



# Cation Effects On Interfacial Water Organization Of Aqueous Chloride Solutions.

## I. Monovalent Cations: $\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ , And $\text{NH}_4^+$ .

Soft-matter Optical Spectroscopy Laboratory

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2014.06.24

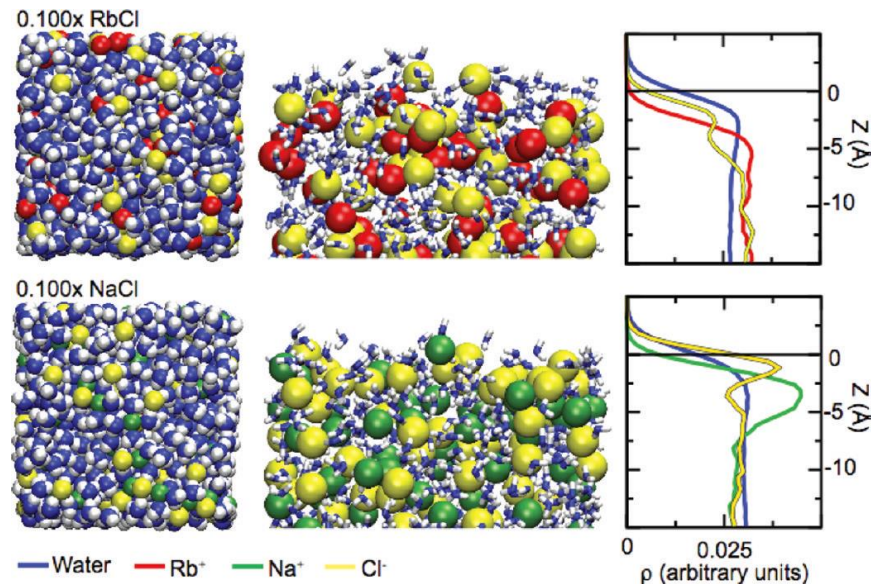


# Introduction

Here we have restricted our attention to atomic anions which, according to simulations, can be either repelled from or adsorbed to the interface, depending on the ion. A similar analysis could be carried out for cations, but since inorganic cations are generally repelled from the interface, their behavior does not appear to contradict the conclusion drawn from a straightforward analysis based on the Gibbs adsorption equation. Note, however, that, for electroneutrality of the interfacial region, the Gibbs surface excesses of the anions and cations must be equal. For this reason, there is a subsurface sodium peak in the case of, e.g., NaBr or NaI solutions.<sup>132</sup>

Jungwirth & Tobias, *Chem. Rev.* 2006

Hemminger, *J. Phys. Chem. C* 2012



The appearance of an enhancement in the halide/cation ratios in integrated density profiles can result not only from anion enhancement but also from cation depletion.

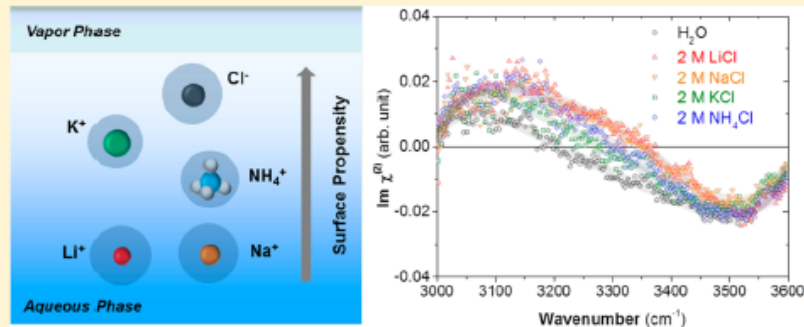
# Cation Effects on Interfacial Water Organization of Aqueous Chloride Solutions. I. Monovalent Cations: $\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ , and $\text{NH}_4^+$

Wei Hua, Dominique Verreault, Zishuai Huang, Ellen M. Adams, and Heather C. Allen\*

