

Supporting Information

Experimental and *Ab Initio* Core-Level Photoelectron Spectroscopy Elucidate the H-Bonding of Ammonia with the Hydroxyls of the (H,OH)-Si(001) Model Surface

Lucía Pérez Ramírez¹, Jean-Jacques Gallet^{1,2}, Fabrice Bournel^{1,2}, Florence Lim¹, Stéphane Carniato¹, François Rochet^{1*}, Oleg V. Yazyev³, Alfredo Pasquarello³, Elena Magnano^{4,5} and Federica Bondino⁴*

¹ Sorbonne Université, CNRS, Laboratoire de Chimie Physique matière et Rayonnement,
UMR 7614, 4 place Jussieu, 75005 Paris, France

² Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin - BP 4891192 Gif-sur-Yvette
CEDEX, France

³ Chaire de Simulation à l'Echelle Atomique (CSEA), Ecole Polytechnique Fédérale de
Lausanne (EPFL), CH-1015 Lausanne, Switzerland

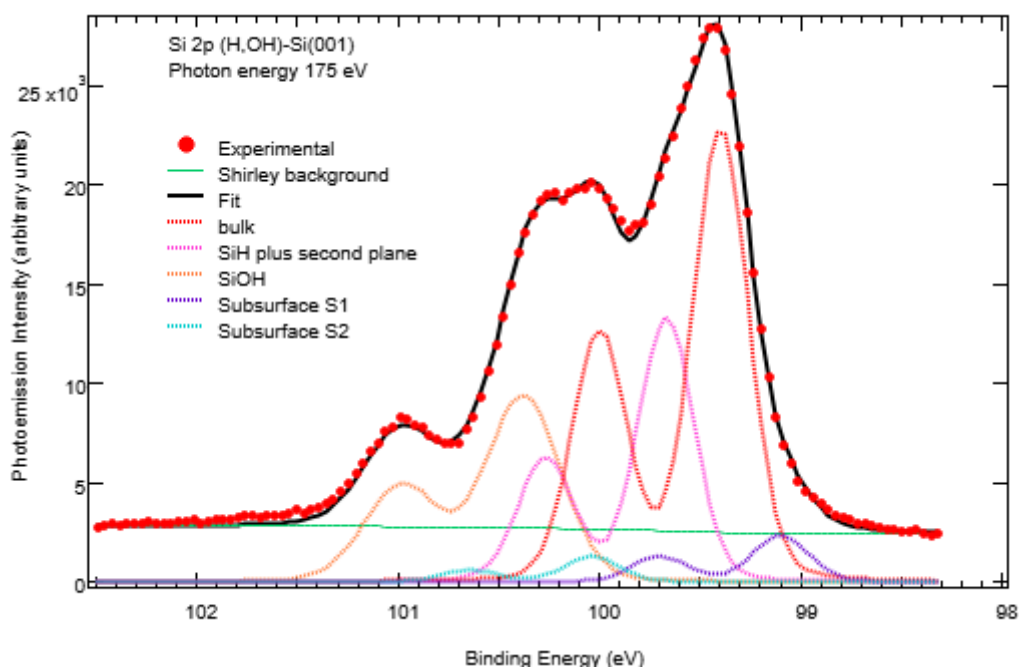
⁴ IOM-CNR, Laboratorio TASC, 34149 Basovizza, Trieste, Italy

⁵ Department of Physics, University of Johannesburg, PO Box 524, Auckland Park 2006,
South Africa

*Corresponding authors: francois.rochet@sorbonne-universite.fr; jean-jacques.gallet@sorbonne-universite.fr

Content: 13 pages, 5 figures and 1 table.

S1. The Si 2p spectrum of (H,OH)-Si(001)



Component	Si 2p _{3/2} Binding Energy (eV)	Lorentzian FWHM (eV)	Gaussian FWHM (eV)	Spectral weight (%)	Core Level shifts (eV)
Si ⁰	99.40	0.045	0.300	44.63	0
SiH/2 nd plane	99.67	0.045	0.300	24.60	0.27
SiOH	100.38	0.045	0.414	23.90	0.98
S1	99.10	0.045	0.300	4.5	-0.30
S2	100.04	0.045	0.300	2.4	0.64

Figure S1. Si 2p spectrum of the (H,OH)-Si(001) surface at 300 K. The table below the spectrum collects the binding energy positions (eV), the Lorentzian and Gaussian full widths at half maximum (FWHM) and the spectral weights of each component.

