Point of zero charge at pH ~ 6.7 • Bands at ~3230 and ~3490 cm⁻¹ associated with interfacial water molecules and H-bonded hydroxyls associated with AlOH₂ groups • pK values of 4.9 and 9.2 for protonation/deprotonation of Al₃OH and AlOH₂ groups
	Amorphous and (0001)	pH 3.5 -10.1 no salt vs 50 mM NaCl	Shen 2008, ^[41]	SFG (OH stretch) ssp, ppp, sps + phase resolved	SA	<ul style="list-style-type: none"> • Spectrum shows typical double feature plus a predominant band in the “free-OH” region • From polarization combination, average tilt angle of ~26° are deduced for the free-OH • pzc is found around pH 6.3 which is lower than for amorphous alumina or powder • Addition of salt reduces H-bonded signal significantly, if pH far away from the pzc
	(0001)	Surface roughness pH 0.8 – 14	Daum 2008, ^[42]	SFG (OH stretch) ssp	SA	<ul style="list-style-type: none"> • Surface disorder affects molecular structure • On a nanorough surface presence of uncoupled hydroxyls groups, presumably in hydrophobic nanopores • Different pK value for deprotonation of surface hydroxyl groups at smooth and rough surface

		Surface preparation Water vapor	Campan 2015, ^[43]	SFG (OH and Al-O stretch) ssp		<ul style="list-style-type: none"> Hydroxylated surface in ambient air shows a 3700 cm⁻¹ band, while this band is absent for the 1-Al terminated surface prepared in UHV
(11 $\bar{2}$ 0)		pH 2.5 – 11 no salt vs 50 mM	Waychunas, 2012 ^[44]	SFG (OH stretch) phase-resolved	SA	<ul style="list-style-type: none"> Sign change of Im$\chi^{(2)}$ spectrum indicates pzc for pH ~ 6.7 Upon adding salt signal decrease at low and high pH Spectral changes due to protonation and deprotonation
		pH 2 – 12 no salt vs 0.1 and 0.5 M NaCl	Borguet 2016, ^[45]	SFG (OH stretch) ssp and ppp static spectra t-resolved	EW	<ul style="list-style-type: none"> ~3200 and ~3400 cm⁻¹ attenuated by the addition of salt Largely salt concentration-independent feature at 3000 cm⁻¹ assigned to surface aluminol groups and/or interfacial water molecules strongly H-bond to alumina Fast (bulk waterlike) vibrational relaxation dynamics, insensitive to changes in surface charge and ionic strength
(1120)		pH 13, KOH	Borguet 2014, ^[46]	SFG (OH stretch) Free Induction Decay	EW	<ul style="list-style-type: none"> OH oscillators from interfacial water, centered at 3679 cm⁻¹, dephase on a ~90 fs timescale Dephasing of interfacial alumina hydroxyls with a resonance at 3644 cm⁻¹, is an order of magnitude slower

	0001 vs. (11 $\bar{2}$ 0)	pH 2 – 12 no salt vs 0.1 M NaCl	Borguet 2017, ^[47]	SFG (OH stretch) ppp static spectra t-resolved	EW	<ul style="list-style-type: none"> • H-bonded OH stretch is blue-shifted for 0001 compared to (11$\bar{2}$0) • For neutral alumina, the dynamics are slower by a factor of 2 for 0001 compared to (11$\bar{2}$0) • For charged 0001, the dynamics are faster than in bulk or at charged silica • The addition of salt has little to no effect on the dynamics
	Sapphire (0001)	pH 3 – 9 T-dependent	Bonn 2017, ^[48]	SFG (OH stretch) ssp	EW	<ul style="list-style-type: none"> • Upon freezing, the 3200 cm⁻¹ band increases and the 3400 cm⁻¹ band decreases • At neutral surface (~pH 7) ice nucleation is most efficient
