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Binding of Mg^{2+} and Ca^{2+} to Palmitic Acid and Deprotonation of the COOH Headgroup Studied by Vibrational Sum Frequency Generation Spectroscopy

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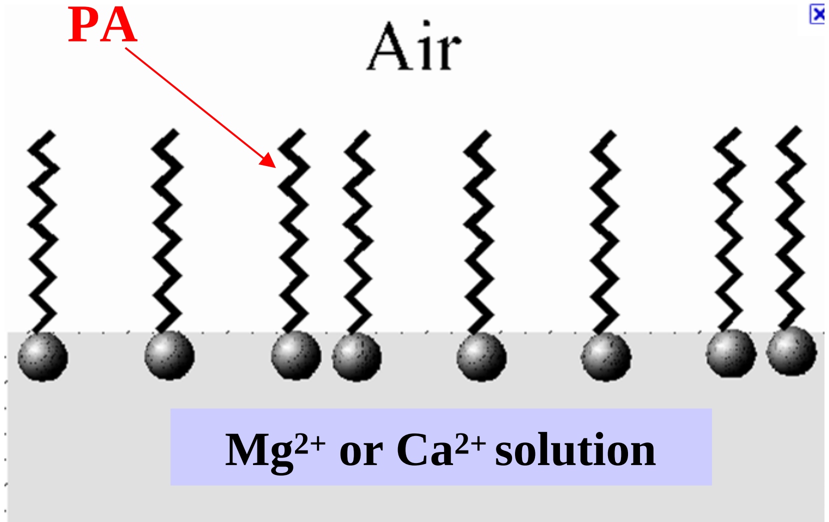
At the air/liquid interface, cation binding specificity of alkaline earth cations, Mg^{2+} and Ca^{2+}, with the biologically relevant ligand carboxylate (COO^-) using vibrational sum frequency generation spectroscopy is reported. The empirical evidence strongly supports that the ionic binding strength is much stronger for Ca^{2+} to COO^- than that for Mg^{2+}. We conclude that at a near-neutral pH, the mechanism that governs Ca^{2+} binding to COO^- is accompanied by commensurate deprotonation of the carboxyl headgroup. In addition, surface molecular structure and ion concentration influence the cation binding behavior at the air/liquid interface. In a 0.1 M Ca^{2+}(aq) solution, Ca^{2+} initially favors forming ionic complexes in a 2:1 bridging configuration ($2Ca^{2+}$:$1COO^-$) but 1:1 chelating bidentate complexes ($1Ca^{2+}$:$1COO^-$) gradually emerge as secondary species as the system reaches equilibrium. As the Ca^{2+} concentration rises to 0.3 M, the primary complexed species exists in the 2:1 bridging configuration. Unlike Ca^{2+}, Mg^{2+} at 0.1 and 0.3 M favors a solvent-separated ionic complex with COO^-.

Methods

$C_{15}H_{31}COOH$

Palmitic Acid (PA)

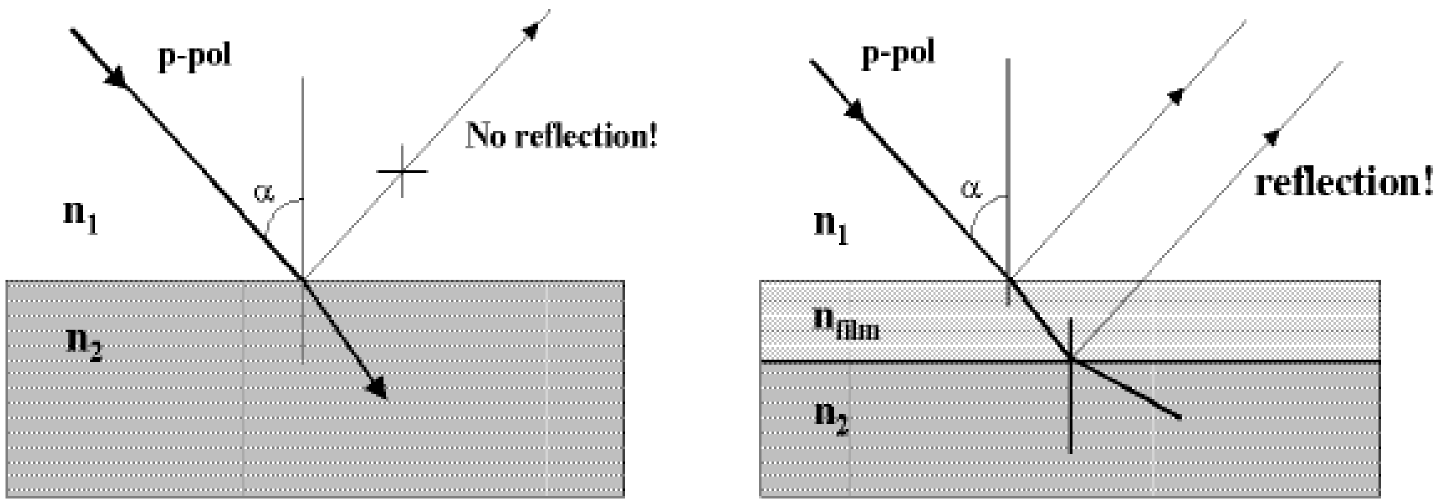
- **$MgCl_2$**
- **$CaCl_2$**



- Langmuir Film Balance
- Monolayer at Equilibrium Pressure
- Brewster Angle Microscopy
- Vibrational Sum Frequency Generation Spectrometer

