Hydrophobic silica/H_2O interface studied by sum-frequency vibrational spectroscopy (SFVS)

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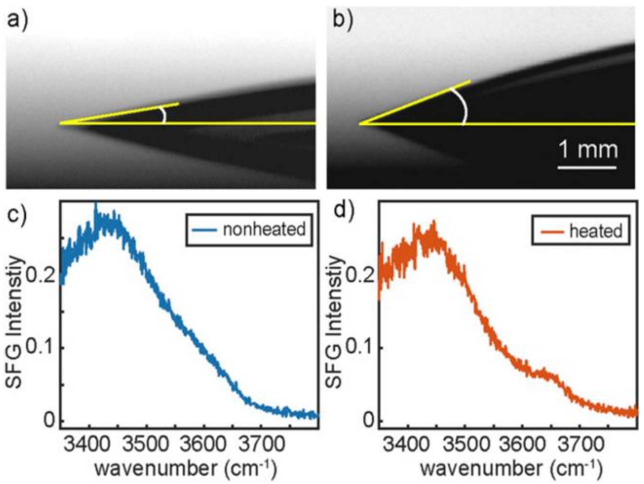
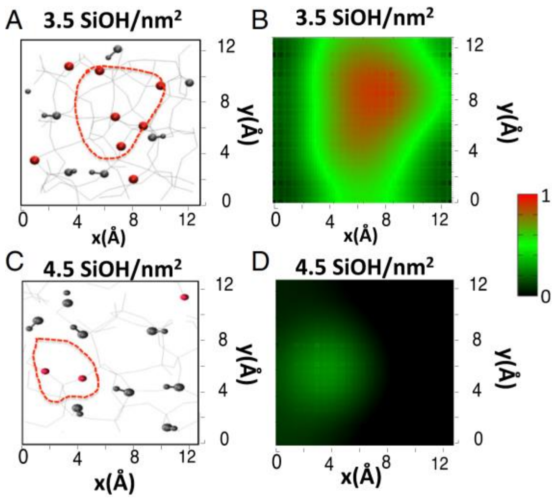
Introduction

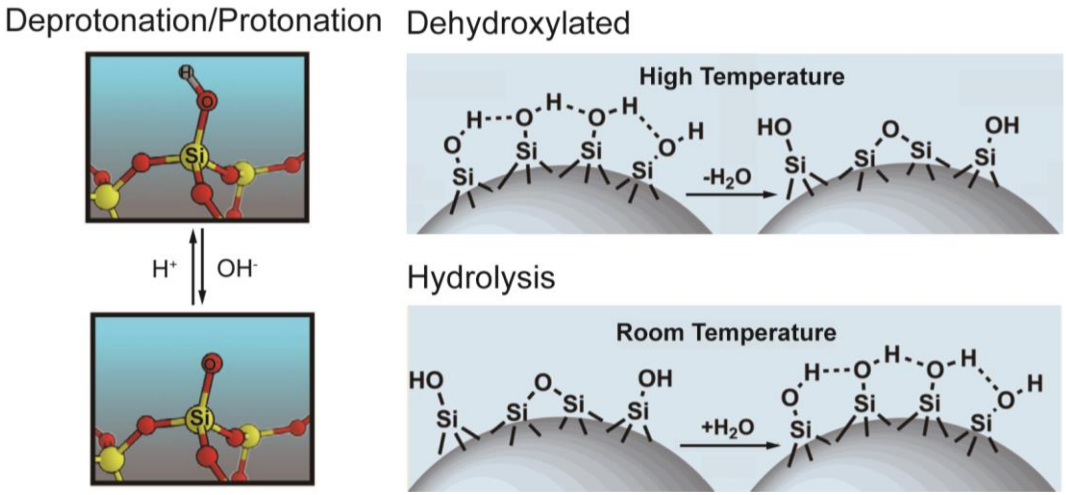
Hydrophobic and hydrophilic interactions are ubiquitous at metal, protein, and mineral oxide/water interfaces. The essential physical and chemical reactions involved are affected by the microscopic hydrophobic and hydrophilic interactions that are not easily extracted by macroscopic measurements such as the contact angle.