		pH 4, 10 halide ions	Borguet 2018, ^[49]	SFG (OH stretch) ppp static spectra t-resolved	EW	<ul style="list-style-type: none"> • Attenuation of SFG signal at positively charged surface followed the sequence F⁻>>Br⁻>Cl⁻>I⁻ • At negative surface attenuation follows Br⁻>I⁻≈Cl⁻>F⁻ • Only F⁻ perturbs the vibrational lifetime of water next to positively charged surface
		Monovalent vs divalent cations pH 4, 6, 10	Borguet 2019, ^[50]	SFG (OH stretch) ppp static spectra t-resolved	EW	<ul style="list-style-type: none"> • Lower binding affinity at the interface for monovalent compared to divalent cations • At pH 10, negatively charged surface, addition of divalent cations increases spectral intensity at 3400 cm⁻¹; monovalent cations only attenuated SFG intensity

						<ul style="list-style-type: none"> • Presence of NaCl and BaCl₂ does not change the vibrational lifetime
Calcium Fluoride		pH dependent, with addition of NaF	Richmond 2001, ^[51]	SFG (OH stretch) ssp	EW	<ul style="list-style-type: none"> • The signal is largest under acidic conditions and vanishes around neutral pH • At basic pH the signal increases again and an additional free-OH feature appears • Upon addition of NaF, this free-OH band decreases
		@pH 5.8 10 ⁻⁵ – 1 M of Na ⁺ and Ca ²⁺ salts	Richmond 2010, ^[52]	SFG (OH stretch)	EW	<ul style="list-style-type: none"> • Signal is more sensitive to the presence of NaF and Na₂SO₄ than to that of NaCl and NaBr
		@pD 3.7	Benderskii 2005, ^[53]	SFG (OD stretch) ssp Free Induction Decay	SA	<ul style="list-style-type: none"> • Exciting the weaker hydrogen bond ensemble shows monotonic decay and shift to lower frequency on a 100 fs time scale • Exciting stronger hydrogen bond ensemble results in shift to higher frequency and time scale of 125 fs • Dynamical heterogeneity of water hydrogen bonding network
		no salt added @pH 3, 9.5, 12 Water flow vs resting	Bonn 2014, ^[31]	SFG (OH stretch) ssp	EW	<ul style="list-style-type: none"> • signal is large under acidic conditions, minimum around neutral pH and increases again towards alkaline conditions • Upon flow, signal increases at low pH, decreases at high pH and is only affect in spectral shape around neutral pH

			no salt added pH 2, 7, 13	Sulpizi 2016, [54]	SFG (OH stretch) phase-resolved	SA	<ul style="list-style-type: none"> • Large signal at pH 2 • Lower signal at higher pH values • pH 13: A “free OH” band is present
			No salt added	Borguet 2016, [55]	SFG (OH stretch) ppp Free Induction Decay	EW	<ul style="list-style-type: none"> • two featured bands at 3140 cm⁻¹ and 3410 cm⁻¹ show a 70 fs and 50 fs dephasing time, respectively
			Flow perturbed @different flow rates (with varying pH and salt concentration	Abdelmonem, 2018 [56]	SHG (@400 nm) ssp, ppp	EW	<ul style="list-style-type: none"> • The SHG response for the flow perturbed steady-state increases with increasing flow rate
			pD/pH 2	Sulpizi and Backus 2019, ([57])	Time-dependent 2D-SFG (OD/OH stretch) ssp	EW	<ul style="list-style-type: none"> • Fast vibrational relaxation and spectral diffusion for strongly hydrogen-bonded OD groups
Titanium Dioxide	Thin film on fused silica: 0.9 – 3.9 nm		@30mM salt (NaCl vs. PBS) pH 2 - 12	Cremer 2004, [58]	SFG (OH stretch) ssp	SA	<ul style="list-style-type: none"> • Typical double featured band • With NaCl: SFG minimum at pH 4-6 (known as the isoelectric point of TiO₂) • Towards lower/higher pH, the 3200 cm⁻¹ band increases relative to the 3400 cm⁻¹ band • PBS buffer shift the minimum to pH 2, similar to titration curve for silica