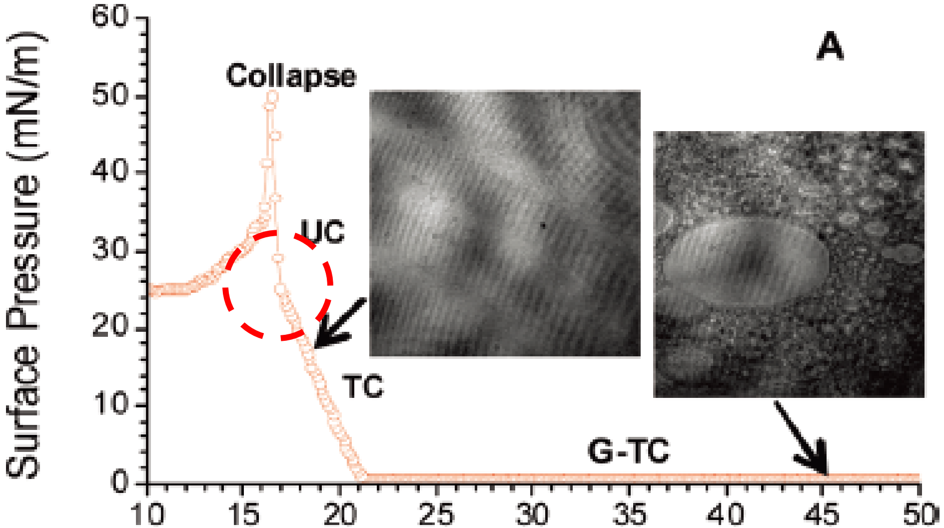
Brewster Angle Microscopy and Compression Isotherms

Brewster Angle



$$\alpha = \arctan(\frac{n_2}{n_1})$$

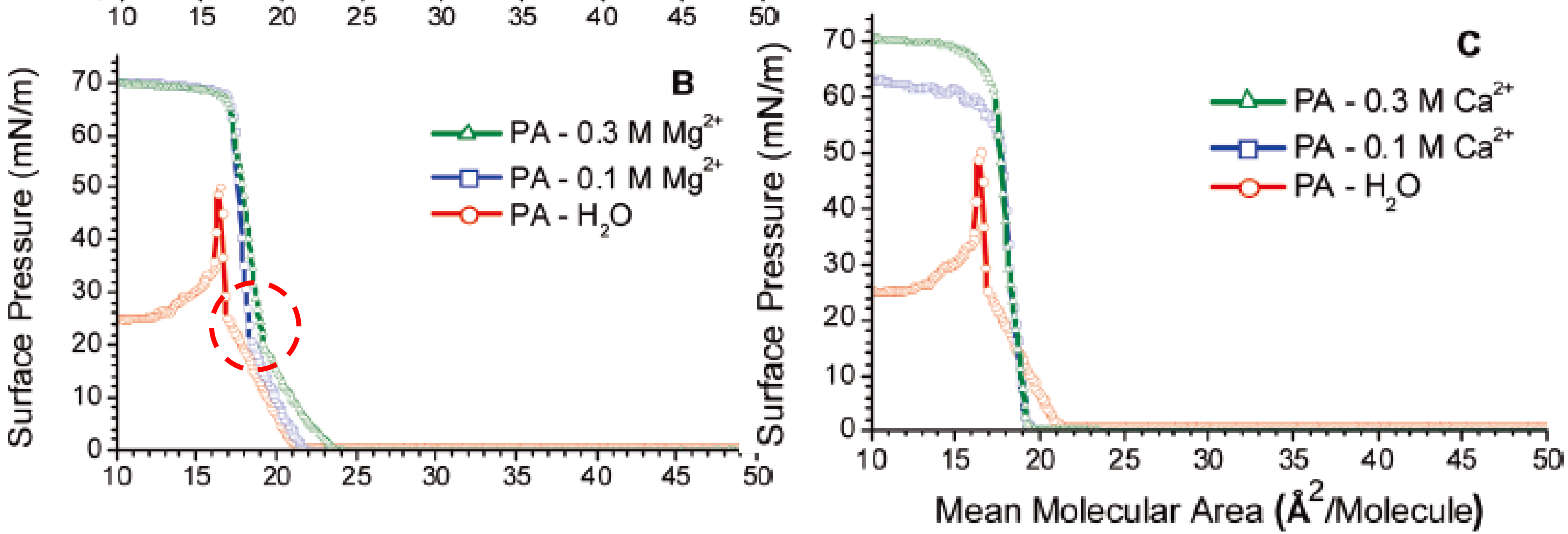
Brewster Angle Microscopy and Compression Isotherms