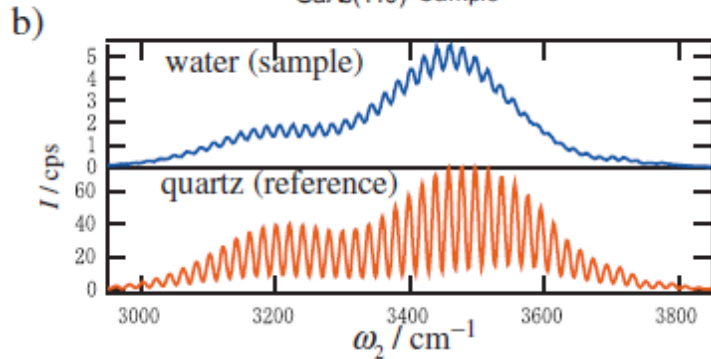
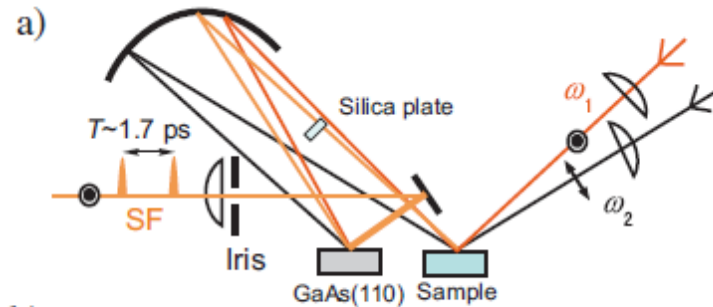
Department of Chemistry & Biochemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210, United States

## Supporting Information

**ABSTRACT:** The influence of monovalent cations on the interfacial water organization of alkali ( $\text{LiCl}$ ,  $\text{NaCl}$ , and  $\text{KCl}$ ) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ) salt solutions was investigated using surface-sensitive conventional vibrational sum frequency generation (VSFG) and heterodyne-detected (HD-)VSFG spectroscopy. It was found in the conventional VSFG spectra that  $\text{LiCl}$  and  $\text{NH}_4\text{Cl}$  significantly perturb water's hydrogen-bonding network. In contrast,  $\text{NaCl}$  and  $\text{KCl}$  had little effect on the interfacial water structure and exhibited weak concentration dependency. The  $\text{Im } \chi_s^{(2)}(\omega_{\text{IR}})$  spectra from HD-VSFG further revealed that, for all chloride solutions, the net transition dipole moments of hydrogen-bonded water molecules ( $\text{O} \rightarrow \text{H}$ ) are oriented more toward the vapor phase relative to neat water. This suggests the presence of an interfacial electric field generated from the formation of an ionic double layer in the interfacial region with a distribution of  $\text{Cl}^-$  ions located above the countercations, in agreement with predictions from MD simulations. The magnitude of this electric field shows a small but definite cation specificity and follows the order  $\text{Li}^+ \approx \text{Na}^+ > \text{NH}_4^+ > \text{K}^+$ . The observed trend was found to be in good agreement with previously published surface potential data.

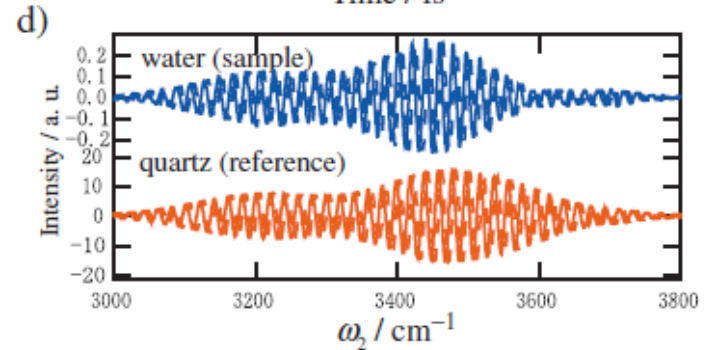
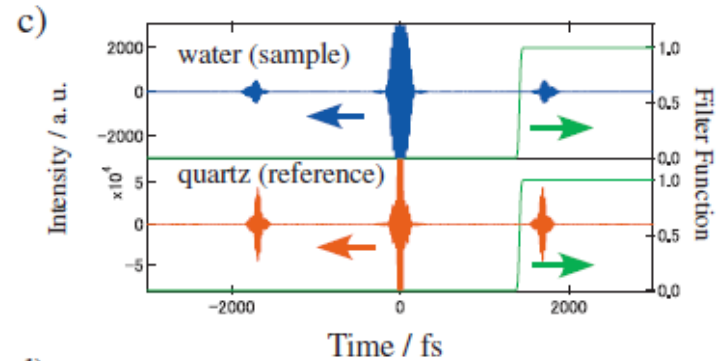


