Sum-Frequency Generation Study of Divalent Ion Effects at Silica/Water Interface

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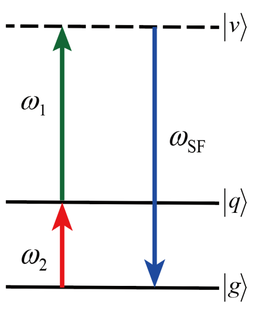
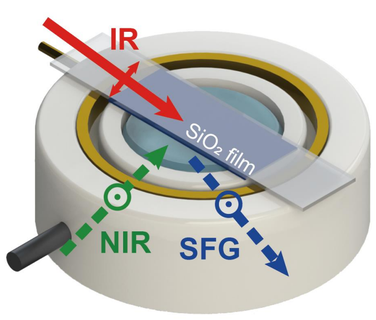
Introduction

- Ion adsorption at mineral/water interfaces is central to environmental chemistry, geochemistry, electrochemistry, and biological interfaces [1]. Divalent cations such as Ca^{2+} and Mg^{2+} are particularly important because their high charge density and strong hydration produce interfacial behavior distinct from monovalent ions [2]. At silica/water and quartz-related interfaces, Ca^{2+} adsorption can also promote carbonate enrichment and $CaCO_3$ nucleation [3].
- Negatively charged silica attracts cations and reorganizes the electrical double layer. SHG studies show that divalent electrolytes induce responses beyond simple point-charge electrostatics. Although Mg^{2+} and Ca^{2+} are strongly hydrated kosmotropes, weakly hydrogen-bonded OH features suggest disruption of interfacial hydrogen-bond networks, whose molecular origin remains unresolved.
- Here, in situ SFVS probes Si–O lattice vibrations at buried silica/water interfaces. We show that divalent ions perturb the oxide surface itself, causing pH- and concentration-dependent blue shifts of $Si–O^-$ modes. Experiments and DFT reveal weakened $Si–O^-$–water hydrogen bonding, heterogeneous dehydration, and locally hydrophobic-like environments.

