

Supporting information

Trimethylamine Probes Isolated Silicon Dangling Bonds and Surface Hydroxyls of (H,OH)-Si(001)

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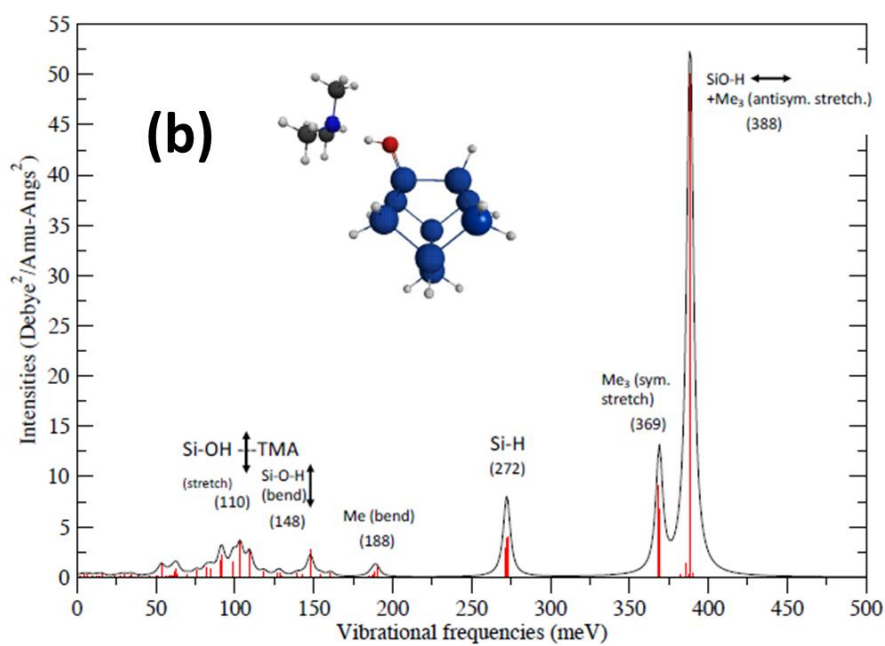
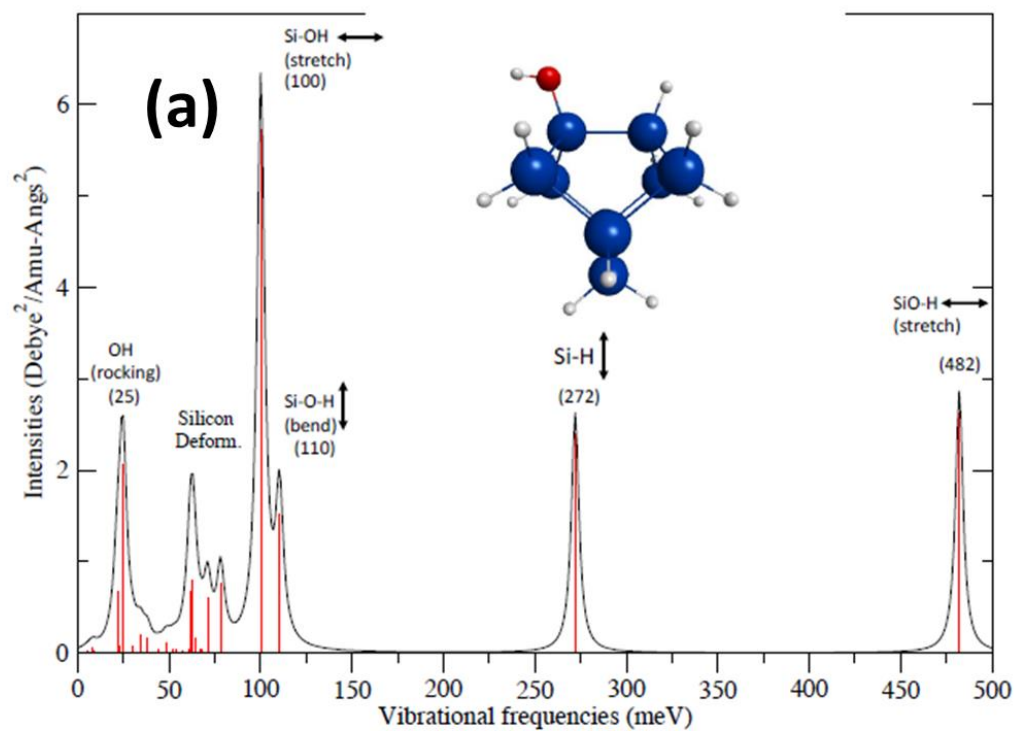
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S1. DFT Simulation of vibrational spectra and table of peak assignments