Correlation between molecular and macroscopic hydrophobicity



Hydrophobic patches at macroscopic hydrophilic silica/water interface



Surficial reactions at silica/water interface

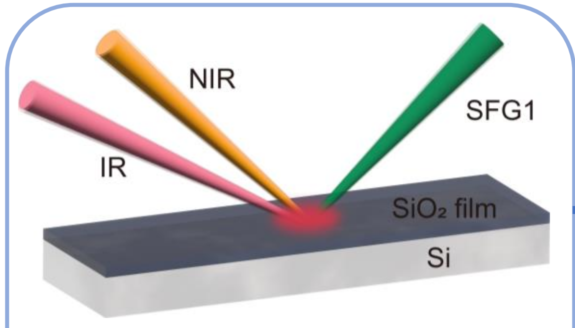
Results

Samples(SiO_2) treatment

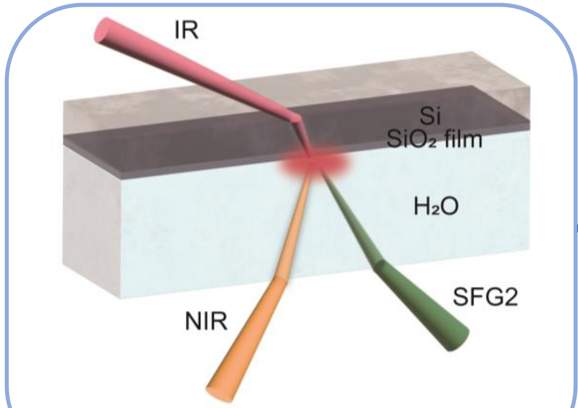
- ✓ Hydrophilic film :
  UV 30min and soaked in H_2SO_4 for 2h