	Thin film on fused silica		Water vapor on UV-irradiated surface	Nihonyanagi 2004, ^[59]	SFG (OH stretch) ppp	EW	<ul style="list-style-type: none"> UV-irradiation increases the H-bonded OH-stretch signal substantially as well as a third “free-OH” feature
	Thin film on quartz: 1 nm		@ pH 10, With 0.33 and 0.033 mM of: CsCl, RbCl, LiCl, NH ₄ Cl, KCl, NaCl CaCl ₂ , MgCl ₂ , ZnCl ₂	Cremer 2012, ^[6]	SFG (OH stretch)	SA	<ul style="list-style-type: none"> Signal intensity is in direct relation to the Hofmeister trend from ZnCl₂ giving the weakest response to CsCl with the largest signal
	Thin film on CaF ₂ : 50 – 200 nm		Isotopic dilution	Backus 2017, ^[60]	SFG (OH stretch) ssp static spectra phase-resolved	SA	<ul style="list-style-type: none"> Double feature: 2 bands of opposite sign Negative high-frequency feature and positive low-frequency feature Shape changes upon isotopic dilution
	Thin-film on CaF ₂ : 85, 150 nm		@0, 10, 100 mM of NaCl pD 3 - 11	Backus 2019, ^[61]	SFG (OD stretch) Static spectra Phase-resolved	SA (Two VIS angles)	<ul style="list-style-type: none"> Intensity minimum at pD 5 Spectral differences from sample to sample High-frequency part of the double band flips sign when pD crosses pzc, low-frequency part keeps sign across full pD range

Mica	Cleaved		Water vapor on the surface	Salmeron 1998, ^[62]	SFG (OD stretch) ssp	SA	<ul style="list-style-type: none"> • With increasing humidity, the typical double feature arises with the low-frequency band being predominant • Also, a “free OD” is present
	Cleaved		pH-dependence using D ₂ SO ₄	Chou 2011, ^[63]	SFG (OD stretch) ssp	SA	<ul style="list-style-type: none"> • SFG signal decreasing with the addition of D₂SO₄ and is drastically diminished from c > 0.5 M
	Muscovite (001) With IMG fixed on sapphire		T-dependent	Leisner 2015, ^[36]	SHG (@400 nm)	EW	<ul style="list-style-type: none"> • The non-linear properties change way before freezing point
	Adhered onto a sapphire prism		T-dependent and ice formation	Dhinojwala, 2016 ^[64]	SFG (OH stretch) ssp, ppp	EW	<ul style="list-style-type: none"> • Upon freezing, the water signal in front of a mica surface drops • The hysteresis of this drop is about 10°C between cooling and heating the cycles
	Cleaved (001)		T-dependent and ice formation	Abdelmonem, 2017 ^[65]	SHG (@400 nm) SM polarization	EW	<ul style="list-style-type: none"> • The SHG signal drops upon formation of a thin film of water on the mica surface, regardless of the formed phase and freezing path
	Muscovite (001)		Azimuthal angle dependence	Wang 2019, ^[66]	SFG (OH stretch)	SA: multiple layer reflections	<ul style="list-style-type: none"> • Signal highly anisotropic • SFG can be used to discriminate bottom from top mica face
	Muscovite (001)		Cationic termination: Cleaved, H ⁺ , Na ⁺ , K ⁺ , Cs ⁺	Zeng, Bonn and Wang, ^[67]	SFG (OH stretch)	SA	<ul style="list-style-type: none"> • H-mica induces less orientational order on interfacial water than Na- and K-mica as indicated by a lower SFG response in the OH stretching band

References

- [1] S. Ong, X. Zhao, K. B. Eisenthal, *Chem. Phys. Lett.* **1992**, *191*, 327-335.
