

# Interfacial Water Structure and Effects of $Mg^{2+}$ and $Ca^{2+}$ Binding to the COOH Headgroup of a Palmitic Acid Monolayer Studied by Sum Frequency Spectroscopy

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## Abstract

The interfacial hydrogen-bonding network that uniquely exists in between a palmitic acid (PA) monolayer and the underneath surface water molecules was studied using vibrational sum frequency generation (VSFG) spectroscopy.

Perturbations due to cation binding of  $Mg^{2+}$  and  $Ca^{2+}$  were identified

the polar ordering of the interfacial water molecules was observed under the influence of the surface field of dissociated PA headgroups.

negatively charged PA headgroups induces considerable polar ordering on the interfacial water molecules relative to the neat water surface without the PA film.

$Ca^{2+}$  was observed to have the greater impact on the interfacial hydrogen-bonding network relative to  $Mg^{2+}$ , consistent with the greater binding affinity of  $Ca^{2+}$  toward the carboxylate group relative to  $Mg^{2+}$  and thereby modifying the interfacial charge

At high-salt concentrations, the already disrupted hydrogen-bonding network reorganizes and reverts to its original hydrogen-bonding structure as that which appeared at the neat salt solution surface without a PA monolayer.

# Introduction

- Vicinal water molecules differ to the bulk water  
(density, specific heat, viscosity, and other physical properties)
  
- Advantage of Langmuir monolayers :
  - reflection of real biological and atmospheric aerosol processes
  - easy manipulation of experimental parameters  
(surface pressure, molecular coverage, film morphology)
  
- Strong point of vibrational sum frequency generation (VSFG) spectroscopy :
  - study of Interfacial hydrogenbonded water structure at interfaces
  - reseach on Hydrogenbonded water structure at buried interfaces

this study provide :

water molecular structure of interfacial hydrogen-bonding network underneath a palmitic acid ( $C_{16}$ ; PA) monolayer

- under Influence of two salts  $MgCl_2$  and  $CaCl_2$
- by varying the cation **concentrations**

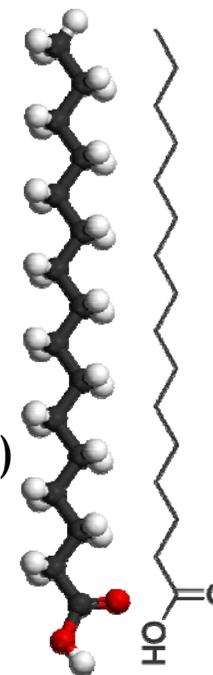
Perturbations of interfacial hydrogen-bonding network :

- influence of the **surface field** of dissociated PA headgroups
- $Mg^{2+}$  and  $Ca^{2+}$  **binding** effects at a near neutral pH (6.0)
- Surface charge **neutralization** effect