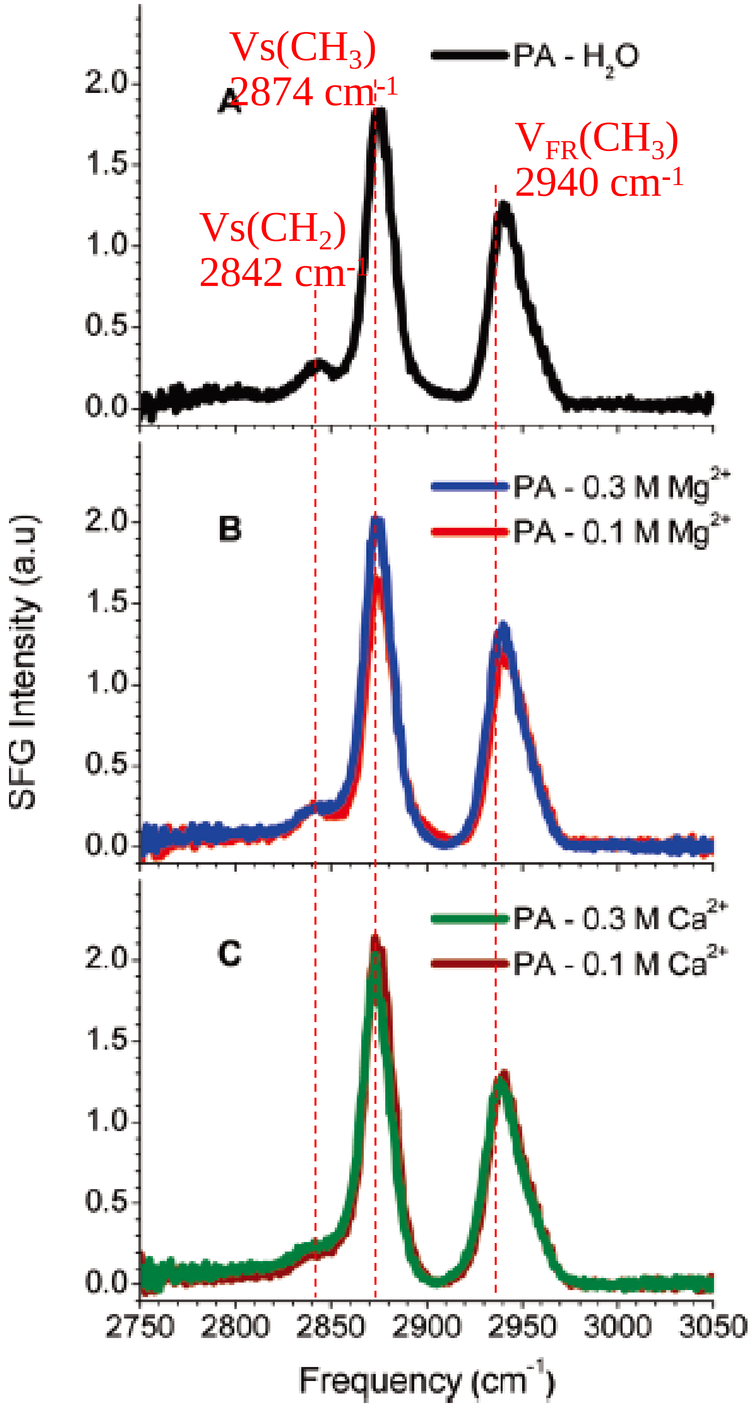
G-TC: gas and tilted condensed coexistence phase