- [2] Z. Yang, Q. Li, K. C. Chou, *The Journal of Physical Chemistry C* **2009**, *113*, 8201-8205.
- [3] K. C. Jena, D. K. Hore, *J. Phys. Chem. C* **2009**, *113*, 15364-15372.
- [4] K. C. Jena, P. A. Covert, D. K. Hore, *J. Phys. Chem. Lett.* **2011**, *2*, 1056-1061.
- [5] A. Eftekhari-Bafrooei, E. Borguet, *J. Phys. Chem. Lett.* **2011**, *2*, 1353-1358.
- [6] S. C. Flores, J. Kherb, N. Konelick, X. Chen, P. S. Cremer, *The Journal of Physical Chemistry C* **2012**, *116*, 5730-5734.
- [7] J. Schaefer, G. Gonella, M. Bonn, E. H. G. Backus, *Phys. Chem. Chem. Phys.* **2017**, *19*, 16875-16880.
- [8] M. D. Boamah, P. E. Ohno, F. M. Geiger, K. B. Eisenthal, *J. Chem. Phys.* **2018**, *148*, 222808.
- [9] S.-h. Urashima, A. Myalitsin, S. Nihonyanagi, T. Tahara, *The Journal of Physical Chemistry Letters* **2018**, *9*, 4109-4114.
- [10] M. D. Boamah, P. E. Ohno, E. Lozier, J. van Ardenne, F. M. Geiger, *The Journal of Physical Chemistry B* **2019**, *123*, 5848-5856.
- [11] D. K. Hore, E. Tyrode, *J. Phys. Chem. C* **2019**, *123*, 16911-16920.
- [12] M. S. Azam, C. Y. Cai, J. M. Gibbs, E. Tyrode, D. K. Hore, *J. Am. Chem. Soc.* **2020**, *142*, 669-673.
- [13] V. Ostroverkhov, G. A. Waychunas, Y. R. Shen, *Chemical Physics Letters* **2004**, *386*, 144-148.
- [14] J. A. McGuire, Y. R. Shen, *Science* **2006**, *313*, 1945-1948.
- [15] A. Eftekhari-Bafrooei, E. Borguet, *J. Am. Chem. Soc.* **2009**, *131*, 12034-12035.
- [16] A. Eftekhari-Bafrooei, E. Borguet, *J. Am. Chem. Soc.* **2010**, *132*, 3756-3761.
- [17] M. S. Azam, C. N. Weeraman, J. M. Gibbs-Davis, *J. Phys. Chem. Lett.* **2012**, *3*, 1269-1274.
- [18] S. Dewan, M. S. Yeganeh, E. Borguet, *J. Phys. Chem. Lett.* **2013**, *4*, 1977-1982.
- [19] M. S. Azam, C. N. Weeraman, J. M. Gibbs-Davis, *J. Phys. Chem. C* **2013**, *117*, 8840-8850.
- [20] M. S. Azam, A. Darlington, J. M. Gibbs-Davis, *J. Phys.-Condens. Mat.* **2014**, *26*, 244107.
- [21] A. M. Darlington, J. M. Gibbs-Davis, *J. Phys. Chem. C* **2015**, *119*, 16560-16567.
- [22] L. Dalstein, E. Potapova, E. Tyrode, *Phys. Chem. Chem. Phys.* **2017**, *19*, 10343-10349.
- [23] J. D. Cyran, M. A. Donovan, D. Vollmer, F. Siro Brigiano, S. Pezzotti, D. R. Galimberti, M.-P. Gaigeot, M. Bonn, E. H. G. Backus, *Proceedings of the National Academy of Sciences* **2019**, *116*, 1520-1525.
- [24] K. A. Lovering, A. K. Bertram, K. C. Chou, *The Journal of Physical Chemistry C* **2016**, *120*, 18099-18104.