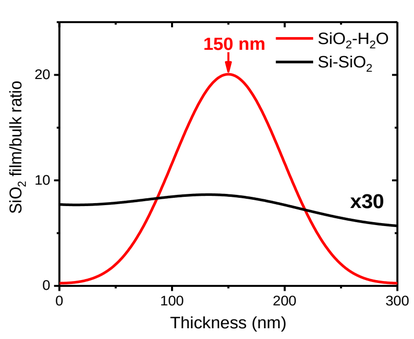
Methods



SFG energy level diagram



Experimental geometry



Film structure enhancement at the SiO_2 / water interface

Results

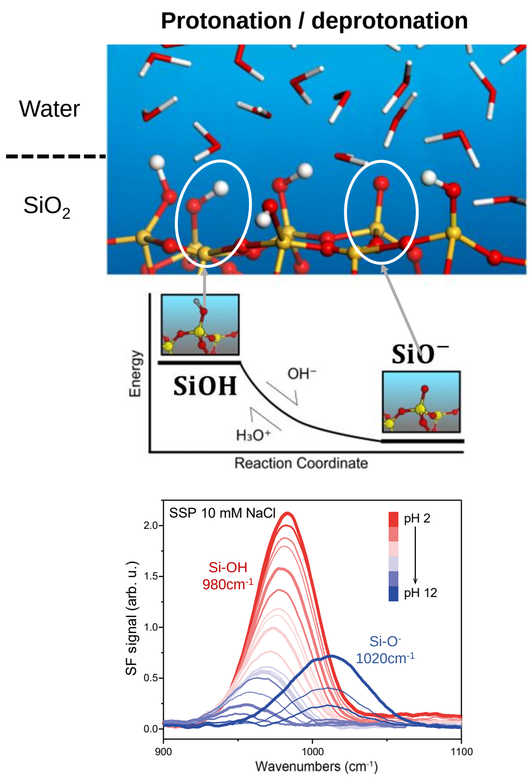


Fig. 1. Silanol deprotonation schematic and SFG spectra

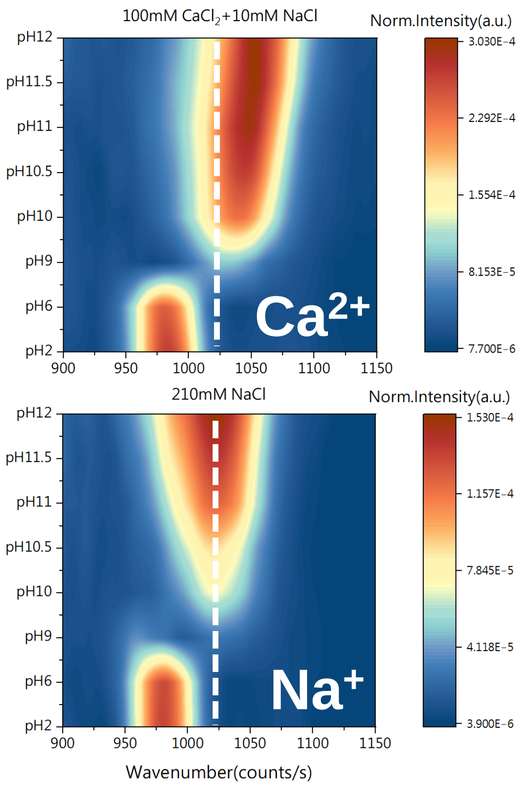


Fig. 2. Two-dimensional spectra of two solutions

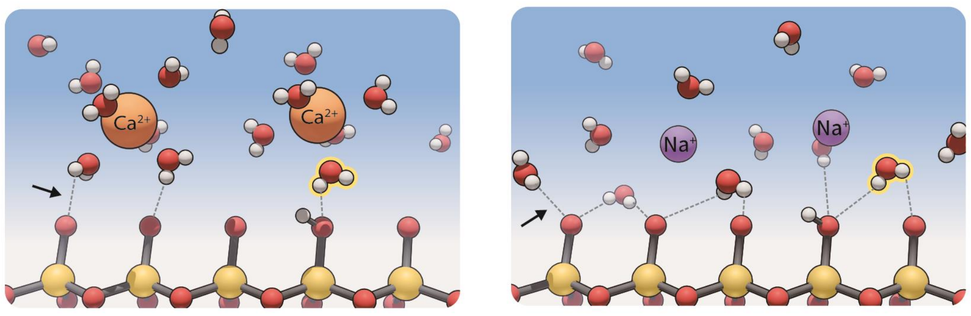


Fig. 3. Schematic diagram of adsorption of two ions

At high pH, divalent cations induce a blue shift in the Si-O⁻ peak, a phenomenon not seen with monovalent ions. This may be attributed to the strong hydration ability of divalent cations and their close adsorption to the silica surface via electrostatic interactions under alkaline conditions.

Results

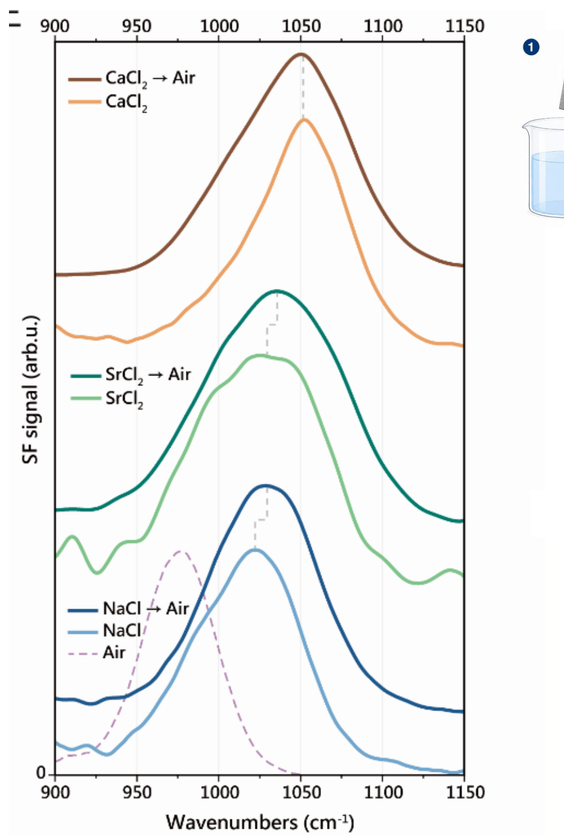


Fig. 4. SFG spectra of solid/liquid interfaces and solid/air interfaces after solution immersion.

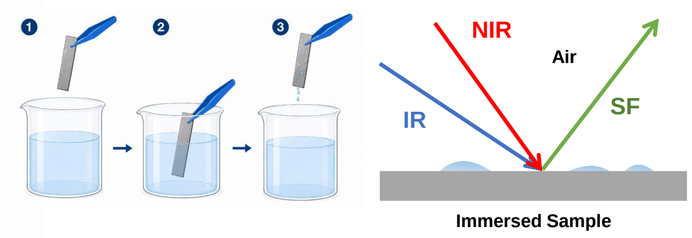


Fig. 5. Air interface experimental geometry

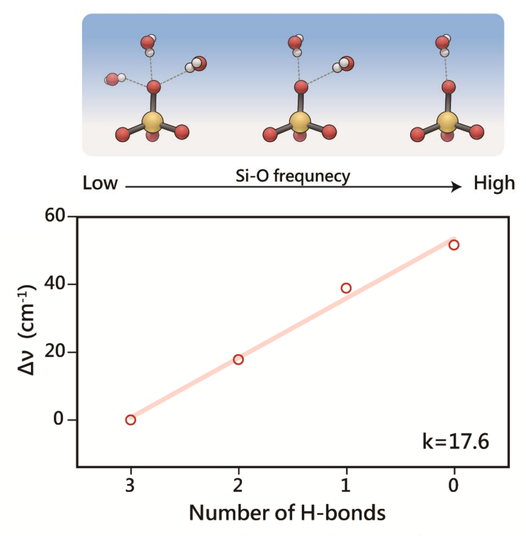
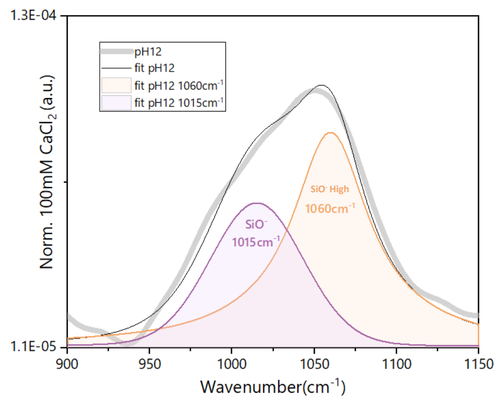