# Experimental Section

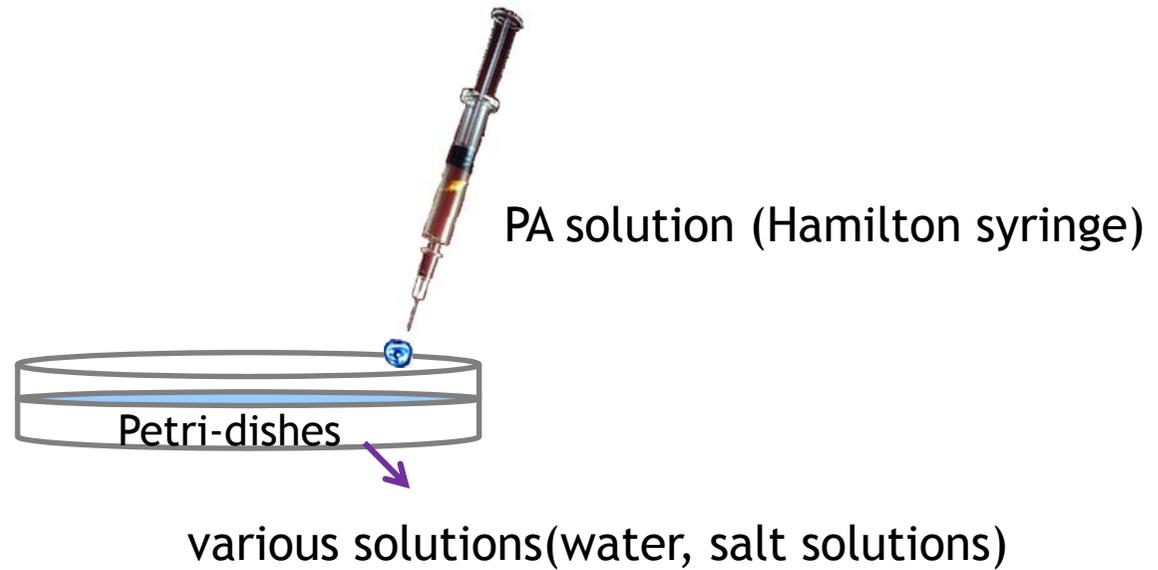
## Materials

- Palmitic acid ( $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$ ) solution :  $\sim 1.5$  mM (by chloroform)  
(the majority of the PA headgroups is protonated (99.8%) at PH 6.0)
- Salt solutions :
  - Magnesium chloride hexahydrate ( $\text{MgCl}_2(\text{H}_2\text{O})_x$ )
  - Calcium chloride dihydrate (by deionized water, pH 6.0)
- Filter out impurities(organic contaminants ):
  - Twice
  - Whatman Carbon-Cap activated carbon filter
- Concentrations :
  - Mohr titration technique  
(silver nitrate(a titrant ) and potassium chromate(indicator))
  - 0.1, 0.3, 1.5, and 1.8 M (molarity) (by dilution)
  - 2.6 M  $\text{Mg}^{2+}$  (by evaporation)

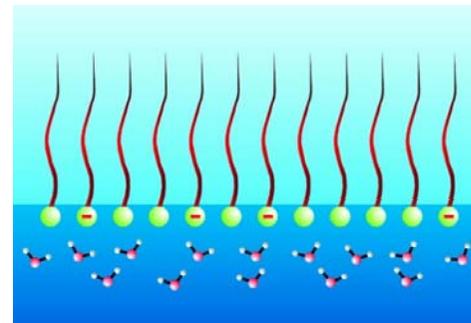


## Methods

- Dropwise method :



- Form highly ordered condensed phase :