TC: tilted condensed phase

UC: untilted condensed phase



VSFG (2800 – 3000 cm^{-1}) C-H stretching region

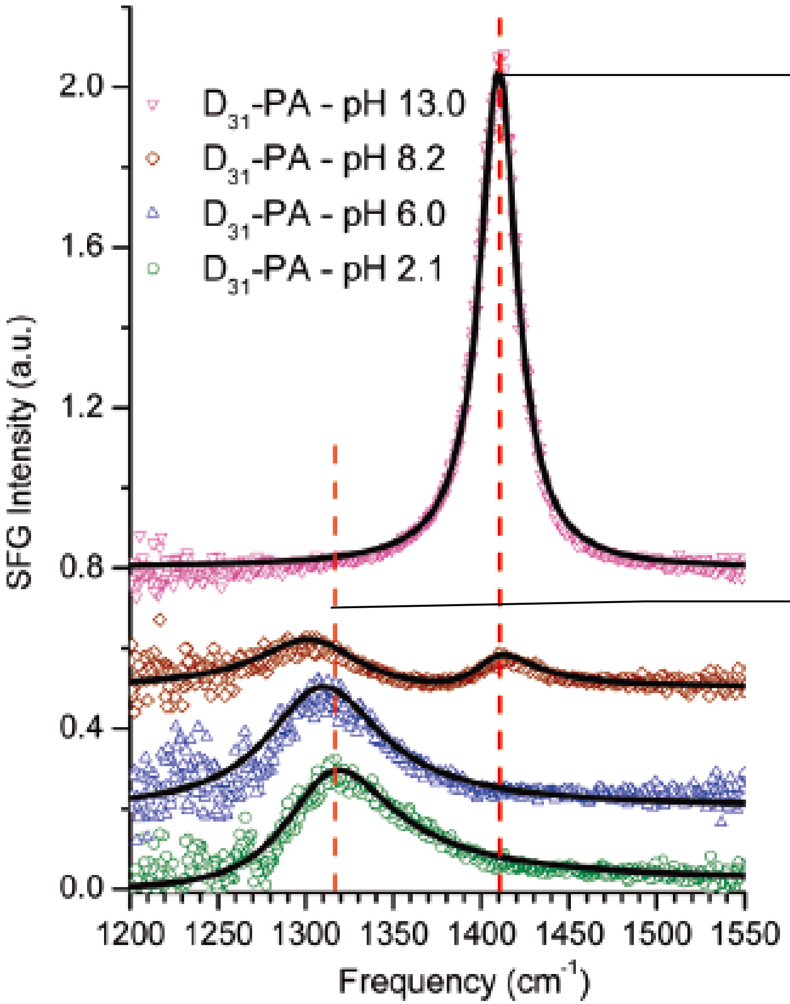


Acyl chain of PA is more ordered at higher Mg^{2+} concentration

A condensing effect is much more pronounced in Ca^{2+} than in Mg^{2+}

VSFG (1300-1500 cm^{-1})
-COOH and -COO^- Vss Region

1. pH Control Study



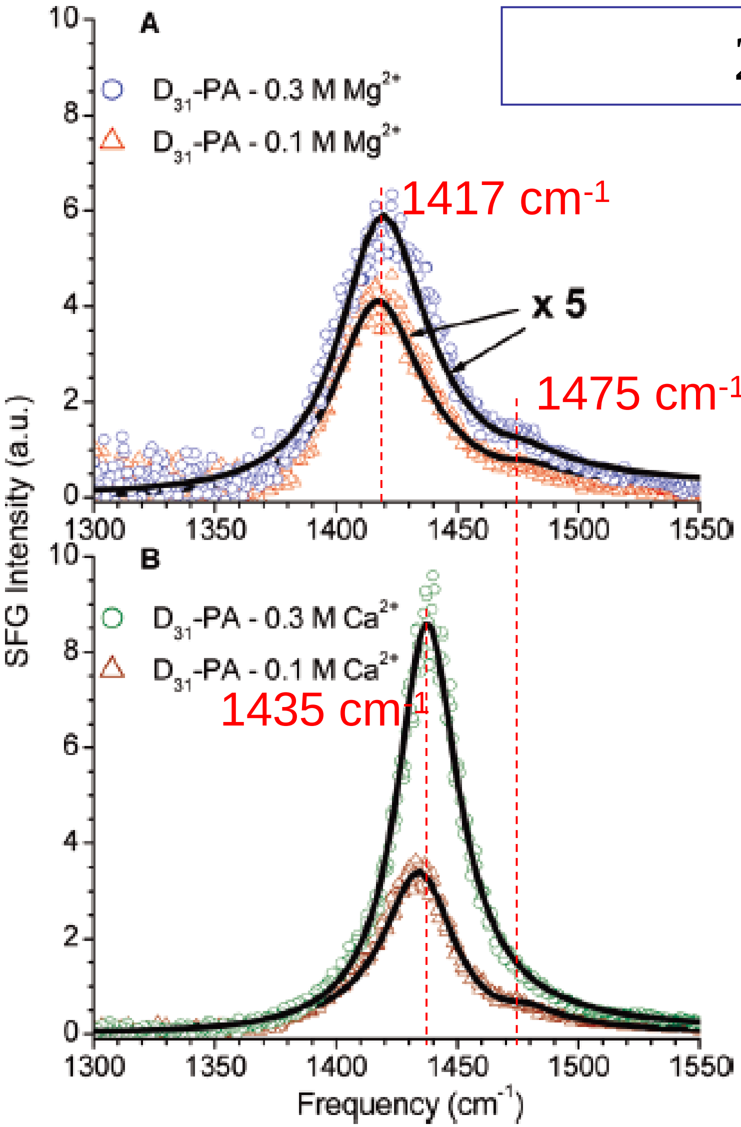
1410 cm^{-1} hydrated form of -**COO^-** group