- ✓ Hydrophobic film :
  Hydrophilic film annealed in vacuum at 1223K for 4h

SFVS experiment scheme

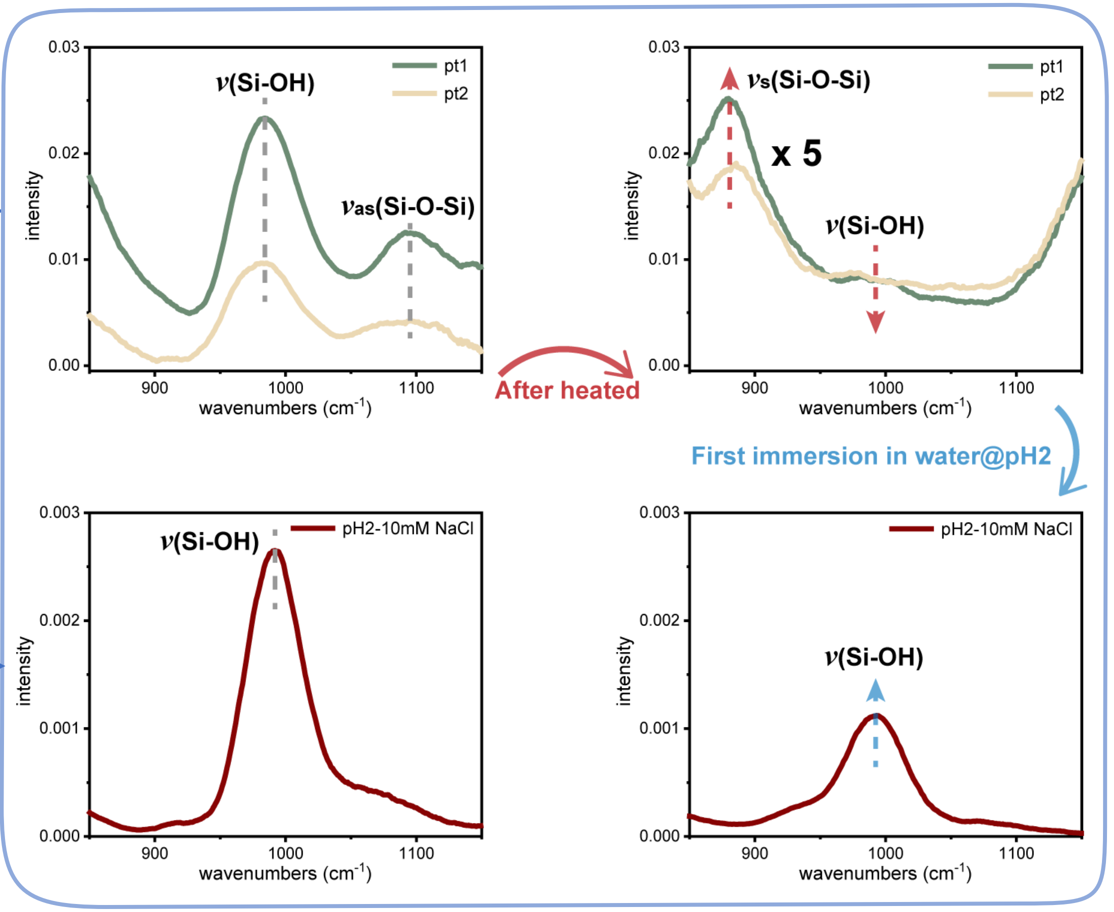


SFVS @ SiO_2/Air interface



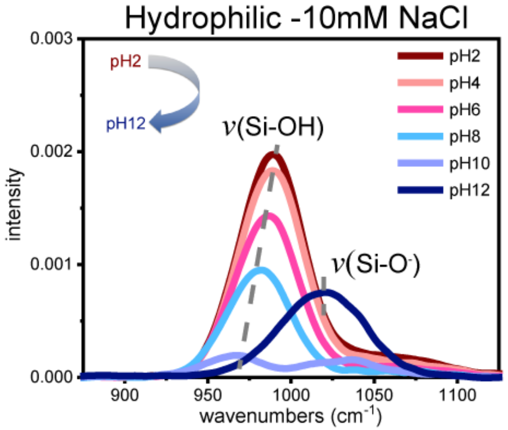
SFVS @ SiO_2/H_2O interface

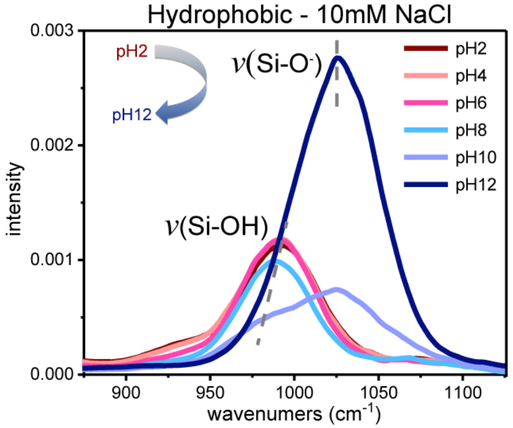
Hydrophilic vs. Hydrophobic



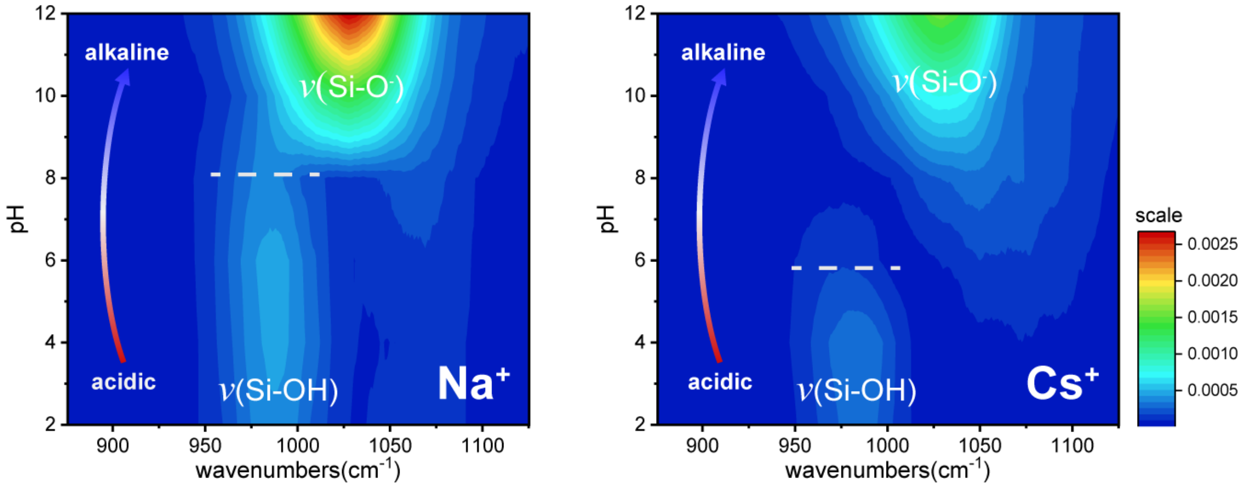
Results

Deprotonation — Hydrophilic vs. Hydrophobic





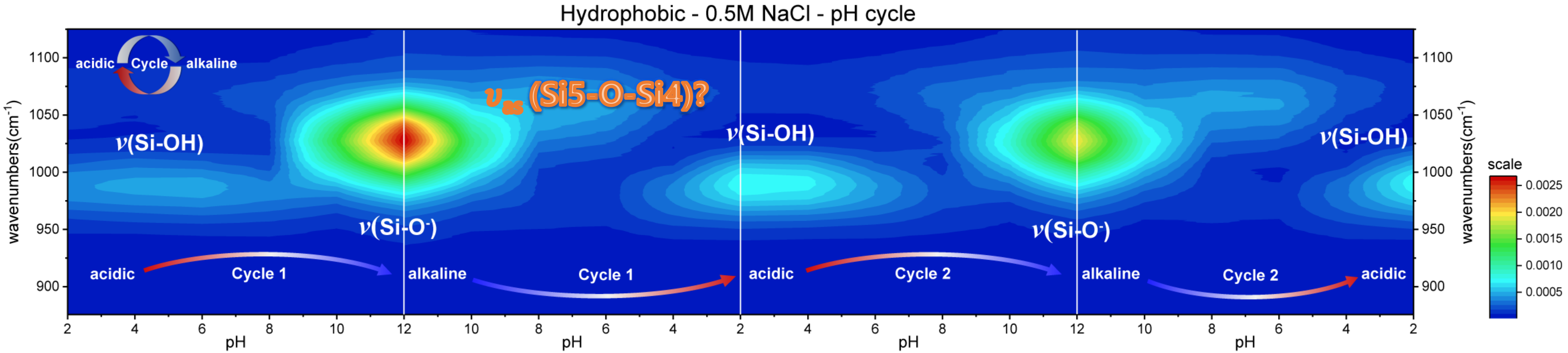
Cation effect @ hydrophobic SiO_2/ H_2O interface



The deprotonation process ($Si\text{-}OH \rightarrow Si\text{-}O^- + H^+$) is hindered (<pH8) at hydrophobic SiO_2/ H_2O interface in Na^+ but accelerated in Cs^+.

Results

pH cycle



☐ It takes multiple acid-base cycles to fully re-hydroxylate the SiO_2 surface.

☐ a ~1060cm-1 peak appears consistently in the protonation/deprotonation gap (neither Si-OH nor SiO^-) during the pH cycle, which is not observed at the hydrophilic SiO_2 /H_2O interface.

Summary

- Most of the Si-OHs are dehydroxylated and converted to metastable Si-O-Si rings at the hydrophobic SiO_2/Air interface.
- High-pKa Si-OHs with weak H-bond recover partly in water at pH2 because of the hydrolysis of metastable Si-O-Si rings.
- Cs^+ has a specific interaction with the hydrophobic SiO_2/H_2O interface, which promotes the deprotonation process.
- pH cycle results suggest that different protonation/deprotonation mechanisms at the hydrophobic SiO_2/H_2O interface.

References

1. E. H. G. Backus et al. In: *Proc. Natl. Acad. Sci* **116** (5 2019), p. 1520-1525.
2. A. J. Mcquillan et al. In: *Langmuir* **32**, (6 2016), p. 1568–1576
3. N. G. Green et al. In: *J. Colloid. Interf. Sci* **451**, (2015), p. 231-244.

Thank you