The Si 2p core level of the (H,OH)-Si(001) surface (shown in Figure S1) is measured at $h\nu = 175$ eV. At a kinetic energy of ~ 75 eV, the inelastic mean free path λ is ~ 4.8 nm.¹ Considering the exit angle of the photoelectrons with respect to the surface normal (60°), the effective escape depth $\lambda \cos(60^\circ)$ is small ~ 2.4 Å, which ensures a good surface sensitivity (a surface plane is worth 46% of the spectral weight). The spectrum is very similar to those shown in our previous publications.^{2,3} It is fitted with five doublets (the spin-orbit splitting is 0.602 eV and the $2p_{1/2}:2p_{3/2}$ branching ratio is 0.5). We use true Voigt functions with a Lorentzian FWHM of 0.045 eV. Gaussian widths are indicated in the table. We find the Si $2p_{3/2}$ component of bulk silicon Si^0 component at 99.40 eV. The “SiH *plus* 2nd plane” component is at +0.27 eV from Si^0 , the SiOH (Si^{1+}) component at +0.98 eV. As the SiOH coverage is 0.5 ML, 48% of the spectral weight corresponds to the surface plane, which shows the high surface sensitivity. Note the absence of the Si^{2+} oxidation state at about +1.8 eV from Si^0 (and of higher oxidation states). This proves the absence of subsurface oxidation. Only OHs are present on the surface. Two more small subsurface components are needed to obtain a good fit. The “S1” component at -0.30 eV, distinct from that of the “up” dimer atom component of the clean surface that appears at -0.57 eV,^{3,4} and the “S2” component at +0.64 eV.

S2. O 1s and N 1s normalization with respect to Si LVV

Figure S2 presents the N 1s spectra of a Si(001)- 2×1 surface after saturation with NH_3 at a pressure of 5×10^{-9} mbar (blue), and a silicon surface after 10 minutes of water dosing ($P=5\times 10^{-9}$ mbar) plus approximately 20 minutes of ammonia dosing ($P=5\times 10^{-9}$ mbar) (red). The spectra are normalized using the Si LVV Auger edge to evaluate the variation of ammonia quantities on the surface. The area under the N 1s peak of the blue curve, measured from the (H, NH_2)-Si(001) surface,⁵ corresponds exactly to 0.5 ML. Taking this as a standard, we find that the

calculated area under the N 1s peak of the red curve is 0.40 ML. Since the red spectrum is taken just after the end of the ammonia dosing process given in Figure 4 of the article, we deduce from the normalized N 1s intensity the nitrogen coverages as a function of time for the different species.

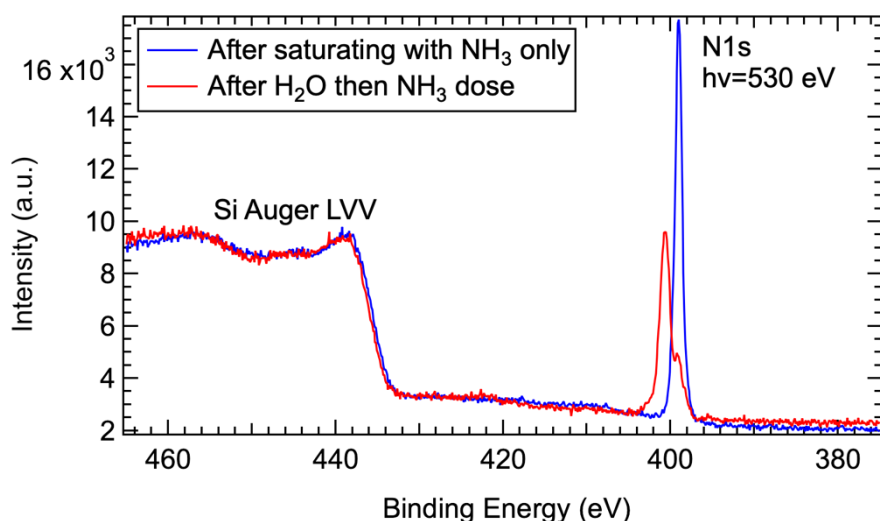


Figure S2. Si Auger LVV and N 1s core level peak recorded at $h\nu = 530$ eV from the NH_3 -covered silicon surface and the NH_3 -(H,OH)-covered surface.