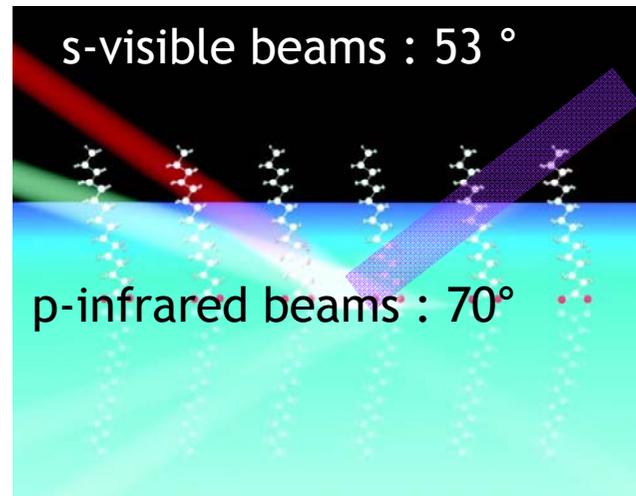


mean molecular area (MMA) coverage :  $\sim 21 \text{ \AA}^2/\text{molecule}$

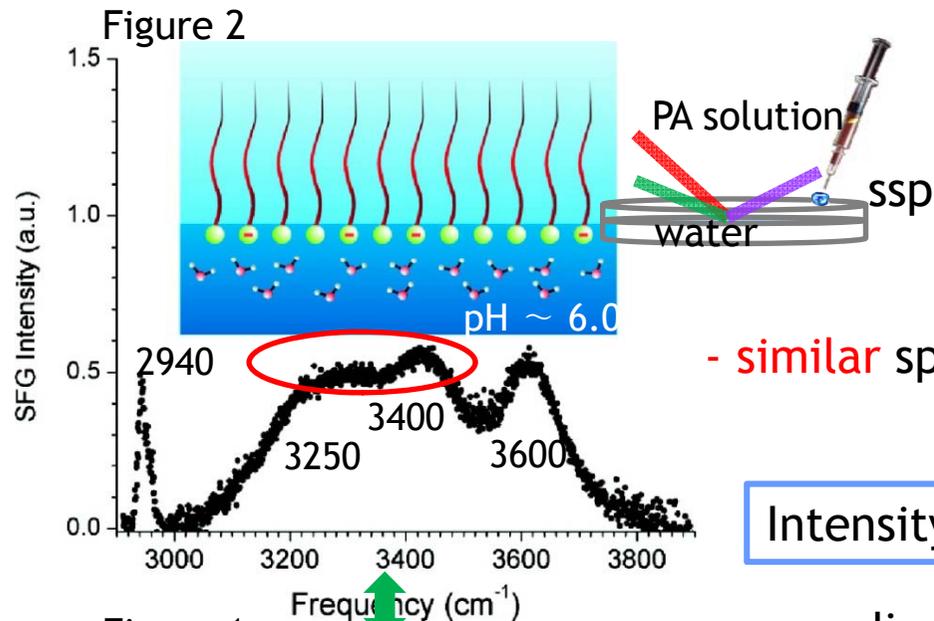
## Broad Bandwidth Sum Frequency Generation Instrumentation

- Spectral bandwidth (broadband infrared beam) :  $\sim 450 \text{ cm}^{-1}$
- Optimize:  $\sim 3300 \text{ cm}^{-1}$
- Polarization combinations : **ssp** (s-SFG; s-visible; p-infrared)
- Temperature :  $23 \text{ }^\circ\text{C}$

Visible beams energy :  $300 \text{ } \mu\text{J}$   
Infrared beams energy :  $\sim 10 \text{ } \mu\text{J}$   
(Purge dry nitrogen gas)

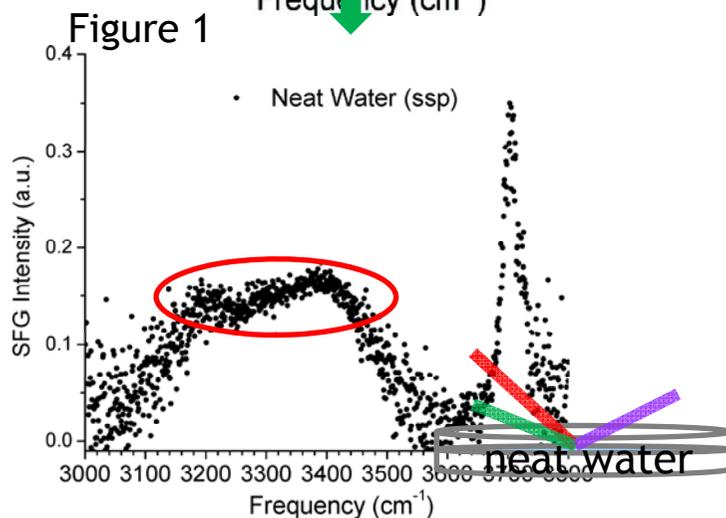


# Results and Discussion



- similar spectral features in the two bands

Intensity improvement :



dissociation of PA headgroups ( $pK_a \sim 8.7$  % at pH 6.0)



presence of negative charges (headgroup)

surface field effect

intensity growth

the O-H oscillators associate with the interfacial hydrogen-bonded water molecules