deprotonation

1300 cm^{-1} C-O stretch of **-COOH** group

protonation

VSFG (1300-1500 cm^{-1})
-COOH and -COO^- Vss Region



2. Mg^{2+} vs Ca^{2+}

1417 cm^{-1} hydrated form of COO-

1475 cm^{-1} 1:1 ionic complex

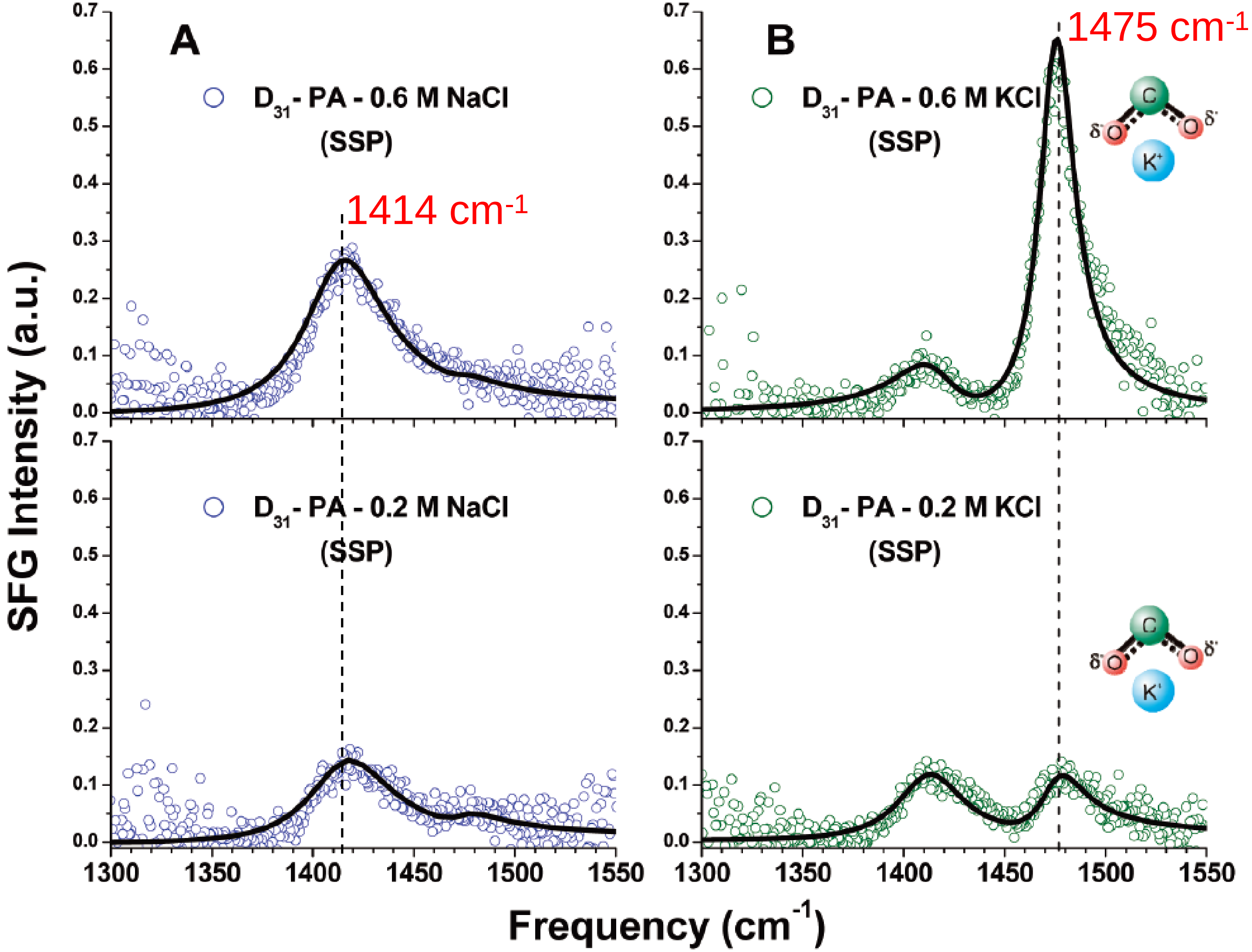
Mg^{2+}

COO- exists as a hydrated species accompanied by a smaller fraction of 1:1 ionic complex

Ca^{2+}

1435 cm^{-1} 2:1 ($2Ca^{2+}/1COO^-$) bridging ionic complex

Na^+ vs K^+



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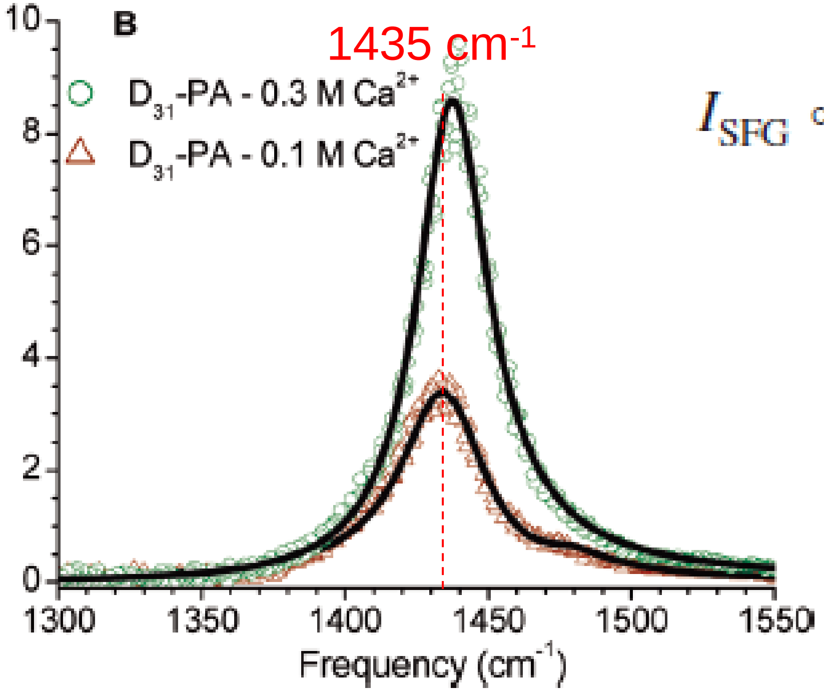
VSFG (1300-1500 cm^{-1})
-COOH and -COO^- Vss Region