Fig. 6. DFT-calculated Si–O frequencies with 0–3 H-bonded water molecules

- In Fig. 4, $Si–O^-$ vibrational responses vary with divalent ions and interfacial environments. The blue shift follows the order $Na^+ < Sr^{2+} < Ca^{2+}$, indicating that stronger ion hydration more effectively disrupts $Si–O^-$–water hydrogen bonding. After air exposure, Na^+- and Sr^{2+}-treated surfaces show additional blue shifts, confirming that reduced hydrogen bonding leads to higher $Si–O^-$ vibrational frequencies. In contrast, the Ca^{2+} spectrum changes little, suggesting that Ca^{2+} already creates a partially dehydrated, air-like interface.
- In Fig. 6, DFT calculations show that fewer hydrogen-bonded water molecules shorten the Si–O bond and increase its stretching frequency. On average, the loss of one hydrogen bond corresponds to a $Si–O^-$ blue shift of 17.6 cm^{-1}.



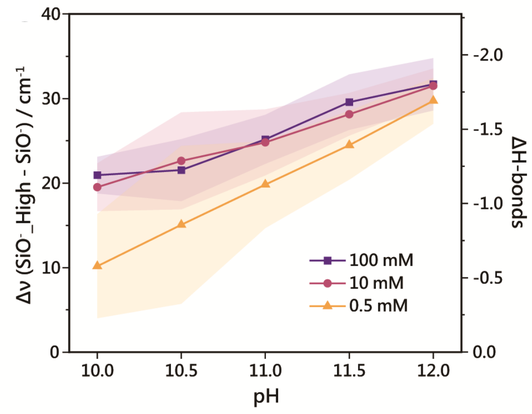


Fig. 7. Spectra Fitting of $CaCl_2$ Solutions

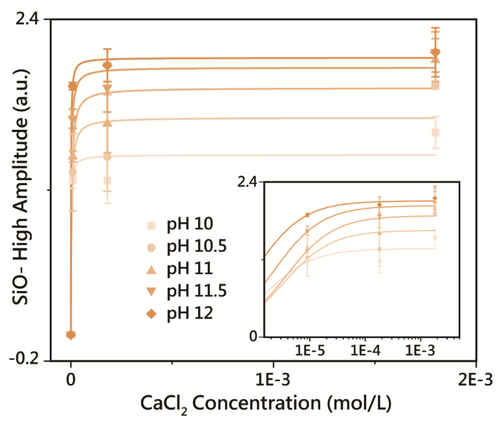


Fig. 8. Langmuir Model Fitting

ΔG ~ −31.8 kJ/mol

pH	A_m	ΔG (KJ/mol)
10	0.01368	-32.5441
10.5	0.01652	-30.7965
11	0.01878	-30.5173
11.5	0.02033	-31.7628
12	0.02107	-33.5753

Langmuir model: $A = \frac{A_m K C_e}{1 + K C_e}$

- SiO^- spectra in NaCl solutions of varying concentration and pH were fitted using two peaks.
- The magnitude of the blue shift suggests that, at pH 12, some SiO^- groups lose as many as 1.7 hydrogen bonds.
- The high-frequency peak reflects Ca^{2+} adsorption, from which the adsorption free energy was obtained.

Summary

- Both experimental results and theoretical calculations demonstrate that weaker hydrogen bonding of surface $Si–O^-$ groups leads to higher vibrational frequencies.
- Divalent cations compete with surface $Si–O^-$ groups for interfacial water, thereby reducing $Si–O^-$–water hydrogen bonding and causing a blue shift of the $Si–O^-$ peak. Cations with more compact hydration shells induce larger blue shifts, consistent with their stronger ability to perturb interfacial hydration.
- Langmuir fitting of the SFG spectra yields an adsorption free energy of approximately –31.8 kJ/mol for Ca^{2+} adsorption on the silica surface.

References: [1] **Backus, E.H.G. et al., 2021.** *Angewandte Chemie International Edition*, **60**, 10482–10501.
[2] **Patra, A. et al., 2020.** *The Journal of Physical Chemistry C*, **124**, 3028–3036.
[3] **Li, Q. et al., 2014.** *Environmental Science & Technology*, **48**, 5745–5753.