Figure S3 shows the O 1s spectra of the silicon surface after 10 minutes of water dosing at room temperature ($P = 5 \times 10^{-9}$) (blue), after cooling down to 130 K (red), and, finally, after 20 minutes of NH_3 dosing at $P = 5 \times 10^{-9}$ (green) at 130 K. Given that the dissociation of water on the silicon dimers at room temperature leads to the formation of half a monolayer (ML) of SiH and half a monolayer of SiOH, the area under the O 1s peak of the blue curve correspond to 0.5 ML of OH species exactly. The (H,OH)-Si(001) surface formed at 300 K serves as standard to estimate the oxygen coverages. Therefore, the calculated oxygen coverage after cooling down in UHV is 0.57 ML, and after ammonia dosing is 0.50 ML.

Both for N and O coverages, the relative uncertainty due to adjusting the Si LVV edges is about 5% and that due to measuring the spectral intensity is 3%. The overall error in measuring is estimated to be ~8%.

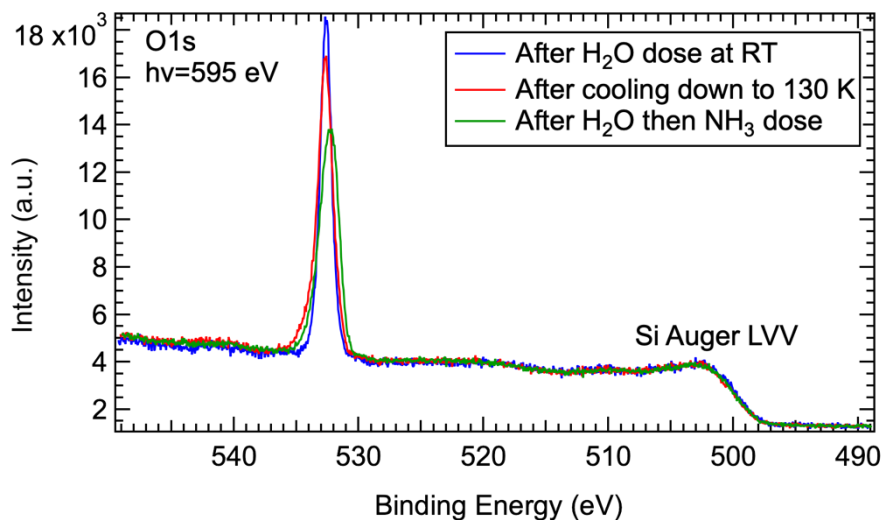


Figure S3. Si Auger LVV and O 1s core level peak recorded at $h\nu = 595$ eV from the silicon surface after water saturation at room temperature (blue), then cooling down to 130 K (red), and after NH₃ dosing under a pressure of 5×10^{-9} mbar (green).

S3. Cluster QC DFT O 1s Ionization energies (IE_{QC}^{th})

Single dimer clusters

The results of the O 1s cluster QC DFT calculations obtained for single-dimer clusters, Si₉H₁₂ (OH,H) (single OH) and Si₉H₁₂ (2OH) (ODIM OH pairs), are collected in Table S1 for various configurations. Calculations of O 1s ionization energies IE_{QC}^{th} were limited to this small cluster. While such an approach obviously cannot represent the variety of configurations encountered on the real surface, trends can be highlighted that are useful for interpreting the experimental spectra.

The IE_{QC}^{th} of isolated the isolated hydroxyl is found at 537.86 eV. It is used as an energy reference to calculate ΔIE_{QC}^{th} of other configurations.

Configuration	Cluster	H-bond length (Å)	O1s IE_{QC}^{th} (eV)	ΔIE_{QC}^{th} (eV)
Free H ₂ O	NA	NA	539.78	1.92
Single OH	Si ₉ H ₁₂ (H,OH)	NA	537.86	0
Single OH(D)...NH ₃ (A)	Si ₉ H ₁₂ (H,OH,NH ₃)	O-H...NH ₃ 1.84	536.55	-1.31
Single OH(a)...NH ₃ (d)	Si ₉ H ₁₂ (H,OH,NH ₃)	H-O...H-NH ₂ 2.17	537.84	-0.02
ODIM pair OH(D)...OH(A)	Si ₉ H ₁₂ (2OH)	O-H...O-H 1.64	536.28	-1.58
ODIM pair OH(D)...OH(A)			538.20	0.34
ODIM OH(D)...NH ₃ (A,d)...OH(A)	Si ₉ H ₁₂ (2OH,NH ₃)	O-H...NH ₃ 1.77	536.50	-1.36
ODIM OH(D)...NH ₃ (A,d)...OH(A)		H ₂ NH...O-H 2.10	538.00	0.14
ODIM OH(d)...OH(a,D)...NH ₃ (A)	Si ₉ H ₁₂ (2OH,NH ₃)	O-H...NH ₃ 1.84	536.84	-1.02
ODIM OH(d)...OH(a,D)...NH ₃ (A)		O-H...OH 2.64	537.36	-0.5