2. Mg^{2+} vs Ca^{2+}

1435 cm^{-1} 2:1 ($2Ca^{2+}/1COO^-$) bridging ionic complex**?**



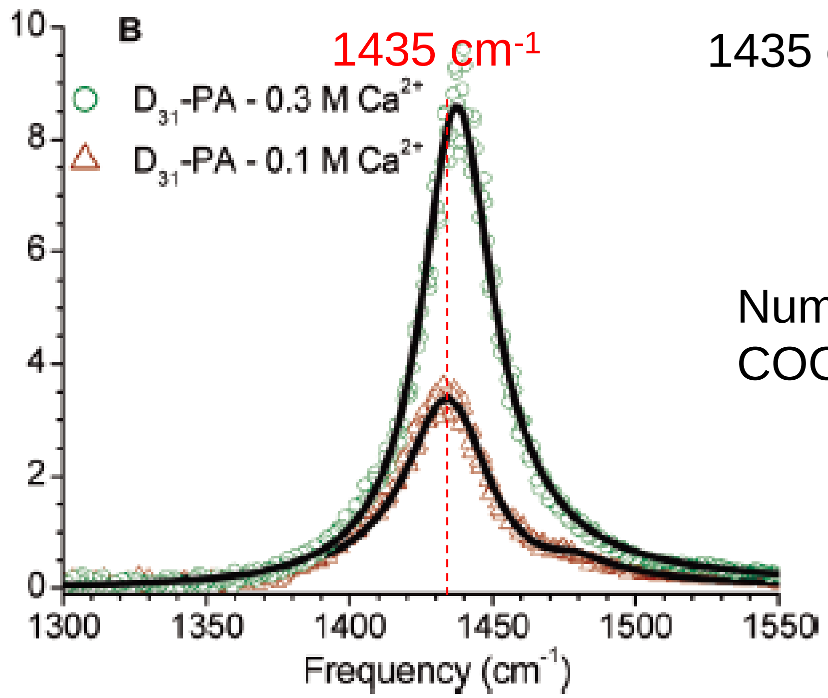
$$I_{\text{SFG}} \propto |P^{(2)}|^2 \propto |\chi_{\text{NR}}^{(2)} e^{i\phi_{\text{NR}}} + \sum_v \chi_v^{(2)}|^2 I_{\text{vis}} I_{\text{IR}}$$

