Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Observing Different Dynamic Behaviors of Weakly and Strongly Adsorbed Polystyrene Chains at Interfaces

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We applied a film thickness gauge (SCREEN SPE USA, LLC, Lambda Ace VM-1200) to measure the PS layer thicknesses. For the weakly adsorbed layer, the measured thickness was 2.4±1.2 nm; and for the strongly adsorbed layer, the measured thickness was 2.7±0.4 nm, as shown in Figure S1. The results are consistent with the reported data in the literatures.[S1,S2]

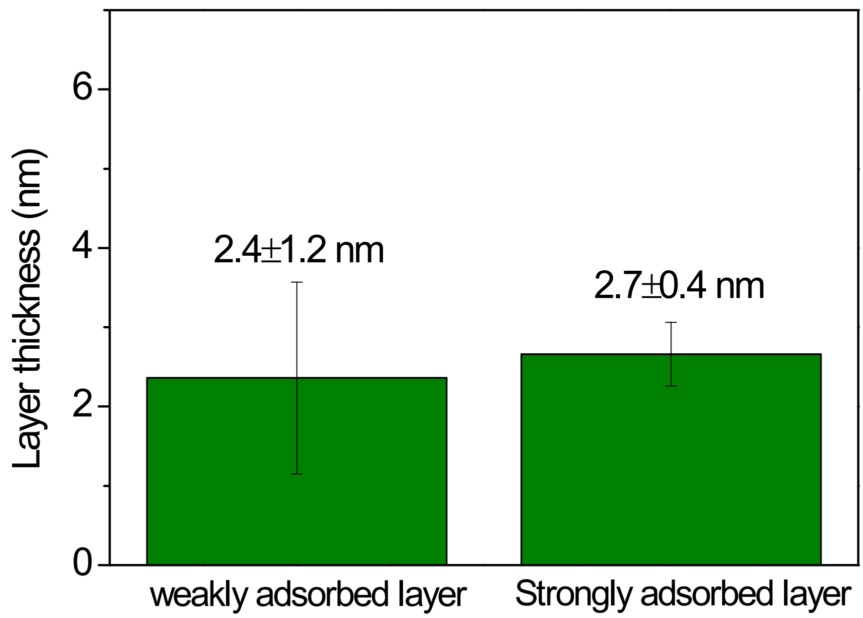

Figure S1. The thicknesses of weakly and strongly adsorbed layers measured by a film thickness gauge (each averaged from three independent measurements).

In Figure S2, the interfacial deuterated water (D_2O) spectra were shown for both the weakly and strongly adsorbed layers in *ssp* polarization combination. The results indicated that D_2O were orderly arranged at the interface for both layers.

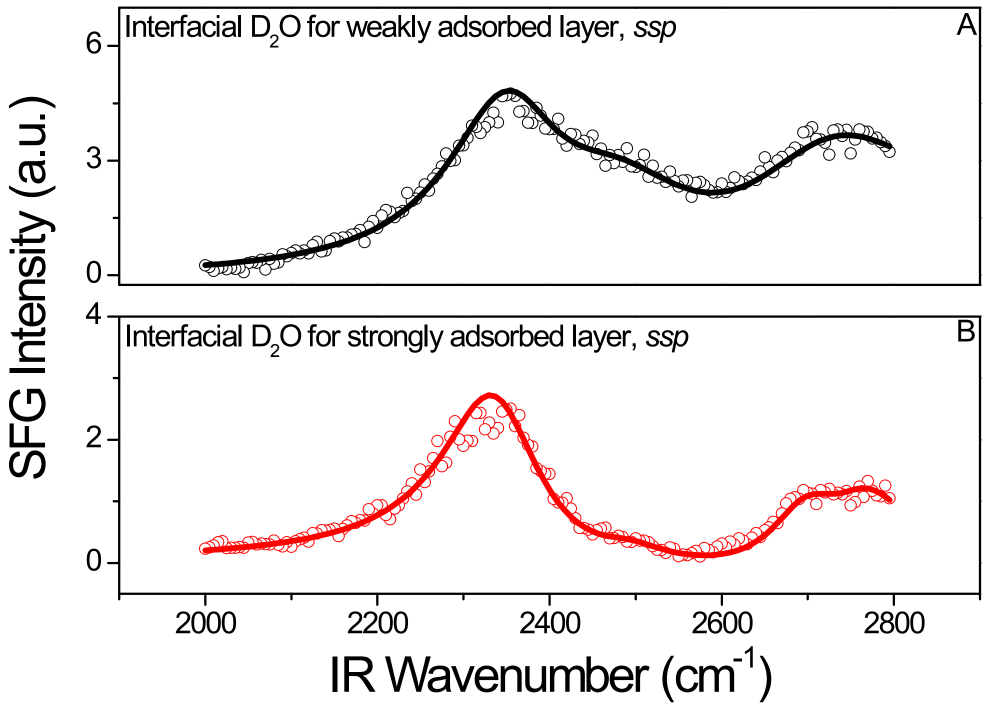

Figure S2. Normalized SFG spectra of the weakly and strongly adsorbed layers on sapphire in contact with D_2O in the OD stretching frequency range with *ssp* polarization combination. Panel A shows the spectrum of D_2O for the weakly adsorbed layer and Panel B shows the spectrum of D_2O for the strongly adsorbed layer. The solid lines were plotted to guide eyes.