# Heterodyne-Detected VSFG Spectroscopy



$$I = |\tilde{E}_{\text{tot}}(\omega)|^2 = |\tilde{E}_{\text{sample}}|^2 + |\tilde{E}_{\text{LO}}|^2 + \tilde{E}_{\text{sample}}\tilde{E}_{\text{LO}}^* \exp(i\omega T) + \tilde{E}_{\text{sample}}^*\tilde{E}_{\text{LO}} \exp(-i\omega T).$$

» HD-VSFG: vis 300  $\mu\text{J}$ ; IR 10  $\mu\text{J}$



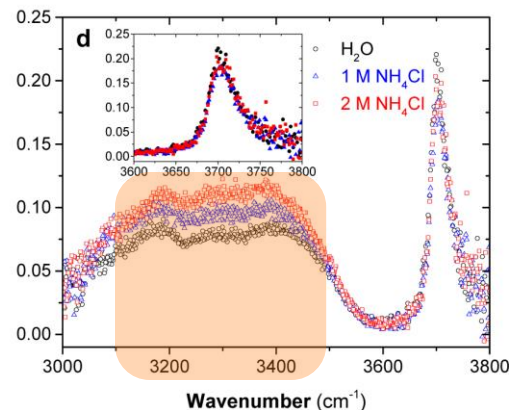
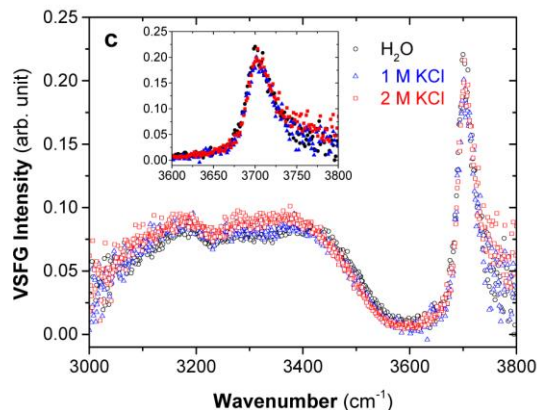
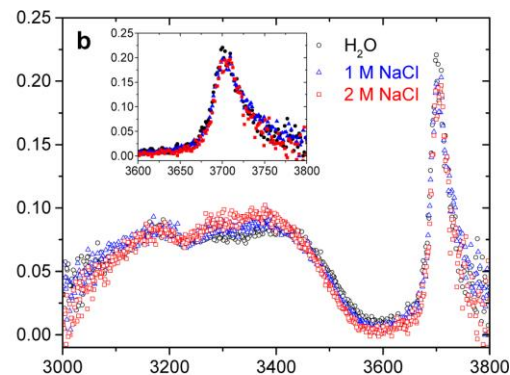
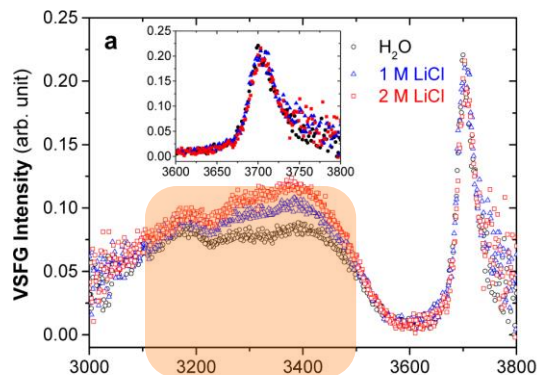
# VSFG of air/aqueous interfaces of 1 & 2 M chloride salt solutions

## NaCl and KCl

The presence of a weak interfacial field due to  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cl}^-$  repelled from the surface.