Table S1. Theoretical O 1s ionization potential energies IE_{QC}^{th} calculated via a DFT QC silicon cluster approach (Si₉H₁₂, the “one-bare-dimer” cluster). ΔIE_{QC}^{th} values are referenced to the IE_{QC}^{th} of the isolated OH (537.86 eV). (...) denotes a H-bond. OH and NH₃ can donate (D or d) or accept (A or a) H atoms. A capital letter corresponds to a strong H bond, a lower case to a weak H bond (the “proxy” of the H bond strength is its length given in the table).

Pairs of OH sitting on the same dimer establish strong H bonds. Indeed, the optimized O-O distance is 2.60 Å (the Si-Si dimer bond length is 2.35 Å). The short H-O...H-O H-bond length (1.64 Å) means that the effect on O 1s IE_{QC}^{th} is large. The IE_{QC}^{th} the OH(A) and OH(D) species are 538.20 eV and 536.28 eV, respectively. This corresponds to an energy splitting of 1.92 eV: the acceptor shifts by $\Delta IE_{QC}^{th} = +0.34$ eV and the donor by $\Delta IE_{QC}^{th} = -1.58$ eV, with respect to the isolated OH case (Table S1). This situation is reminiscent of that of the (H₂O)₂ dimer, see Carniato et al.⁶ and Table 1, where the acceptor moves by +0.56 eV and the donor by 1.17 eV with respect to the case of the isolated water molecule. The same trend in sign for the core

level shifts and a larger shift magnitude for the donor than for the acceptor were also calculated by Garcia-Gil and coworkers in the case intermolecular H-bond in organic molecules.⁷

Adsorption on Si₉H₁₂ (H,OH)

The ammonia molecule can be attached to the single OH of the Si₉H₁₂ (OH,H) cluster. In the OH(D)...NH₃(A) configurations the H-bond length is 1.84 Å, and $\Delta IE_{QC}^{th} = -1.31$ eV. A minimum energy configuration can also be achieved by presenting one hydrogen of the molecule in front of the oxygen of the hydroxyl. The hydrogen bond is then weak (HO(a)...HNH₂(d) is 2.17 Å long) and ΔIE_{QC}^{th} is zero.

Adsorption on Si₉H₁₂ (2OH)

We then investigated the adsorption of an ammonia molecule on Si₉H₁₂ (2OH). Ammonia can be inserted between the two hydroxides, to make a OH(D)...NH₃(A,D)...OH(A) configuration. The “D” and “A” H-bond lengths are 1.77 and 2.10 Å. The ΔIE_{QC}^{th} of OH(D) is worth -1.36 eV and that of OH(A) is $+0.14$ eV. The energy shifts are again non symmetric with respect to the IE_{QC}^{th} of the isolated OH.

The ammonia molecule can also be placed in an end-on position, to make a OH(d)...OH(a,D)...NH₃(A) configuration, with a “d” bond length of 2.64 Å and a “D” one of 1.84 Å. Interestingly we have produced a OH(a,D) hydroxyl making a double H-bond. The ΔIE_{QC}^{th} of OH(a,D) is $= -1.02$ eV, smaller in magnitude than that of OH(D) in the previous, bridge configuration.

S4. Experimental O 1s XPS spectra and their interpretation

We present in Figure S4 the experimental O 1s spectra of the (H,OH)-Si(001) surface at 300 K, at 130 K under vacuum, and then exposed to ammonia. The spectrum of (H,OH)-Si(001) recorded at 300 K (bottom curve) is fitted by a single Gaussian component positioned at a binding energy of 532.62 eV. The FWHM is 1.15 eV. H-bonds are not expected to be stabilized at this temperature.⁸ Therefore the line at 532.62 eV is characteristic of “isolated” OHs.