# Ionic perturbations on the interfacial hydrogen-bonding network

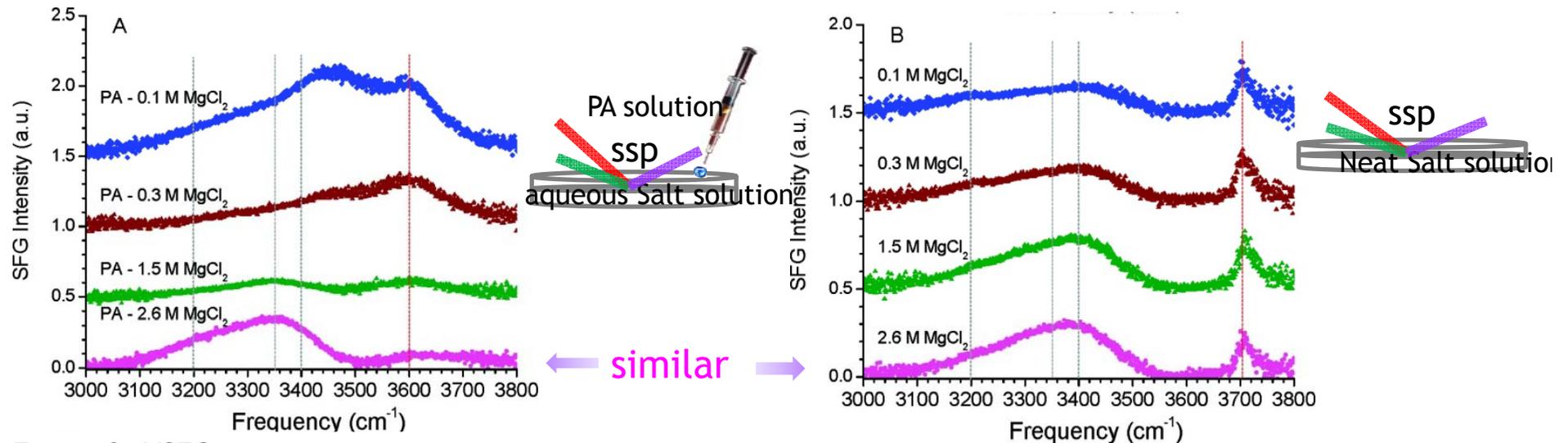


Figure 3. VSGF spectra .

- (A) PA monolayers on aqueous MgCl<sub>2</sub> solutions (0.1, 0.3, 1.5, 2.6 M);
- (B) neat (no monolayer) MgCl<sub>2</sub> solutions (0.1, 0.3, 1.5, 2.6 M)

- reductions of  $\sim 3200$  and  $\sim 3600$  cm<sup>-1</sup> intensities are noticeable
- cation binding to the carboxylic headgroup correlates to the cation concentration

In Figure 3A,

At a low concentration (0.1 M),

intensity attenuation is not overwhelmingly significant

- In  $\sim 3200 \text{ cm}^{-1}$  band, only there is apparent intensity reduction
- $\sim 3450 \text{ cm}^{-1}$  band does not obey the similar trend demonstrated by the  $\sim 3200 \text{ cm}^{-1}$

 Why ?

weak binding strength and insufficient numbers of  $\text{Mg}^{2+}$

At a higher concentration (0.3 M , 1.5M),

- significant decrease of the  $\sim 3450 \text{ cm}^{-1}$  band
- the  $3600 \text{ cm}^{-1}$  band starts to attenuate

 Why ?