- [25] A. Myalitsin, S. H. Urashima, S. Nihonyanagi, S. Yamaguchi, T. Tahara, *J. Phys. Chem. C* **2016**, *120*, 9357-9363.
- [26] A. M. Darlington, T. A. Jarisz, E. L. DeWalt-Kerian, S. Roy, S. Kim, M. S. Azam, D. K. Hore, J. M. Gibbs, *J. Phys. Chem. C* **2017**, *121*, 20229-20241.
- [27] E. L. DeWalt-Kerian, S. Kim, M. S. Azam, H. Zeng, Q. Liu, J. M. Gibbs, *The Journal of Physical Chemistry Letters* **2017**, *8*, 2855-2861.
- [28] B. Reh, M. Rashwan, E. L. DeWalt-Kerian, T. A. Jarisz, A. M. Darlington, D. K. Hore, J. M. Gibbs, *J. Phys. Chem. C* **2019**, *123*, 10991-11000.
- [29] A. Tuladhar, S. Dewan, S. Pezzotti, F. Siro Brigiano, F. Creazzo, M. P. Gaigeot, E. Borguet, *J. Am. Chem. Soc.* **2020**, *142*, 6991-7000.
- [30] J. M. Gibbs-Davis, J. J. Kruk, C. T. Konek, K. A. Scheidt, F. M. Geiger, *J. Am. Chem. Soc.* **2008**, *130*, 15444-15447.
- [31] D. Lis, E. H. G. Backus, J. Hunger, S. H. Parekh, M. Bonn, *Science* **2014**, *344*, 1138-1142.
- [32] J. Schaefer, E. H. G. Backus, M. Bonn, *Nat. Commun.* **2018**, *9*, 3316.
- [33] Q. Du, E. Freysz, Y. R. Shen, *Phys. Rev. Lett.* **1994**, *72*, 238.
- [34] V. Ostroverkhov, G. A. Waychunas, Y. R. Shen, *Phys. Rev. Lett.* **2005**, *94*, 46102.
- [35] M. S. Yeganeh, S. M. Dougal, H. S. Pink, *Phys. Rev. Lett.* **1999**, *83*, 1179-1182.
- [36] A. Abdelmonem, J. Lützenkirchen, T. Leisner, *Atmospheric Measurement Techniques* **2015**, *8*, 3519-3526.
- [37] A. G. Stack, S. R. Higgins, C. M. Eggleston, *Geochimica et Cosmochimica Acta* **2001**, *65*, 3055-3063.
- [38] J. P. Fitts, X. Shang, G. W. Flynn, T. F. Heinz, K. B. Eisenthal, *J. Phys. Chem. B* **2005**, *109*, 7981-7986.
- [39] M. Florsheimer, K. Kruse, R. Polly, A. Abdelmonem, B. Schimmelpfennig, R. Klenze, T. Fanghanel, *Langmuir* **2008**, *24*, 13434-13439.
- [40] J. H. Sung, L. N. Zhang, C. S. Tian, Y. R. Shen, G. A. Waychunas, *J. Phys. Chem. C* **2011**, *115*, 13887-13893.
- [41] L. Zhang, C. Tian, G. A. Waychunas, Y. R. Shen, *J. Am. Chem. Soc.* **2008**, *130*, 7686-7694.
- [42] B. Braunschweig, S. Eissner, W. Daum, *J. Phys. Chem. C* **2008**, *112*, 1751-1754.
- [43] Y. J. Tong, J. Wirth, H. Kirsch, M. Wolf, P. Saalfrank, R. K. Campen, *J. Chem. Phys.* **2015**, *142*, 12.
- [44] J. Sung, Y. R. Shen, G. A. Waychunas, *Journal of Physics-Condensed Matter* **2012**, *24*.
- [45] A. Tuladhar, S. Dewan, J. D. Kubicki, E. Borguet, *J. Phys. Chem. C* **2016**, *120*, 16153-16161.
- [46] A. Boulesbaa, E. Borguet, *J. Phys. Chem. Lett.* **2014**, *5*, 528-533.