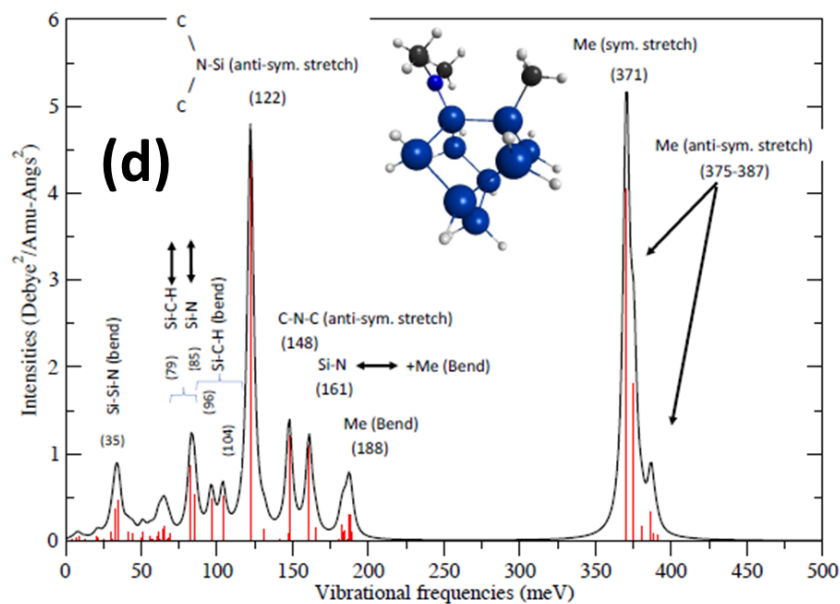
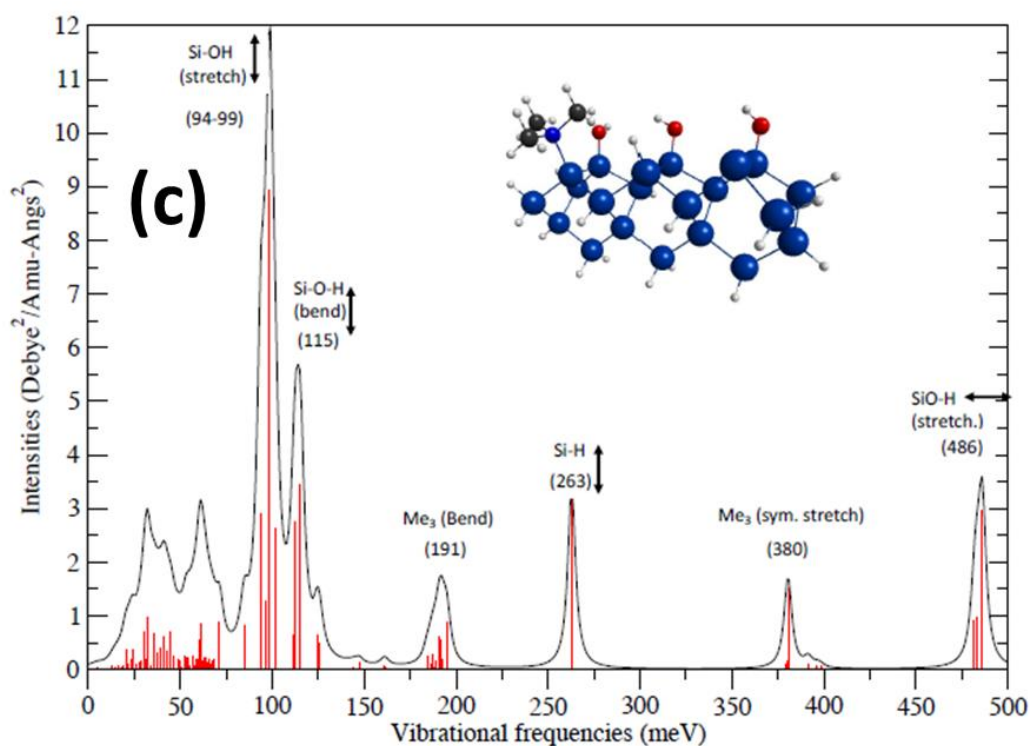