## LiCl and $\text{NH}_4\text{Cl}$

An uneven increase in intensity in the broad OH-bonded region from 3100 to 3500  $\text{cm}^{-1}$

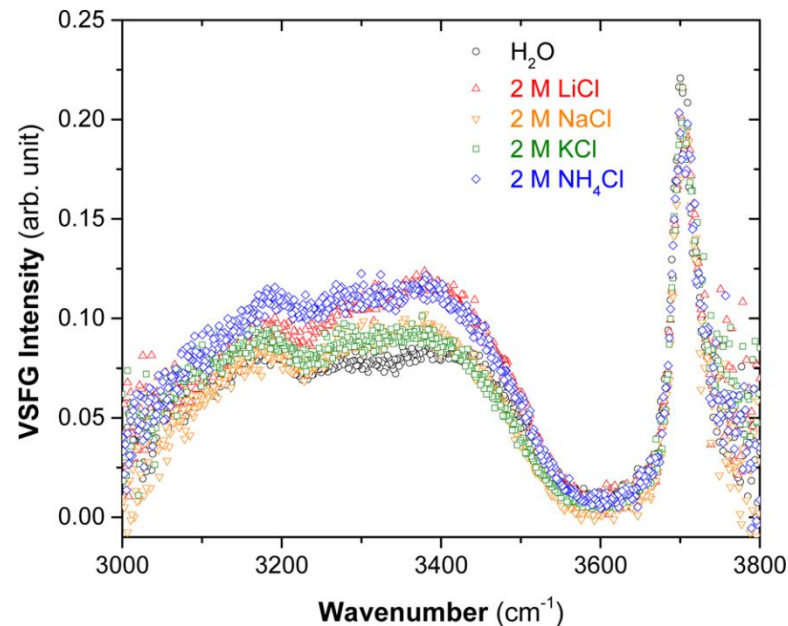


# Comparison between conventional VSFG spectra

A weak cation specificity in the perturbation of interfacial water molecules by monovalent cations following the order (in OH-bonded region):



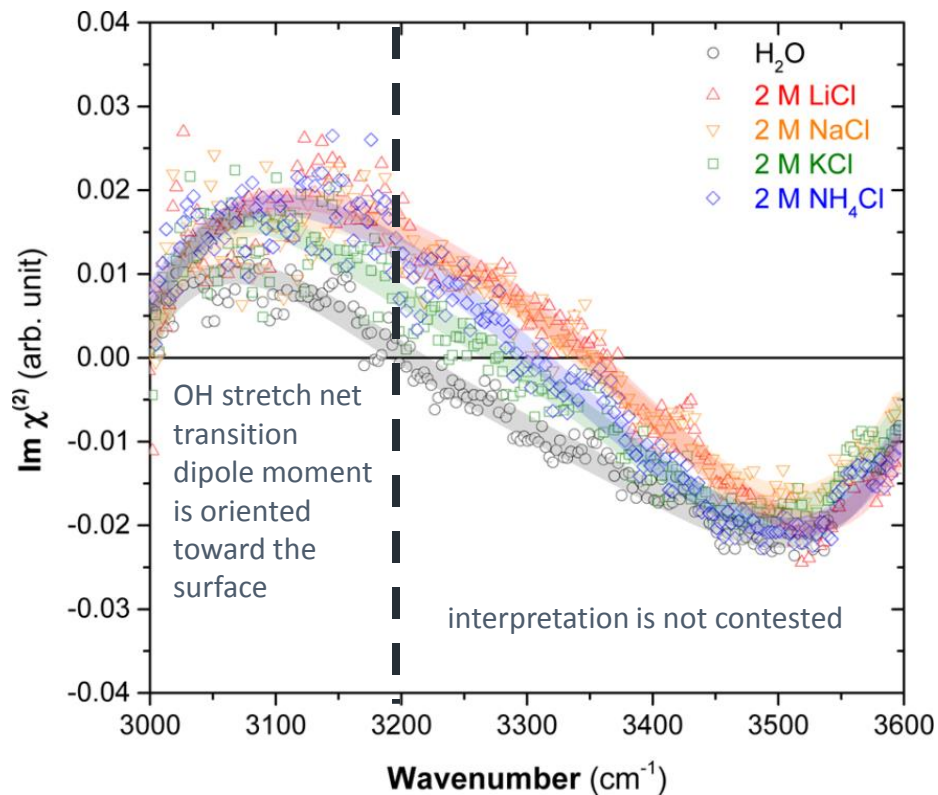
The intensity of the dangling OH peak doesn't change.