- sign of decreasing numbers of protonated headgroups
- small population of bidentate ionic complexes start to emergence

At 1.5M,

- zeropoint- charge ((ZPC);the attenuation of band intensities are maximal)
- decharging mechanism(charge neutralization) affects the signal  
( $\sim 3200$  and  $\sim 3450$   $\text{cm}^{-1}$  bands)
- transition point , reverse trend

At 2.6 M,

reemergence of both  $\sim 3200$  and  $\sim 3400$   $\text{cm}^{-1}$  bands

the  $3600$   $\text{cm}^{-1}$  band becomes reduced compared to that of lower concentrations

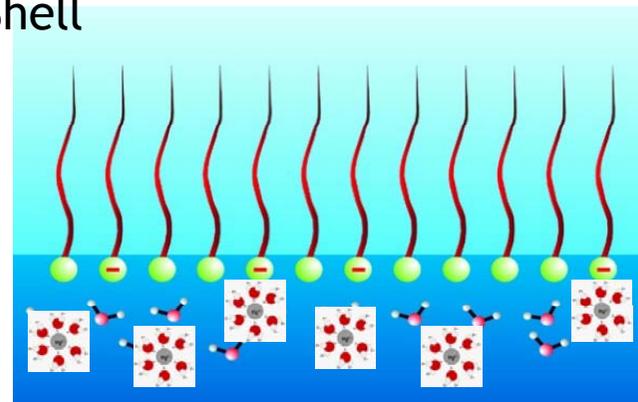
 in a strict sense

an increasing presence of bound ionic complexes at the interface  
(the presence of deprotonated headgroups)

relatively **small** reduction of the  $\sim 3450 \text{ cm}^{-1}$  band (at 0.1 M)  
compare  
**large** reductions of the  $\sim 3450 \text{ cm}^{-1}$  band (at 0.3 and 1.5 M)

↓ Why ?

- $\text{Mg}^{2+}$  become hydrated and combined with water
- solvation shell water molecules of  $\text{Mg}^{2+}$  is unfavorable movement
- the formation of bound ionic complexes ( $\text{Mg}^{2+}/\text{COO}^-$ ) is unlikely  
(order of solvation energy:  $\text{Mg}^{2+} > \text{Ca}^{2+} \gg \text{RCOOH} \gg \text{H}_2\text{O}$ )
- Small fraction of  $\text{Mg}^{2+}$  is interacting with  $\text{COO}^-$  (neutralization)
- majority of  $\text{Mg}^{2+}$  remain intact solvation shell
- Remains the surface field effect



(  $\text{Mg}^{2+}$ ,  $\text{COO}^-$ , water )

At 0.3 and 1.5 M

- the progressive reductions of the overall spectral intensity are indicative of surface charge **neutralization**
- fraction of the headgroups becomes bound with  $\text{Mg}^{2+}$

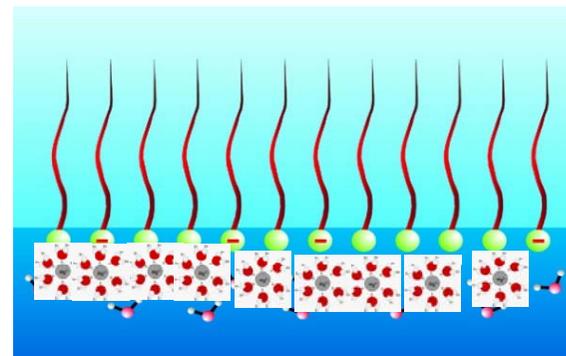


hydrogen-bonding network consist of

**water molecules** participating in the solvation shells of inorganic ions  
and  
the **undissociated PA headgroups**

at 1.5 M  $\text{Mg}^{2+}$

- marks resurgence of the  $\sim 3350 \text{ cm}^{-1}$  band



After surface charge neutralization (1.5M),

- the interfacial hydrogen-bonded water molecules reorganize
- the hydrogen-bonding structure similar to the neat  $\text{Mg}^{2+}$  solution interface