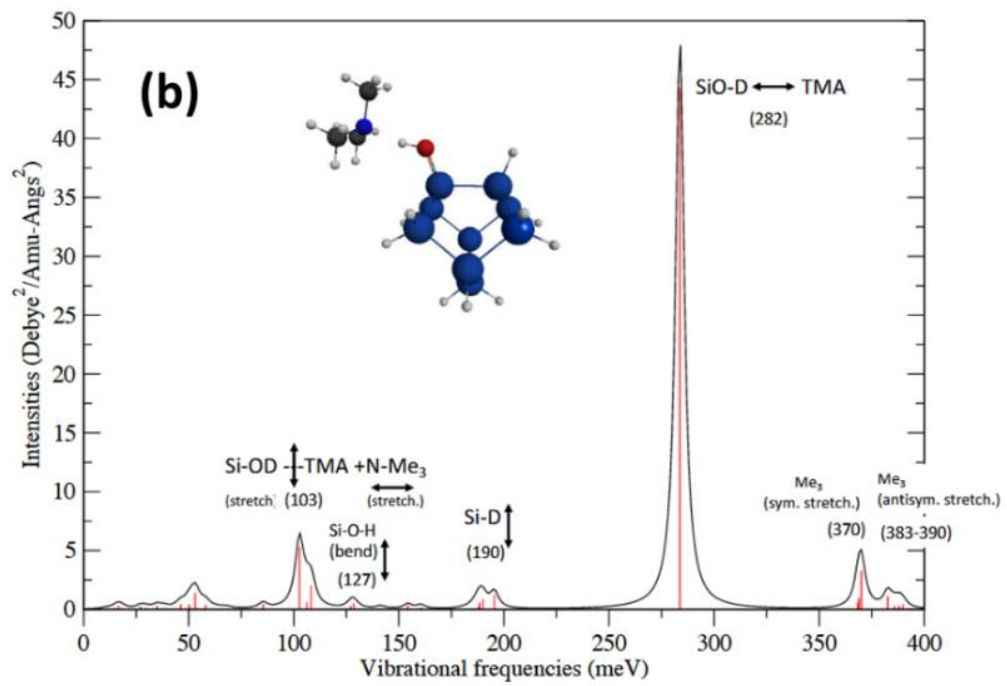
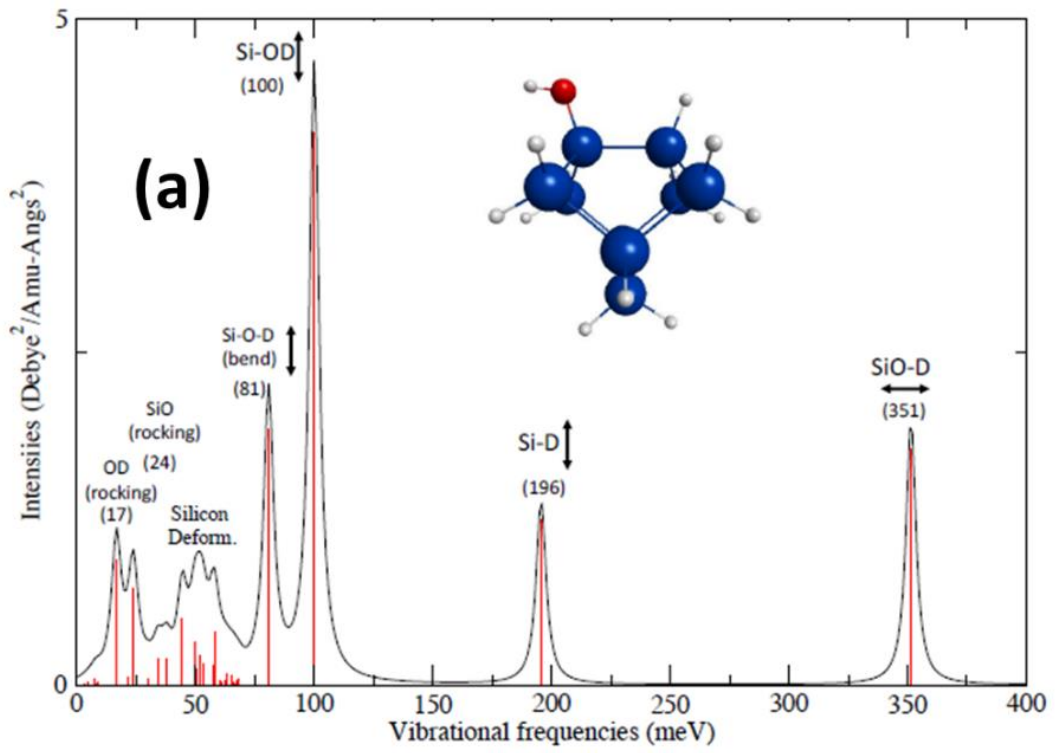


