FEATURE ARTICLE

Unified Molecular Picture of the Surfaces of Aqueous Acid, Base, and Salt Solutions

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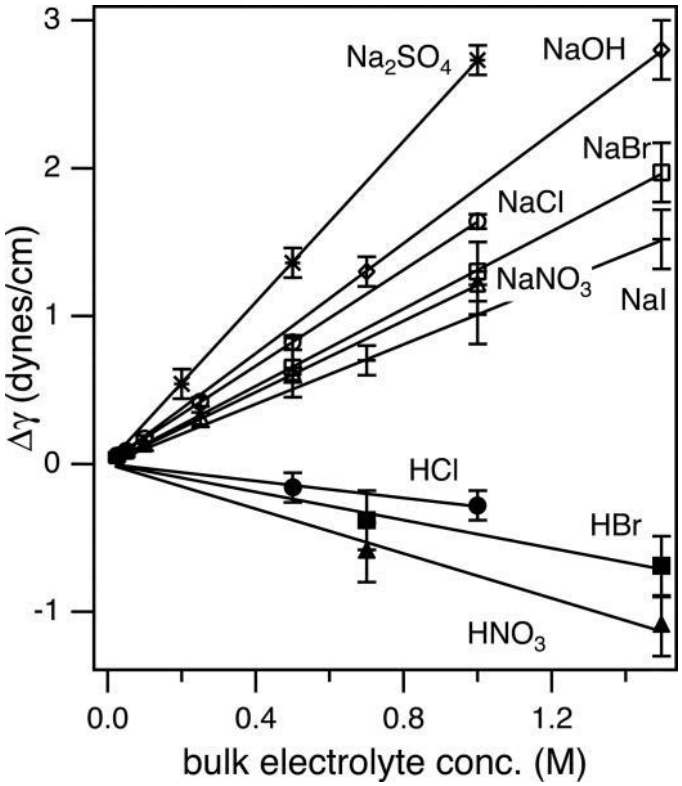
Introduction

Salts and bases increase the surface tension of water

Monovalent inorganic acids decrease it

In present paper

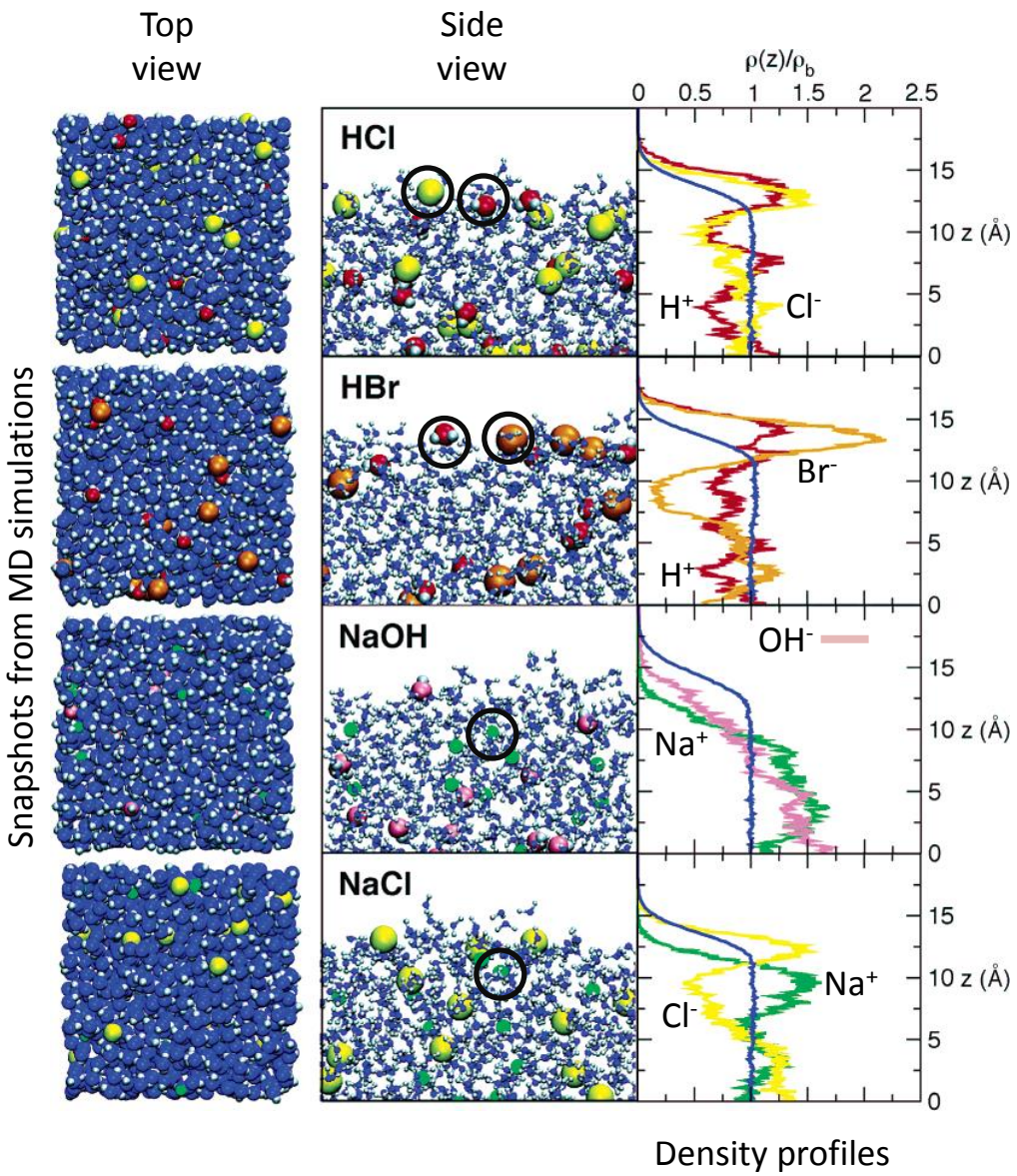
- ✓ MD simulations in slab geometries and VSFG of concentrated acid, base, and salt solutions
- ✓ A unified picture with molecular resolution of the air/solution interface of simple aqueous inorganic electrolytes