As soon as the temperature drops to 130 K (middle curve), the main component remains at the same position (532.64 eV) but broadens (FWHM=1.46 eV). The broadening may be due to stabilization of H bonds between hydroxyls. The effect OH pairing in SP patterns leads to a theoretical IE_{QC}^{th} splitting of 0.25 eV between OH(a) and OH(d).⁶ The OH pairing in CBP should lead to a still smaller splitting. The pairing of ODIM OH pairs leads to very large change in IE_{QC}^{th} (see Section S3), but we see no clear reflection of it in the experimental spectrum (we recall that the effect is asymmetric as the magnitude of the donor shift is greater than that of the acceptor one). In fact, complex H-bonded OH patterns are likely to form on the surface, that are difficult to take into account with cluster methods. In addition, relatively long-distance electrostatic effects between OHs can also complicate the picture. In addition to the main OH component, we need to introduce a Gaussian component at 534.30 eV. The binding energy shift is 1.70 eV with respect to the OH component at 532.62 eV, and this value is close to the ΔIE_{QC}^{th} of molecular water (1.9 eV). H₂O coming from the residual gas in the chamber is likely co-adsorbed on the surface during cooling in UHV. The component represents 9% of the spectral weight (i.e. ~0.05 ML). This is in good agreement with the increase in oxygen coverage to 0.57 ML.

When the (H,OH)-Si(001) surface is covered by molecular ammonia at 130 K, we observe sizeable changes in the spectrum (top curve of Figure S4). The coverage of H bonded ammonia

is in the range 0.22-0.37 ML. The spectrum can always be fitted by two Gaussians, but the small peak that accounts for the asymmetry at high binding energy is now positioned at 533.7 eV¹. In fact, the peak attributed to H₂O (at 534.3 eV) has disappeared. This suggests that the water molecules have been displaced by the ammonia molecules and is in line with the fact that the oxygen coverage has returned to 0.5 ML. Concerning the main component, it is strongly broadened (FWHM=1.63 eV) and significantly shifted to lower binding energy (532.30 eV). The large FWHM, much greater than that at 300 K (1.1 eV), suggests it encompasses two or more contributions. The spectrum can be fitted again by substituting the broad main component at 532.30 eV by a doublet consisting in two components of equal intensity, with a FWHM of 1.17 eV each. The resulting fit is shown in Figure S5. The high binding energy component of the doublet is only at +0.1 eV from that of the “isolated” OH, while the low binding energy one is at -0.72 eV. The QC calculations have shown that the magnitude of ΔIE_{QC}^{th} is much less for OH(A) than for OH(D) in the OH(D)...NH₃(A,D)...OH(A) configuration (see Table S1). To ease the comparison between theory and experiment, the theoretical energy positions of OH(A) and OH(D) are indicated by a red and a violet vertical bar, respectively. However, the large IE_{QC}^{th} splitting of 1.5 eV is greater than that obtained from the experimental fit (0.82 eV). This suggests that the H-bonding pattern of OHs is much more complex than the assumption of singly H-bonded OH(A) and OH(D). The green bar in Figure S5 represents the OH(a,D) component and the orange one that of a OH(d) component (see Table S1). To sum up, the global shift of the peak maximum to lower binding energy and its broadening can be explained qualitatively by the QC calculations, assuming a distribution of OH(D), OH(d), OH(a,D) and OH(A) hydroxyls.

¹ One could attribute this peak to an OH sitting close to a datively bonded ammonia which bears a Lewis charge of +1.