Figure S1. DFT calculated vibrational spectra of (a) the H/OH decorated single Si dimer (b) the TMA(A)..HO model configuration, (c) the molecule datively bonded on an “isolated” dangling bond of a three-dimer cluster (2 non-adjacent dangling bonds), (c) the dissociated molecule on a bare dimer. Me is the methyl group. The peaks are plotted with an “artificial” Lorentzian broadening of 5 meV to help their visualization. Calculated energies are not rescaled.



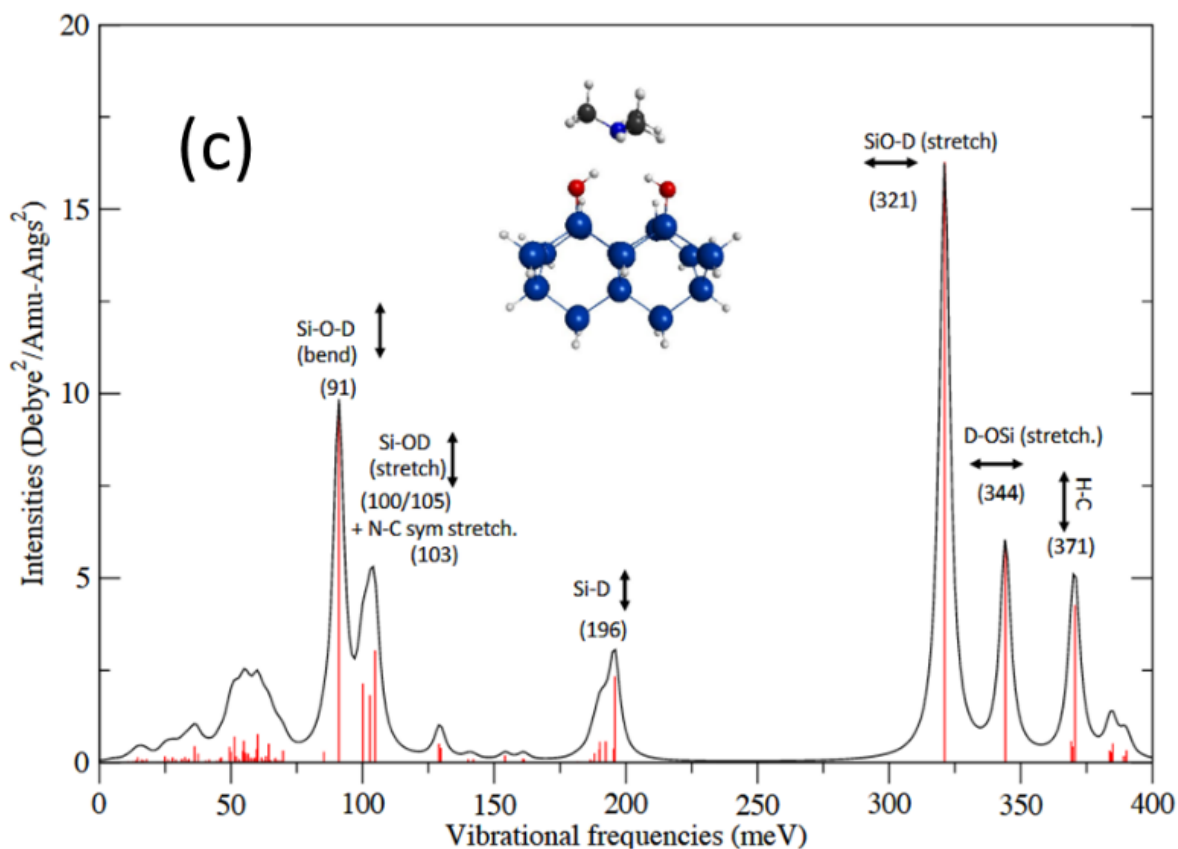


Figure S2. DFT calculated vibrational spectra of (a) of the (D,OD) decorated silicon dimer and (b) of the TMA(A)...DO model and (c) of the TMA(A,A)...2(DO) configuration. Note the redshifts of the SiO-D stretching mode energy (-69 meV) due to the hydrogen-bond with TMA. (Me is the methyl group). The peaks are plotted with an “artificial” Lorentzian broadening of 5 meV to help their visualization. Calculated energies are not rescaled.