We also collected SFG spectrum from the pure sapphire/air interface, as shown in Figure S3. A sharp peak located at ~3720 cm^{-1} was observed, which can be assigned to the free OH vibrational mode on the sapphire surface.[S3-S5]

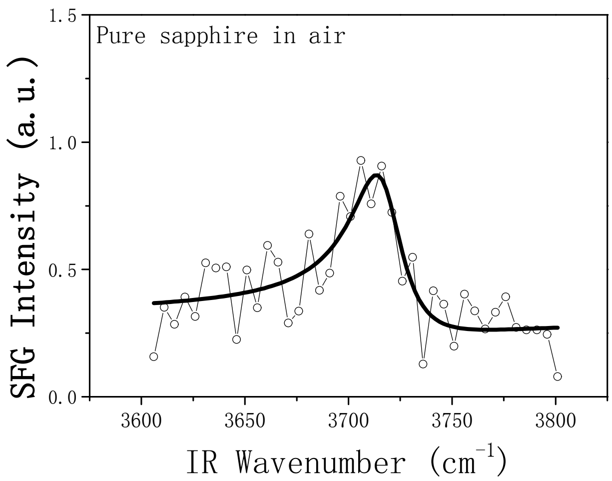

Figure S3. Normalized SFG spectrum of pure sapphire in air in OH stretching frequency range.

Lorentz equation was used for fitting SFG spectra. When the IR frequency is near the vibrational resonance, $\chi_{eff}^{(2)}$ can be written as[S6,S7]:

$$\chi_{eff}^{(2)} = \chi_{nr} + \sum_q \frac{A_q}{w_2 - w_q + i\Gamma_q} \quad \text{(S1)}$$

where χ_{nr} represents the nonresonant background contribution. A_q, w_q and Γ_q represent the amplitude, resonant frequency and damping coefficient of the *qth* vibrational mode, respectively. In Table S1, fitting results were listed for the SFG spectra presented in the main context. In Table S2, the refractive indices of sum-frequency, Vis, and IR beams were listed. In Table S3, the calculated interfacial Fresnel coefficients were listed.

Table S1. The fitting results of the SFG spectra presented in the main text.

ω_q (cm^{-1})	Γ_q (cm^{-1})	Assignment	on sapphire (air)		on sapphire (D_2O)		on sapphire (CCl_4)	
			weakly	strongly	weakly	strongly	weakly	strongly
			A_{ssp}	A_{ssp}	A_{ssp}	A_{ssp}	A_{ssp}	A_{ssp}
2850	10.5	CH_2 ss	3.2	6.0	-	5.5	2.8	8.5
2875	12.3	CH_3 ss	7.1	5.4	-	3.7	8.5	5.8
2910	10.0	CH	4.0	6.3	-	3.2	2.5	6.0
2935	11.5	CH_2 as	-7.2	-7.6	-	-6.5	-13.4	-10.8
2945	8.0	CH_3 Fermi	1.5	-	-	-	-	-
3023	9.0	ν_{20b}						
3032	7.0	ν_{7a}	-	-5.8	-	-	-	-
3050	6.0	ν_{7b}	-	4.4	-	-	-	-
3065	6.0	ν_2	-	8.8	-	-	-	-
3620	80.0	OH	-	-	-	84.1	-	-
3660	80.0	OH	53.2	110.0	-	-	70.7	431.0

Table S2. Refractive indexes of Sum-frequency, Vis, and IR beams

Medium	Refractive indexes at sum frequency	Refractive indexes at visible frequency	Refractive indexes at infrared frequency (2955 cm^{-1})
Air	1.00	1.00	1.00
D_2O	1.33	1.33	1.32
Sapphire	1.78	1.77	1.70
PS adsorbed layer	1.20	1.20	1.20
CCl_4	1.46	1.46	1.44

Note: the refractive indexes were referred to references S8, S9 and S10.

Table S3. The calculated Fresnel coefficient values

	$F_{ssp-yyz}$/|$F_{ssp-yyz}$|
Sapphire (PS)/Air	-0.21+0.05i/0.22
Sapphire (PS)/D_2O	-0.38-0.36i/0.52
Sapphire (PS)/CCl_4	0.02-0.57i/0.57

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