Laurel M. Pegram, M. Thomas Record, Jr

Hydronium cations and large polarizable anions exhibit a propensity for the interface

MD simulations of 1.2 M solutions of HCl, HBr, NaOH, NaCl



HCl: both hydronium cations and chloride anions penetrate into the air/solution interface (enhancement of surface ions)

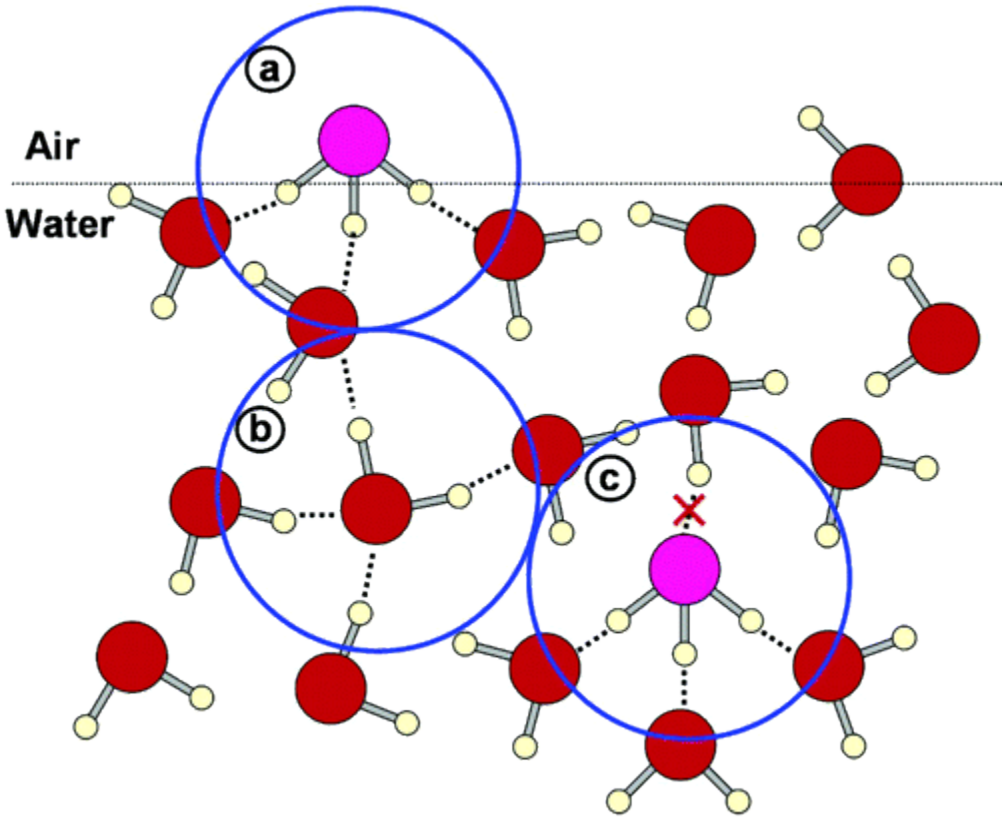
HBr: bromide is more surface enhanced

NaOH and NaCl: sodium cations are repelled from the surface and never penetrate its topmost layer

OH^- - weakly repelled from the surface

Cl^- - weakly attract to the surface

The hydronium cations are preferentially oriented at the surface, with hydrogens pointing toward the aqueous phase and oxygen toward the air