$$\chi_v^{(2)} = N \sum_{lmn} \langle \mu_{IJK:lmn} \rangle \beta_v$$

$$I_{SFG} \sim N^2$$

VSFG (1300-1500 cm^{-1})
-COOH and -COO^- Vss Region

2. Mg^{2+} vs Ca^{2+}

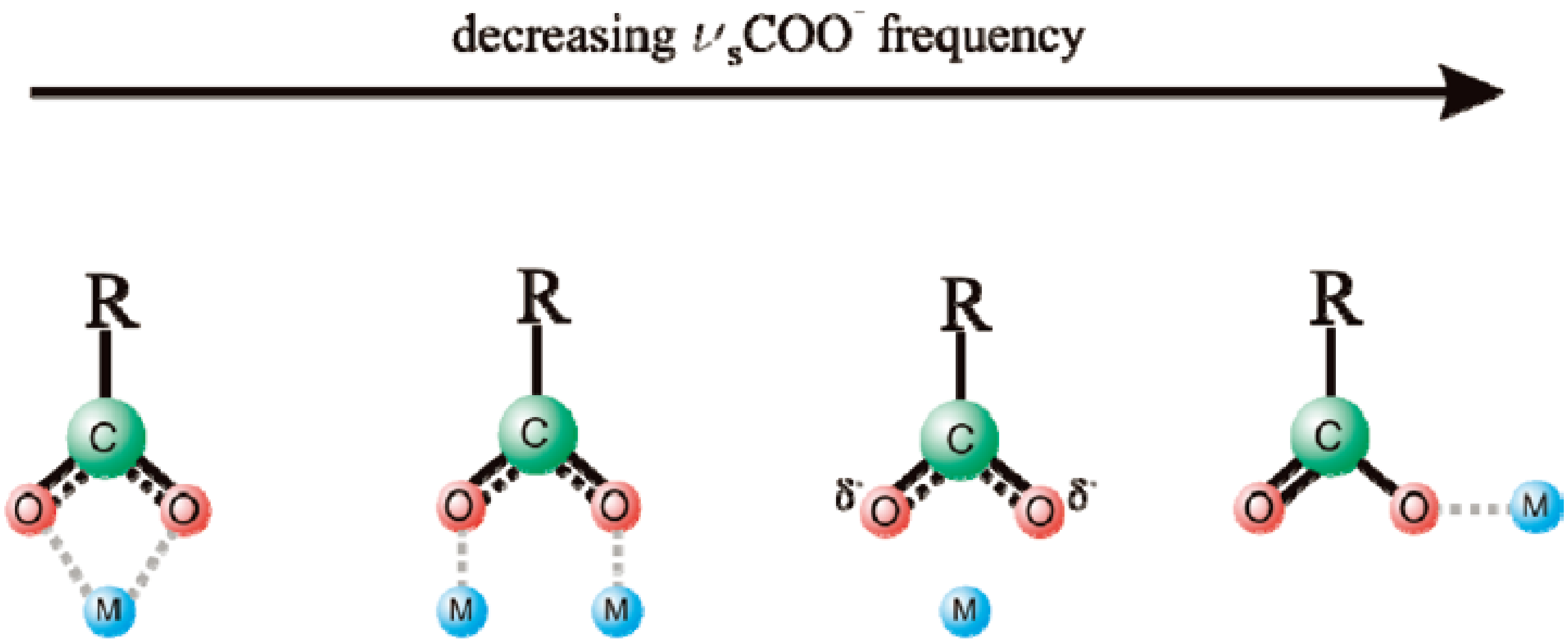


1435 cm^{-1} COO^- intensities ratio 2:1

Number density ratio of COO- is close to 1.5 + Ca^{2+} concentration ratio is 3

1435 cm^{-1} 2:1 ($2Ca^{2+}/1COO^-$) bridging ionic complex