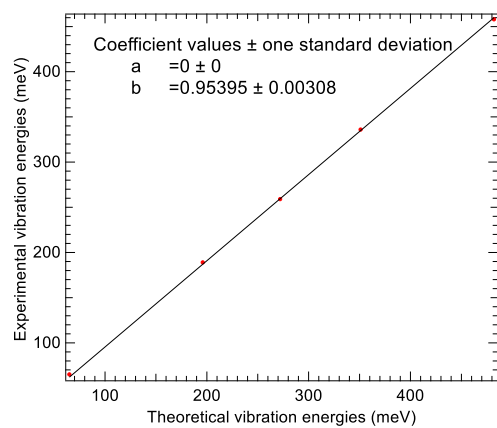


Figure S3. Calculation of the scaling factor (0.9540 ± 0.0031)

Assignment	Energy loss	(a)	(b)	(c)	(d)	(e)
TMA Torsion	35	35	37	36*		
$\delta_s(\text{NC}_3)$	44	45	48	46/48*	47*	
$\delta_d(\text{NC}_3)$	54	52	54			
$\nu(\text{SiN})$	66			65		
$\nu_s(\text{NC}_3)$	99	103	103	100/102*	100	100/103*
	111					
$\rho(\text{CH}_3)$	121			121	121	
$\rho(\text{CH}_3)/\nu_d(\text{NC}_3)$	129	130/129*	129/129	129*	127*	
$\rho(\text{CH}_3)$	136	137				
$\rho(\text{CH}_3)$	144	149	148	148*	147*	
$\rho(\text{CH}_3)/\nu_d(\text{NC}_3)$	152			154/156*		
$\nu_d(\text{NC}_3)$	159	158		154/156*		123/157*
	168					
$\delta_s(\text{CH}_3)$	173	175		136	135	
$\delta_s(\text{CH}_3)$	179	179		180		
$\delta_d(\text{CH}_3)$	183	183		180	180	
overtones/ comb. bands	194-335				218-332	
$\nu_{s,d}^b(\text{CH}_3)$	345-350	344	343			345/350*
$\nu_s(\text{CH}_3)$	355-363	366	365	365	363	353-361/ 356-361*
$\nu_d(\text{CH}_3)$	369-377	370		365	363	370

Table S1: HREELS peak assignments of adsorbed TMA species compared to literature: (a) IR TMA gas,¹ (b) IR TMA solid,² (c) HREELS TMA @ Si(100),³ (d) HREELS TMA @ GaAs⁴ and (e) HREELS TMA @ Ge,⁵ all loss energies are given in meV. *Multilayer.