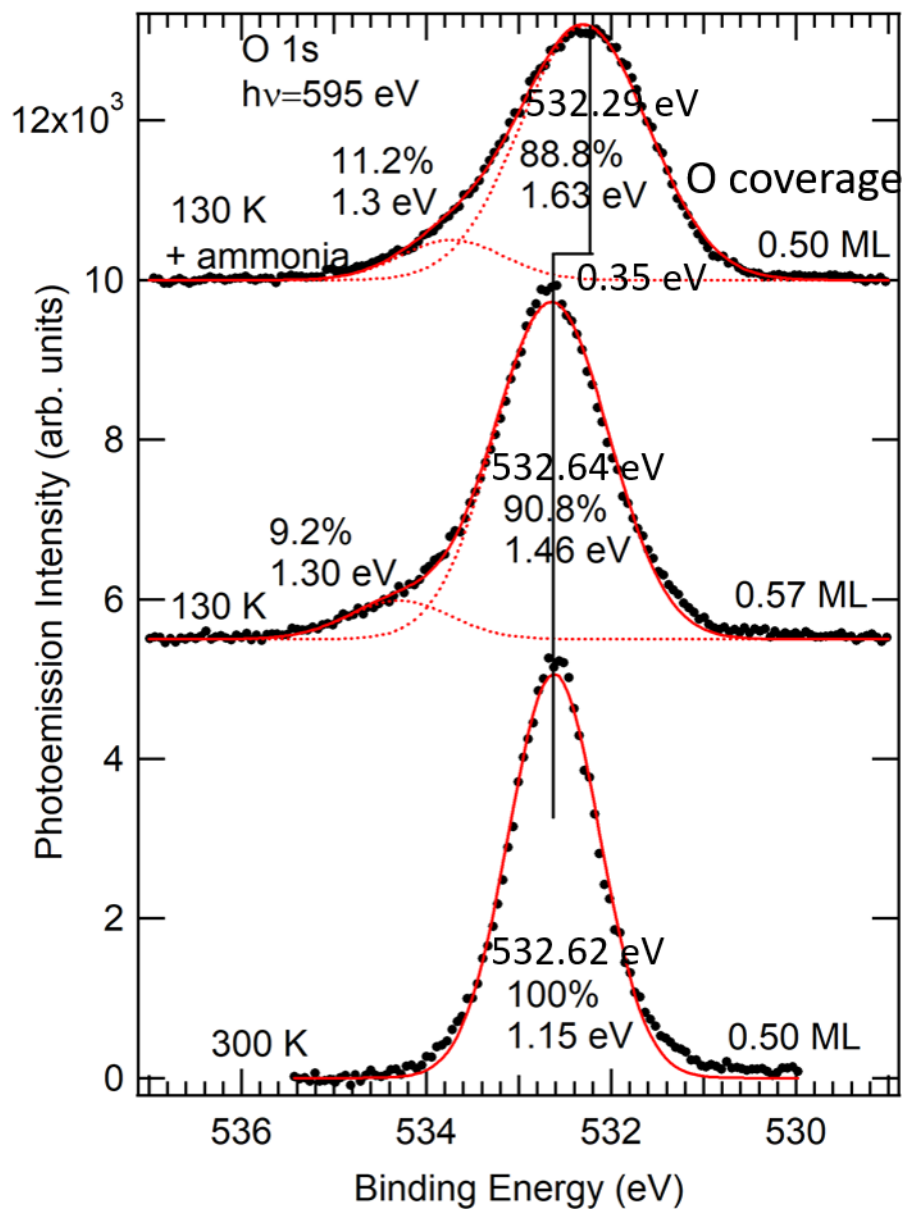


Figure S4. O 1s spectra measured at $h\nu=595$ eV. The spectra are normalized with respect to the O 1s intensity of the (H,OH)-Si(001) surface at 300 K. The oxygen coverage is indicated. Fits (solid red line) are also shown. The spectral weights (%) and FWHM of the Gaussian components (dotted red lines) are indicated.