in a strict sense

- Unlike adsorption
- No the reversal effect

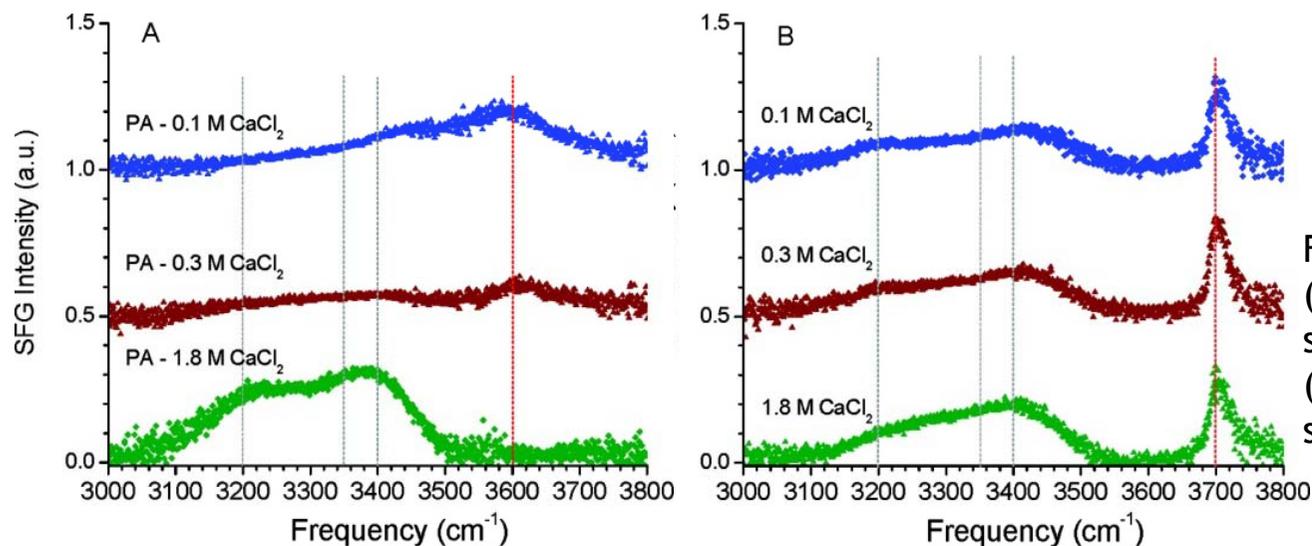


Figure 4. ssp VSG spectra. (A) PA monolayers on aqueous CaCl<sub>2</sub> solutions (0.1, 0.3, and 1.8 M) ; (B) neat (no monolayer) CaCl<sub>2</sub> solutions (0.1, 0.3, and 1.8 M)

At low concentrations (0.1 and 0.3 M),

- the overall signal strength is much weaker than figure 3A

At a concentrated condition (1.8 M),

- spectrum is similar to the neat Ca<sup>2+</sup>
- reemergence of both  $\sim 3200$  and  $\sim 3400$  cm<sup>-1</sup> bands
- disappear  $\sim 3600$  cm<sup>-1</sup> band
- Indicate complete deprotonation
- Ca<sup>2+</sup> interacts much more strongly with COO<sup>-</sup> than Mg<sup>2+</sup>

At the transition point,

- start on reorganization of surface water structures
- occurs at a much lower concentration as compared with  $\text{Mg}^{2+}$

At concentrated conditions,

- reorganize the already disrupted hydrogen-bonding network structure
- similar to hydrogen-bonding network of the neat salt solution interface

# Conclusions

**Surface field** of dissociated PA headgroups influence polar ordering of the interfacial water molecules is observed.

- A small fraction of negative charges induce meaningful polar ordering in the interfacial water molecules

**Cation binding** of  $Mg^{2+}$  and  $Ca^{2+}$  to the PA headgroup has impact on the hydrogen-bonding network

- $Ca^{2+}$  has a much greater binding affinity relative to  $Mg^{2+}$
- $Ca^{2+}$  has a much greater impact on the interfacial hydrogen-bonding network than  $Mg^{2+}$

Surface charge **neutralization effect**