Poul B. Petersen, Richard J. Saykally,
J. Phys. Chem. B, 2005, *109* (16)

Surface tension

Surface tension increases compared to neat water - indicating a net depletion of ions from the interface

Surface tension decreases - a net enrichment of ions in the interfacial layer

Salts such as alkali halides (NaCl, NaBr, NaI) and bases such as alkali hydroxides (NaOH) increase the surface tension of water, whereas acids such as HCl, HBr, or HI slightly decrease it

The density of free OH bonds is higher in the interfacial region than in the bulk.

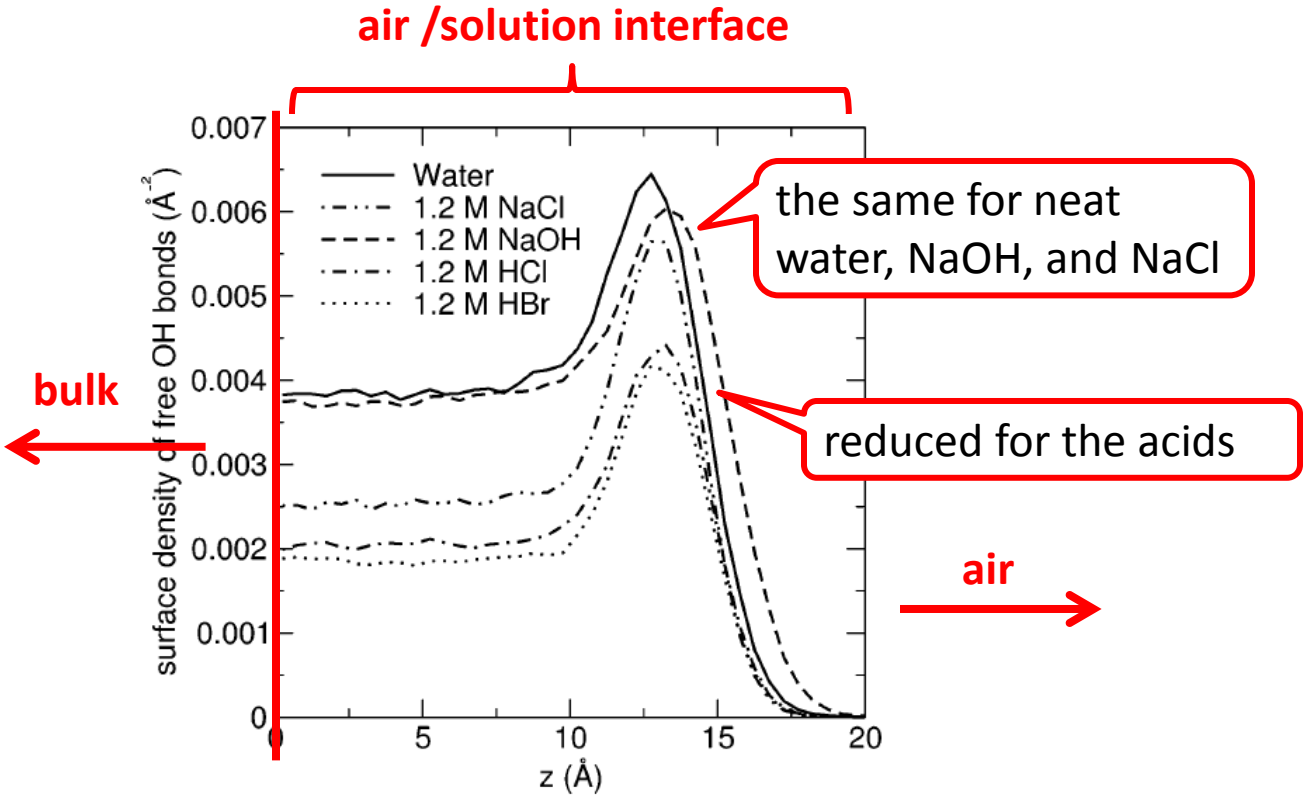
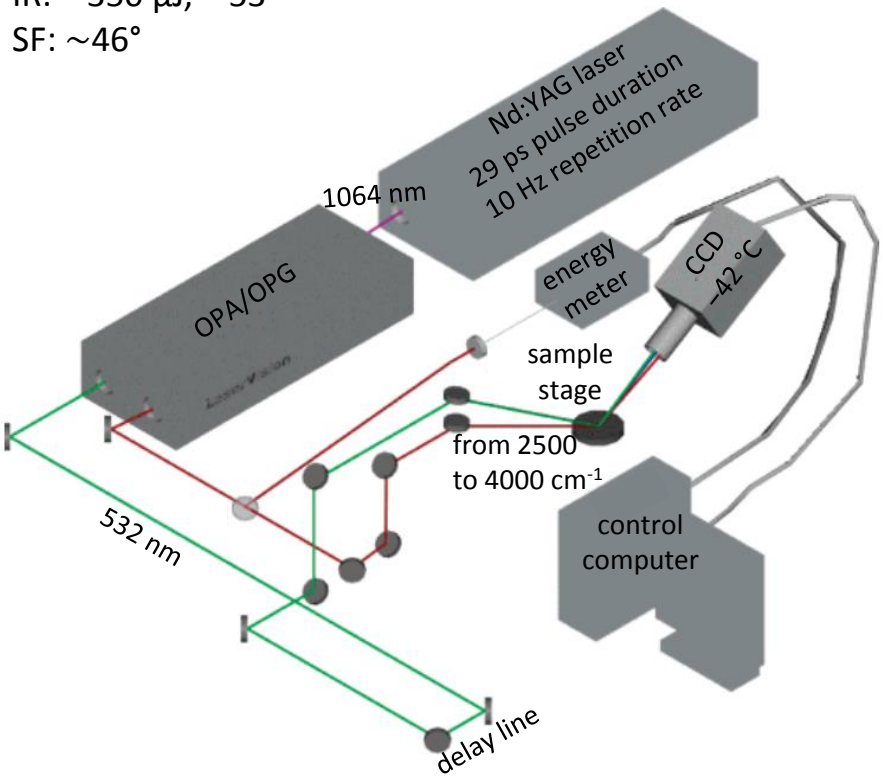