S2. Si 2p and O 1s core-level of the (H,OH)-Si(001) surface

Si 2p core-level

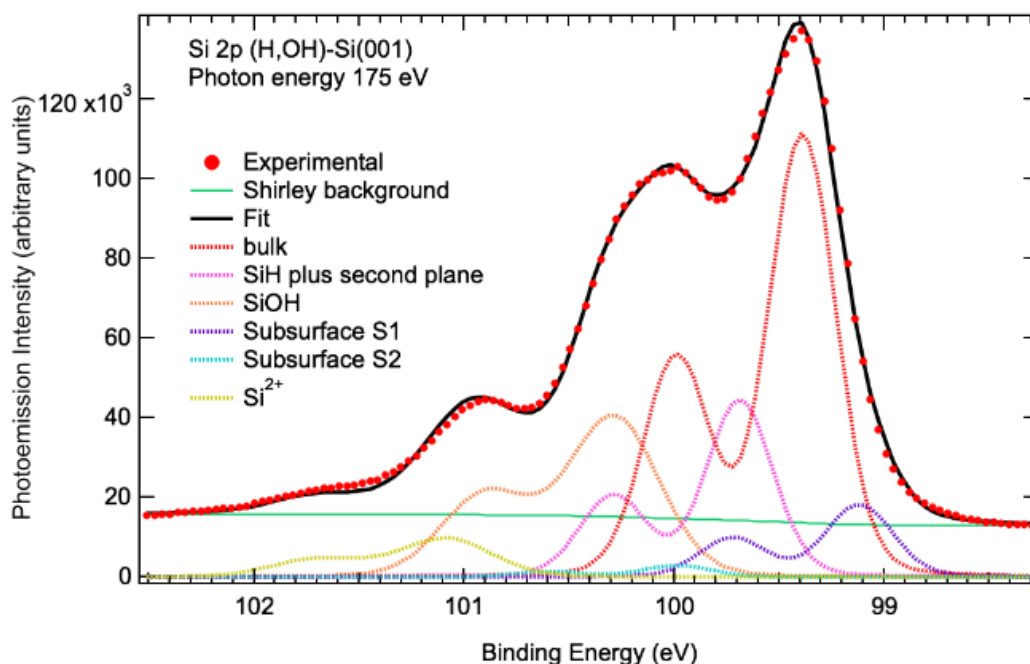


Figure S4: The Si 2p spectrum after water-dosing ($Q_{\text{water}} \geq 2.25$ ML) at 300 K, measured at $h\nu=175$ eV. The photon exit direction is at 60° from the surface normal. The binding energies ($2p_{3/2}$) FWHM and spectral weights of the fitting components are given in Table S2.

Component	Si $2p_{3/2}$ Binding Energy (eV)	Lorentzian FWHM (eV)	Gaussian FWHM (eV)	Weight (%)	Shift* (eV)
Si ⁰	99.40	0.045	0.350	45.62	0
SiH 2 nd plane	99.70	0.045	0.350	17.78	0.30
Si ¹⁺ SiOH	100.30	0.045	0.483	22.45	0.90
Si ²⁺	101.10	0.045	0.490	5.29	1.70
Subsurface S1	99.13	0.045	0.350	7.69	-0.27
Subsurface S2	100.00	0.045	0.350	1.17	0.60

Table S2. Fitting parameters of the Si 2p curve in Figure S4. *Related to Si⁰.

The Si 2p core-level of the pristine (H,OH)-Si(001) surface prepared at 300 K is shown in Figure S4. The spectrum, measured in highly surface sensitive conditions ($h\nu=175$ eV and photoelectron exit angle at 60° from surface normal) exhibits the characteristic Si-OH (Si¹⁺) component of the water-reacted surface at +0.9 eV from the bulk component Si⁰. Its spectral weight (22%) corresponds to 0.5 ML of surface silicon atoms. A small Si²⁺ component is also observed (5% of the spectral weight), which indicates that some O atoms are inserted in the dimer back-bonds. We also see that the surface states of the clean dimerized surface at -0.5 eV from the bulk peak (the outer dimer component^{6,7}) are all quenched, as expected when the surface is saturated by water.