# Comparison between $\text{Im } \chi_s^{(2)}(\omega_{\text{IR}})$ spectra of air/aqueous interfaces

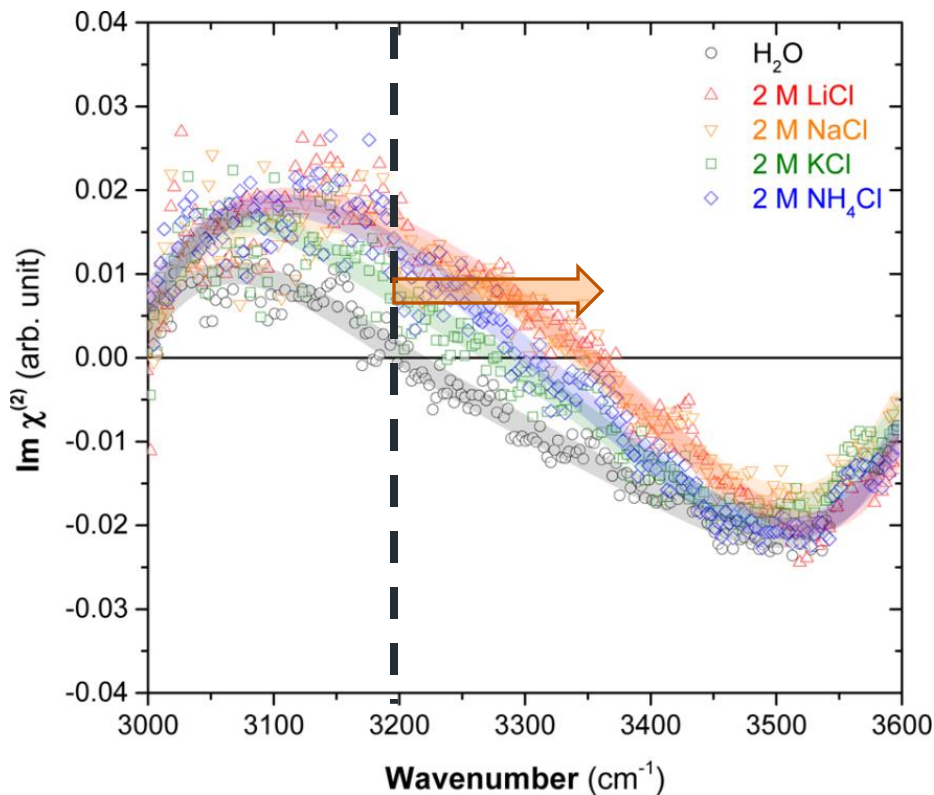
HD-VSFG directly provides the sign and the net orientation of the water OH transition dipole moment of SFG-active OH vibrational stretching modes.



# Comparison between $\text{Im } \chi_s^{(2)}(\omega_{\text{IR}})$ spectra of air/aqueous interfaces

The overall positive enhancement can be interpreted physically by the generation of a positive (here the E-field direction is defined going from positive to negative charge distributions) electric field induced by an ionic double layer formed between  $\text{Cl}^-$  anions located predominantly above their counteranions, closer to the surface. The presence of this ion-induced electric field, in turn, leads to a reorganization of the hydrogen-bonding network and to the reorientation of more interfacial water molecules with their net OH transition dipole moment now preferentially directed toward the surface.

The 3100-3500  $\text{cm}^{-1}$  region definitely reveals the presence of a small cation effect on the magnitude of the interfacial electric field that follows the order:





# Conclusions

- » The influence of LiCl (1<sup>st</sup> time), NaCl, KCl, and NH<sub>4</sub>Cl on interfacial water organization of aqueous chloride solutions
- » VSFG shows significant affect with LiCl and NH<sub>4</sub>Cl
- »  $\text{Im } \chi_s^{(2)}(\omega_{\text{IR}})$  shows a small cation-specific effect for all cations relative to the neat water
- » The positive enhancement of the  $\text{Im } \chi_s^{(2)}(\omega_{\text{IR}})$  signal follows the order  $\text{Li}^+ \approx \text{Na}^+ > \text{NH}_4^+ > \text{K}^+$
- » Cl<sup>-</sup> ions are always located above the countercations in contrast with previously reported HD-VSFG data (direction of the electric fiel)