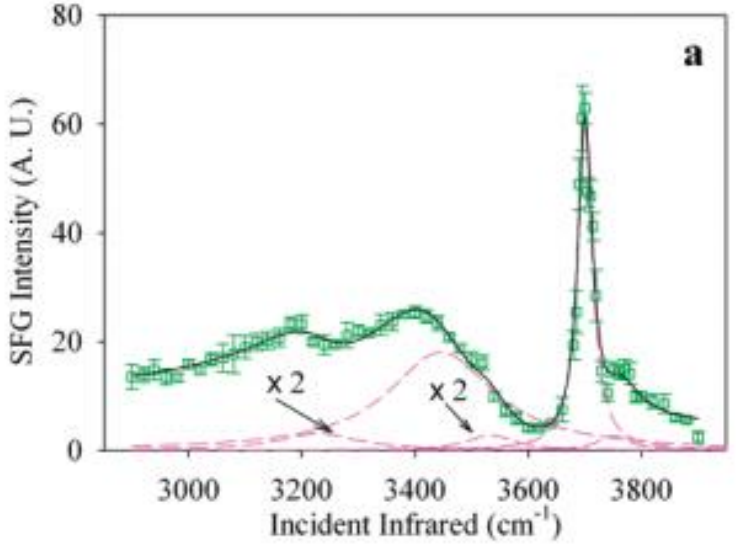
Figure 3. Surface density (number per unit area) of free OH bonds (i.e., water OH bonds that are not hydrogen-bonded to another water molecule or ion) for neat water, HCl, HBr, NaOH, and NaCl, from the center of the slab to the surface.