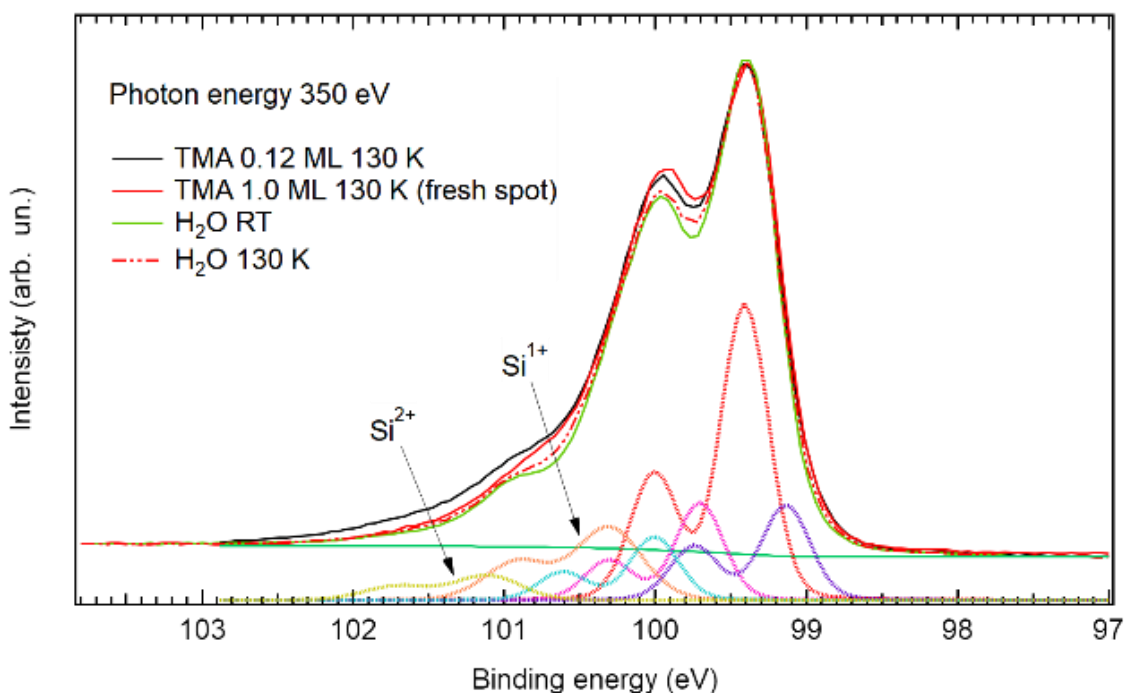


Figure S5. Si 2p core levels measured at $h\nu=350$ eV of the water-covered surface (300 K and 130 K) of the TMA exposed surface ($Q_{TMA}=0.12$ ML) after the real-time XPS run, and of the TMA-exposed surface ($Q_{TMA}=1$ ML), measured on a fresh spot. Components shown in the fit of the green curve: bulk Si^0 (42%), $SiH/2^{nd}$ plane (14%), subsurface S1 (15%), subsurface S2 (9%), $SiOH/Si^{1+}$ (15%), Si^{2+} (5%). FWHM and core-level shifts with respect to Si^0 are the same as those indicated in Table S2.

Effects due to cooling down the sample to 130 K, exposure to TMA and prolonged exposure to the X-ray-beam during the real-time time XPS run were examined at $h\nu=350$ eV (exit angle of 60°). The Si 2p spectra are shown in Figure S5. For spectra measured on “fresh” spots (*i.e.* the irradiation time is limited to the short time necessary to acquire the spectrum 25 s), we see no appreciable change in the Si 2p spectra of the pristine (H,OH)-Si(001) surface at 300 K (green solid curve) and at 130 K (red dash-dotted curve). This means that there is no further oxidation due to water condensed on the surface. Equally, the adsorption of TMA ($Q_{TMA}=1$ ML) does not affect the spectrum (red line) when the measurement is made on a “fresh” spot. In contrast, the curve (black line) acquired immediately at the end of the real-time XPS measurement at 130 K ($Q_{TMA}=0.12$ ML, irradiation time > 1600 s) shows a small but clear increase of the Si^{1+} and Si^{2+} states. This is due to the insertion of the O atom of the hydroxyl within the dimer-bond⁸ and within the back-bonds (the hydroxyl \rightarrow siloxane transformation multiplies the number of Si^{1+} states by a factor of 2). These changes are due to the breaking of the O-H bond in the hydroxyl due to beam damage.

O 1s spectra

The O 1s spectra are shown in Figure S6. The O 1s spectrum of the pristine (H,OH)-Si(001) surface at 300 K is fitted with a single narrow (1.17 eV) component at the characteristic BE of OHs (at 532.7 eV) showing a minor formation of siloxane bridges (at ~ 531.7 eV⁹) corresponding to 9% of the spectral weight. Exposure to TMA (0.12 ML) after cooling down to 130 K results in a broadening of the O 1s peak, as the FWHM increases from 1.2 eV to 1.7 eV. This sizeable broadening cannot be related to surface oxidation, as the corresponding Si 2p spectrum does not show any hint of it (compare the green and red curves in Figure S5). It is rather related to the formation of H bonds between OHs and between OHs and TMA.¹⁰ Upon

TMA adsorption, the binding energy of the centroid shifts down by -0.3 eV. The same shift and broadening were also observed when (H,OH)-Si(001) was exposed to ammonia.¹⁰ The asymmetry of the O 1s peak towards higher binding energy is accounted for by introducing a component at 533.8 eV, similar to what was observed for the ammonia/(H,OH)-Si(001) system.¹⁰ The attribution of this peak is unclear. Note that co-adsorbed molecular water (coming from the residual) is expected at 534.3 eV.¹⁰