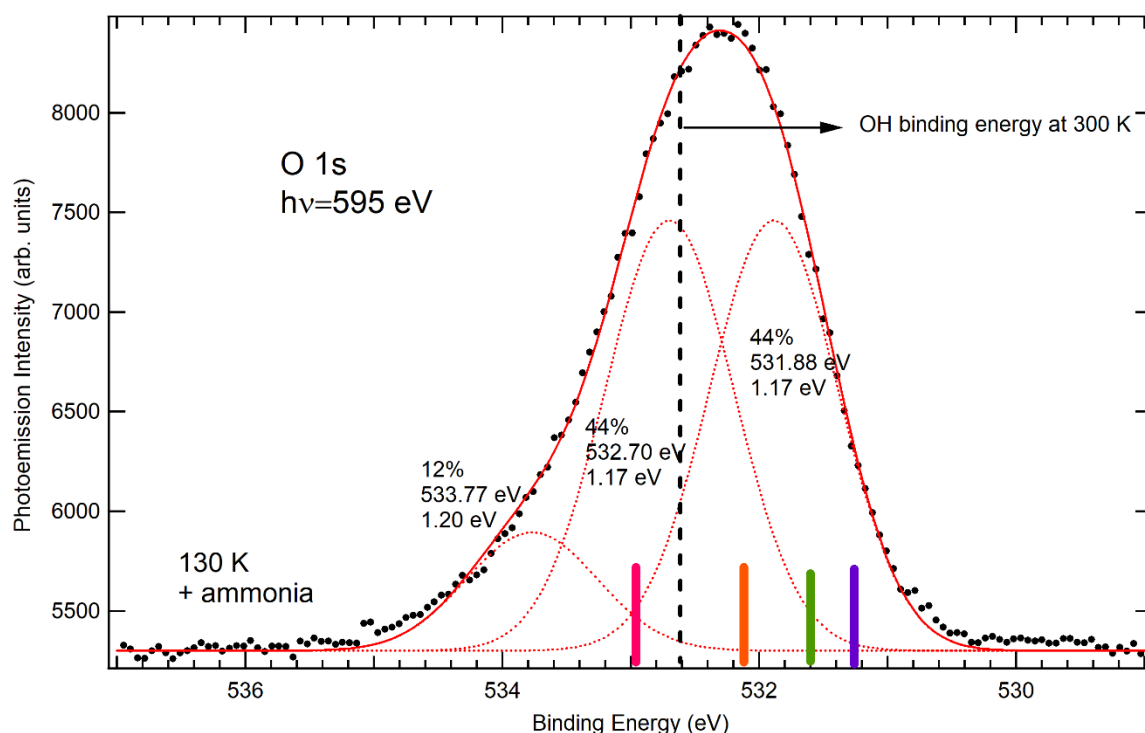


Figure S5. Normalized O 1s spectra of the (H,OH)-Si(001) surface at 130 K covered by ammonia. The dashed vertical line corresponds to the binding energy of the OHs at 300 K (non-interacting OHs). Fits (solid red line) are also shown. The spectral weights (%), energy positions and FWHM of the Gaussian components (dotted red lines) are indicated. The violet and fuschsia vertical bars indicate the ΔE_{QC}^{th} of the OH(D) and OH(A) in a OH(D)...NH₃(A,d)...OH(A) configuration (the reference is the dashed vertical line). Similarly, the orange and the green bars indicate the ΔE_{QC}^{th} of the OH(d) and OH(a,D) in a OH(d)...OH(a,D)... NH₃(A) configuration (see Table S1).

S5. Trimethylamine (TMA) adsorption on (H,OH)-Si(001) at 130 K

We show in Figure S6 the N 1s spectrum measured at $h\nu=455$ eV after exposure of (H,OH)-Si(001) to trimethylamine (TMA) under a pressure of 5.10^{-9} mbar for 140 s. Molecules can make H-bonds with the surface OHs. However, the most interesting observation is that 0.03 ML of molecules can make a dative bonding with the isolated dangling bonds (~ 0.04 ML) present on the surface. Thus, this observation is general for Lewis bases. This suggests that these molecules can dope the surface layers. A detailed report on TMA adsorption on (H,OH)-Si(001) at 130 K is in preparation.