Experimental Method

The energies and the input angles

532 nm: ~1.1 mJ, ~45°
IR: ~350 μJ, ~53°
SF: ~46°





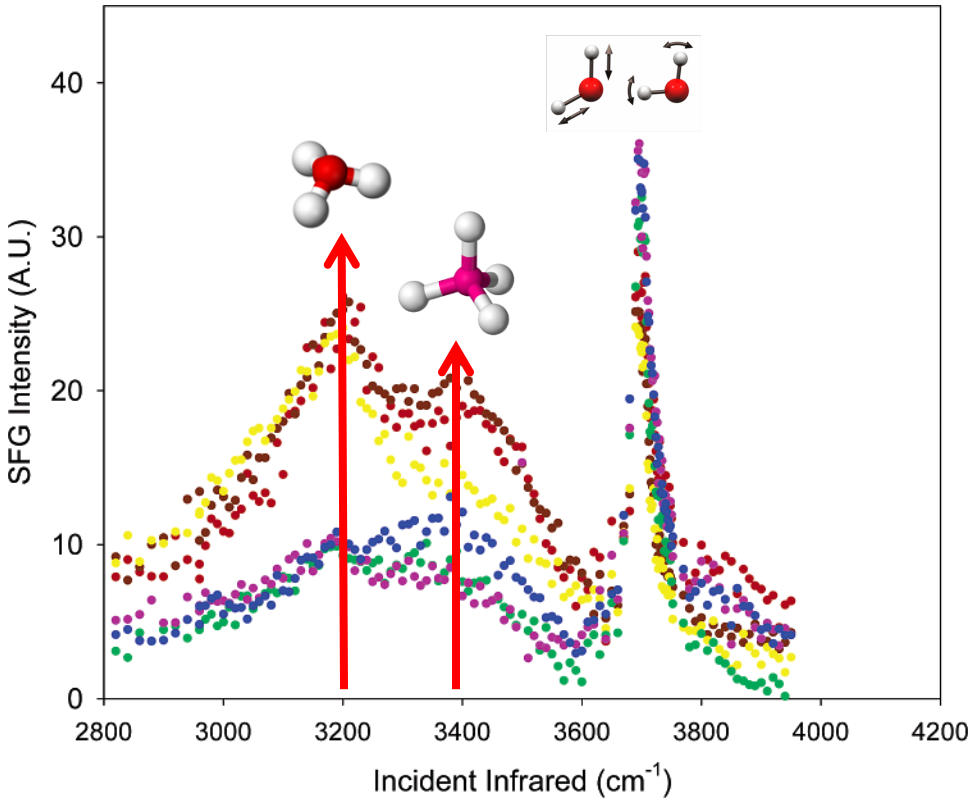
3250 cm^{-1}: the strong intermolecular coupling of water molecule symmetric stretch vibrations within a symmetric hydrogen-bonding network

3450 cm^{-1}: the weaker coupling of the water molecule stretching modes, which is associated with a more disordered and asymmetric 4-coordinate (tetrahedral) hydrogen-bonding network

3700 cm^{-1}: the free OH

Liu et al, J. Phys. Chem. B, 2004, *108* (7)

VSFG surface spectra for 1.2 M HCl, HBr, HI, NaOH, NaCl



ssp polarized

- 1.2 M HI
- 1.2 M HBr
- 1.2 M HCl
- 1.2 M NaCl
- 1.2 M NaOH
- Neat Water

3200 cm^{-1} - response from hydronium

3400 cm^{-1} - oscillating dipoles about the tetra coordinated interfacial water molecules in these acid solutions ($I^- \sim Br^- > Cl^-$)

3700 cm^{-1} - the dangling OH of water

3700 cm^{-1} band increase results on sodium halide air/solution interfaces

3200 cm^{-1} increases and the 3700 cm^{-1} decreases are unique to the acids and are not observed for the base and the sodium salt

Summary

- The air/solution interface of simple inorganic electrolytes observed by MD and VSFG

- Ions can play an active role at the interface and strong ionic specificity in surface propensity

- Monovalent inorganic acids, where both cations and anions exhibit a propensity for the air/solution interface

- In bases and salt solutions cations are repelled from the interface and anions show a varying surface affinity