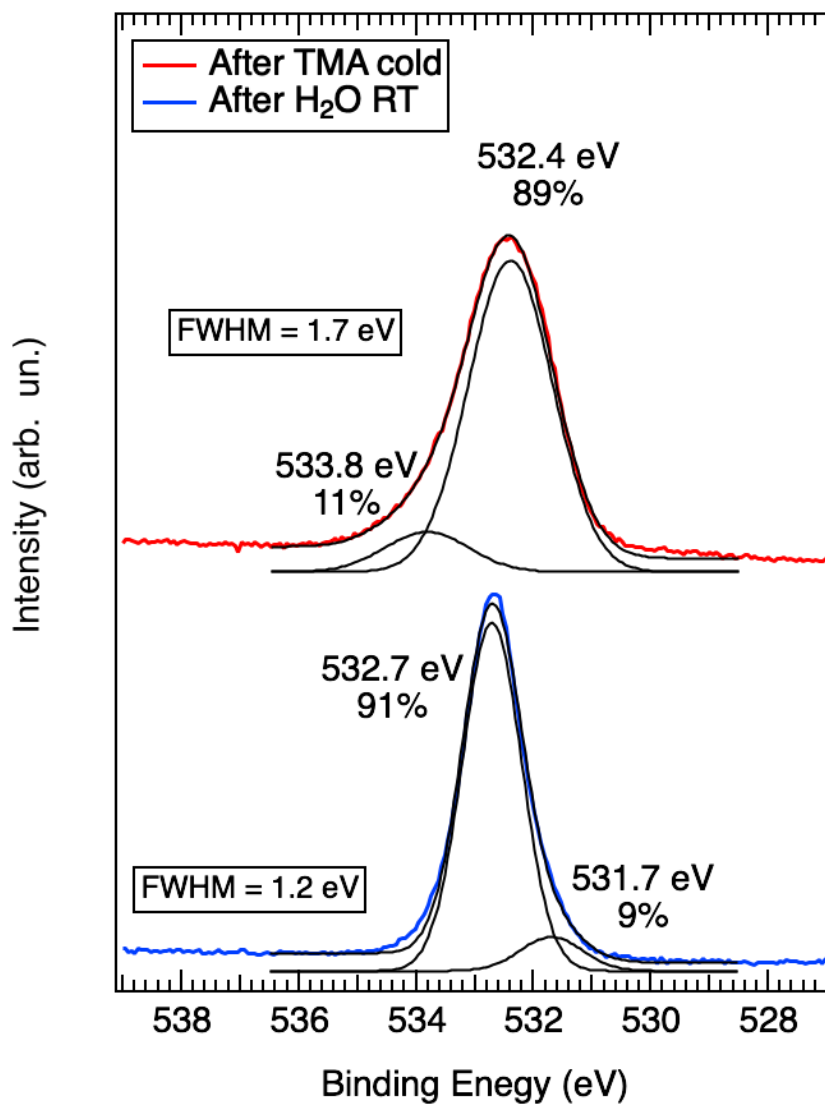


Figure S6. Bottom curve: O 1s spectrum of the (H,OH)-Si(001) measured at room temperature at $h\nu=595$ eV. Top curve: after TMA exposure ($Q_{TMA}=0.12$ ML) at 130 K. All spectra are aligned with respect to that of Si $2p_{3/2}$ positioned at 99.41 eV (because of the surface photovoltage at cryogenic temperature).

S3. Fitting of the C 1s spectra with 4 Gaussians

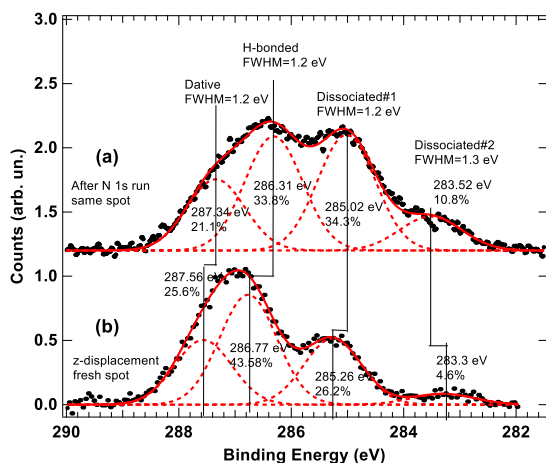


Figure S7. Fitting of the C 1s spectra reported in Figures 4(a,b) in the main paper with a set of four Gaussians. The FWHMs are kept constant, the binding energies are free parameters.

The fitting of C 1s spectra with a restricted set of 4 Gaussians, accounting for the visible shoulder at 287.3 eV, and the three maxima at 287.0-286.3, 285.3-285, 283.5-283.2 eV, leads to broad Gaussians (FWHM of 1.2-1.3 eV) with energy positions that change by 0.2-0.4 eV from curve (a) to curve(b). This is due to the absence of the “diss-SiNC” component at ~386.0 eV, and of the “diss-SiC” component at ~284.2 eV.

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