- [47] A. Tuladhar, S. M. Piontek, E. Borguet, *J. Phys. Chem. C* **2017**, *121*, 5168-5177.
- [48] A. Abdelmonem, E. H. G. Backus, N. Hoffmann, M. A. Sánchez, J. D. Cyran, A. Kiselev, M. Bonn, *Atmos. Chem. Phys.* **2017**, *17*, 7827-7837.

- [49] A. Tuladhar, S. M. Piontek, L. Frazer, E. Borguet, *J. Phys. Chem. C* **2018**, *122*, 12819-12830.
- [50] S. M. Piontek, A. Tuladhar, T. Marshall, E. Borguet, *J. Phys. Chem. C* **2019**, *123*, 18315-18324.
- [51] K. A. Becraft, G. L. Richmond, *Langmuir* **2001**, *17*, 7721-7724.
- [52] A. J. Hopkins, S. Schrödle, G. L. Richmond, *Langmuir* **2010**, *26*, 10784-10790.
- [53] A. N. Bordenyuk, A. V. Benderskii, *J. Chem. Phys.* **2005**, *122*, 134713.
- [54] R. Khatib, E. H. G. Backus, M. Bonn, M. J. Perez-Haro, M. P. Gaigeot, M. Sulpizi, *Scientific Reports* **2016**, *6*, 1-10.
- [55] A. Boulesbaa, E. Borguet, *J. Phys. Chem. Lett.* **2016**, *7*, 5080-5085.
- [56] J. Lutzenkirchen, T. Scharnweber, T. Ho, A. Striolo, M. Sulpizi, A. Abdelmonem, *J. Colloid Interface Sci.* **2018**, *529*, 294-305.
- [57] D. Lesnicki, Z. Zhang, M. Bonn, M. Sulpizi, E. H. G. Backus, *submitted* **2020**.
- [58] S. Kataoka, M. C. Gurau, F. Albertorio, M. A. Holden, S. M. Lim, R. D. Yang, P. S. Cremer, *Langmuir* **2004**, *20*, 1662-1666.
- [59] K. Uosaki, T. Yano, S. Nihonyanagi, *J. Phys. Chem. B* **2004**, *108*, 19086-19088.
- [60] S. Hosseinpour, F. Tang, F. Wang, R. A. Livingstone, S. J. Schlegel, T. Ohto, M. Bonn, Y. Nagata, E. H. G. Backus, *J. Phys. Chem. Lett.* **2017**, *8*, 2195-2199.
- [61] S. J. Schlegel, S. Hosseinpour, M. Gebhard, A. Devi, M. Bonn, E. H. G. Backus, *Physical Chemistry Chemical Physics* **2019**, *21*, 8956-8964.
- [62] P. B. Miranda, L. Xu, Y. R. Shen, M. Salmeron, *Phys. Rev. Lett.* **1998**, *81*, 5876.
- [63] Z. Yang, A. K. Bertram, K. C. Chou, *J. Phys. Chem. Lett.* **2011**, *2*, 1232-1236.
- [64] E. Anim-Danso, Y. Zhang, A. Dhinojwala, *J. Phys. Chem. C* **2016**, *120*, 3741-3748.
- [65] A. Abdelmonem, *Atmos. Chem. Phys.* **2017**, *17*, 10733-10741.
- [66] A. Tuladhar, Z. A. Chase, M. D. Baer, B. A. Legg, J. Tao, S. Zhang, A. D. Winkelman, Z. Wang, C. J. Mundy, J. J. De Yoreo, H. F. Wang, *J. Am. Chem. Soc.* **2019**, *141*, 2135-2142.
- [67] S. Jin, Y. Liu, M. Deiseroth, J. Liu, E. H. G. Backus, H. Li, H. Xue, L. Zhao, X. C. Zeng, M. Bonn, J. Wang, *submitted* **2020**.