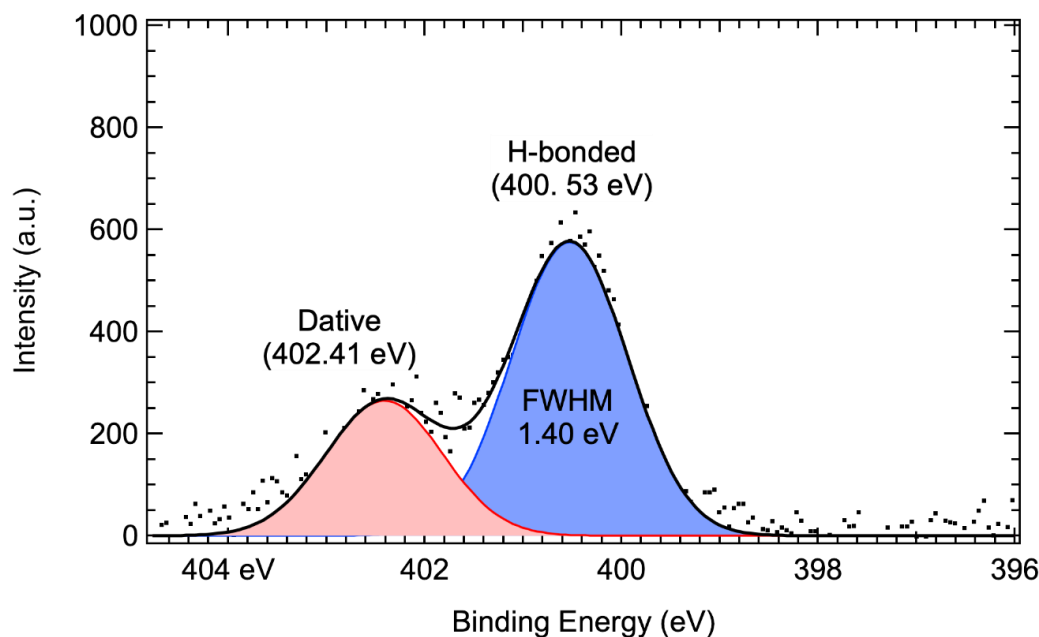


Figure S6: *N 1s* spectrum of the (H,OH)-Si(001) surface exposed to TMA at 130 K under a pressure of 5.10^{-9} mbar for 140 s. The photon energy is 455 eV. The blue component is attributed to TMA molecules making acceptor H-bonds with OHs and corresponds to a coverage of 0.07 ML, while the red component, attributed to dative bonding, corresponds to a coverage of 0.03 ML.

References

- (1) Tanuma, S.; Powell, C. J.; Penn, D. R. Calculations of Electron Inelastic Mean Free Paths. *Surf. Interface Anal.* **2005**, 37 (1), 1–14. <https://doi.org/10.1002/sia.1997>.
- (2) Gallet, J.-J.; Bournel, F.; Rochet, F.; Köhler, U.; Kubsky, S.; Silly, M.; Sirotti, F.; Pierucci, D. Isolated Silicon Dangling Bonds on a Water-Saturated $\langle n \rangle^{+}$ -Doped Si(001)- 2×1 Surface: An XPS and STM Study. *J. Phys. Chem. C* **115** (15), 7686–7693. <https://doi.org/10.1021/jp201262x>.
- (3) Bournel, F.; Gallet, J.-J.; Pierucci, D.; Khaliq, A.; Rochet, F.; Pietzsch, A. Hydrosilylation of Styrene on Water-Saturated Si(001)- 2×1 at Room Temperature. *J. Phys. Chem. C* **2011**, 115 (30), 14827–14833. <https://doi.org/10.1021/jp202913y>.
- (4) Gallet, J. J.; Bournel, F.; Rochet, F.; Köhler, U.; Kubsky, S.; Silly, M. G.; Sirotti, F.;

- Pierucci, D. Isolated Silicon Dangling Bonds on a Water-Saturated N⁺-Doped Si(001)-2 × 1 Surface: An XPS and STM Study. *J. Phys. Chem. C* **2011**, *115* (15), 7686–7693. <https://doi.org/10.1021/jp201262x>.
- (5) Mathieu, C.; Bai, X.; Bournel, F.; Gallet, J.-J.; Carniato, S.; Rochet, F.; Sirotti, F.; Silly, M. G.; Chauvet, C.; Krizmancic, D.; et al. Nitrogen 1s NEXAFS and XPS Spectroscopy of NH₃-Saturated Si(001)-2×1: Theoretical Predictions and Experimental Observations at 300 K. *Phys. Rev. B* **2009**, *79* (20), 205317. <https://doi.org/10.1103/PhysRevB.79.205317>.
- (6) Carniato, S.; Gallet, J.-J.; Rochet, F.; Dufour, G.; Bournel, F.; Rangan, S.; Verdini, A.; Floreano, L. Characterization of Hydroxyl Groups on Water-Reacted Si(001)-2×1 Using Synchrotron Radiation O 1s Core-Level Spectroscopies and Core-Excited State Density-Functional Calculations. *Phys. Rev. B* **2007**, *76* (8), 085321. <https://doi.org/10.1103/PhysRevB.76.085321>.
- (7) Garcia-Gil, S.; Arnau, A.; Garcia-Lekue, A. Exploring Large O 1s and N 1s Core Level Shifts Due to Intermolecular Hydrogen Bond Formation in Organic Molecules. *Surf. Sci.* **2013**, *613*, 102–107. <https://doi.org/10.1016/j.susc.2013.03.017>.
- (8) Larsson, C. U. S.; Johnson, A. L.; Flodström, A.; Madey, T. E. Adsorption of H₂O on Planar and Stepped Si(100): Structural Aspects. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **1987**, *5* (4), 842–846. <https://doi.org/10.1116/1.574322>.