VSFG (1300-1500 cm^{-1})
-COOH and -COO^{-} Vss Region



bidentate complex

bridging complex

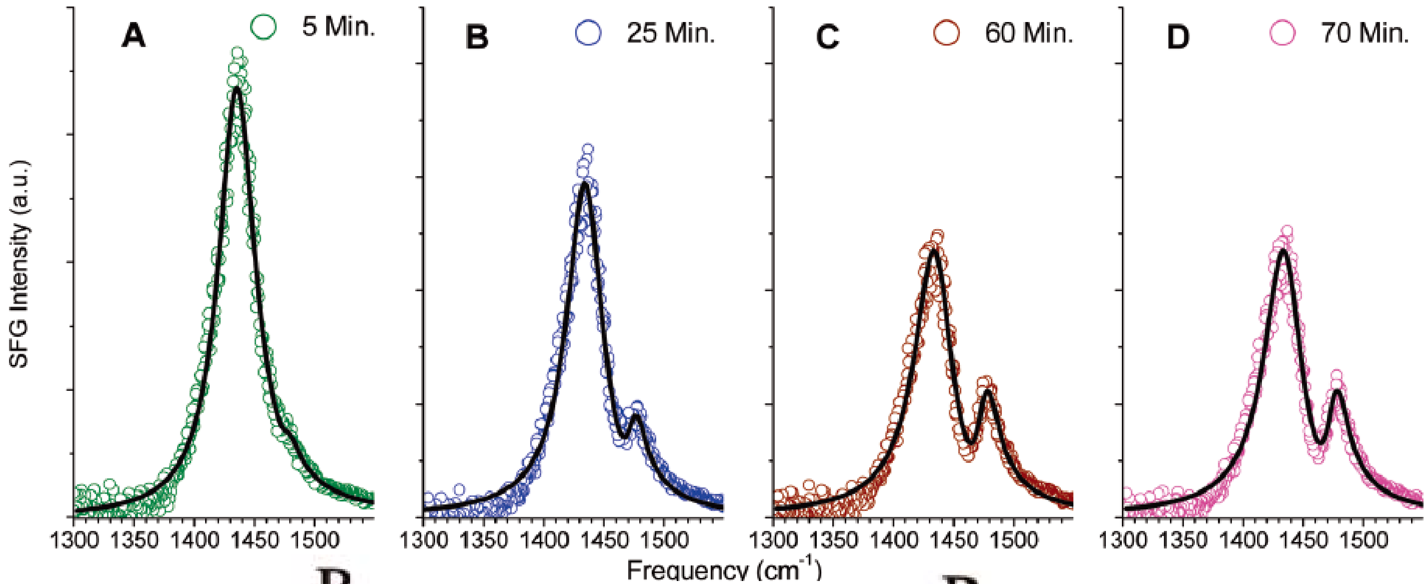
ionic complex

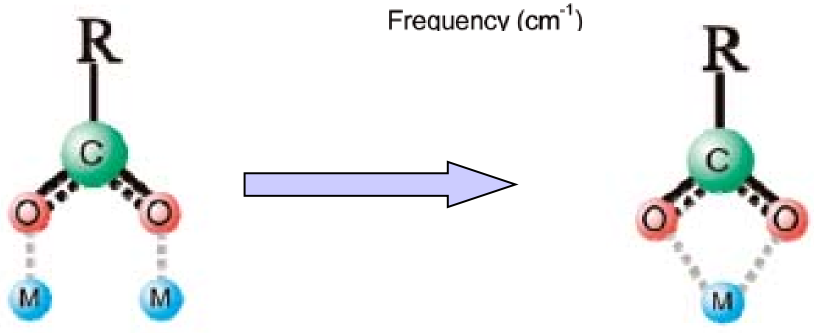
monodentate complex

VSFG (1300-1500 cm^{-1})
-COOH and -COO^- Vss Region

3. Time evolution study

0.1M Ca^{2+}

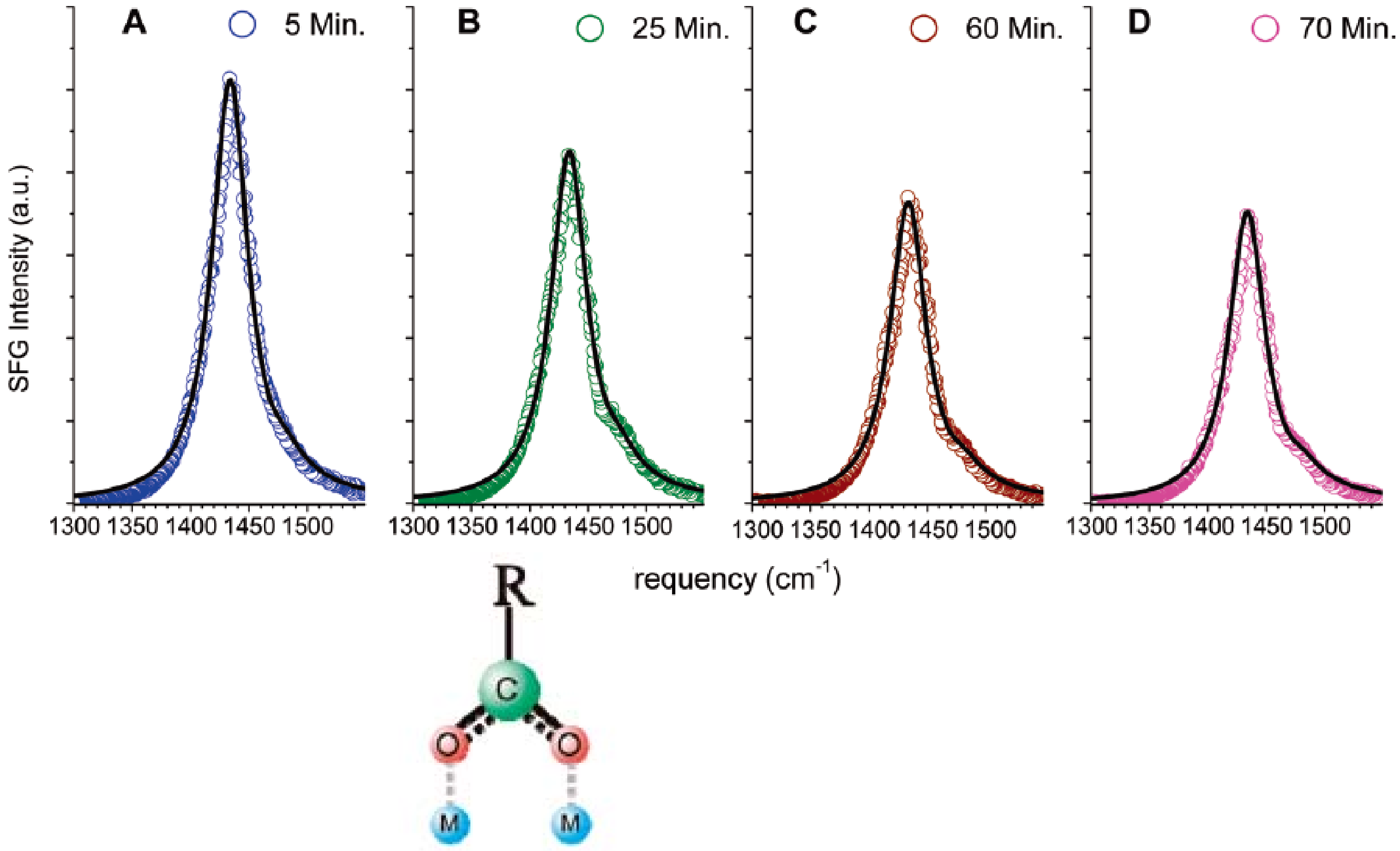




VSFG (1300-1500 cm^{-1}) -COOH and $-COO^{-}$ Vss Region

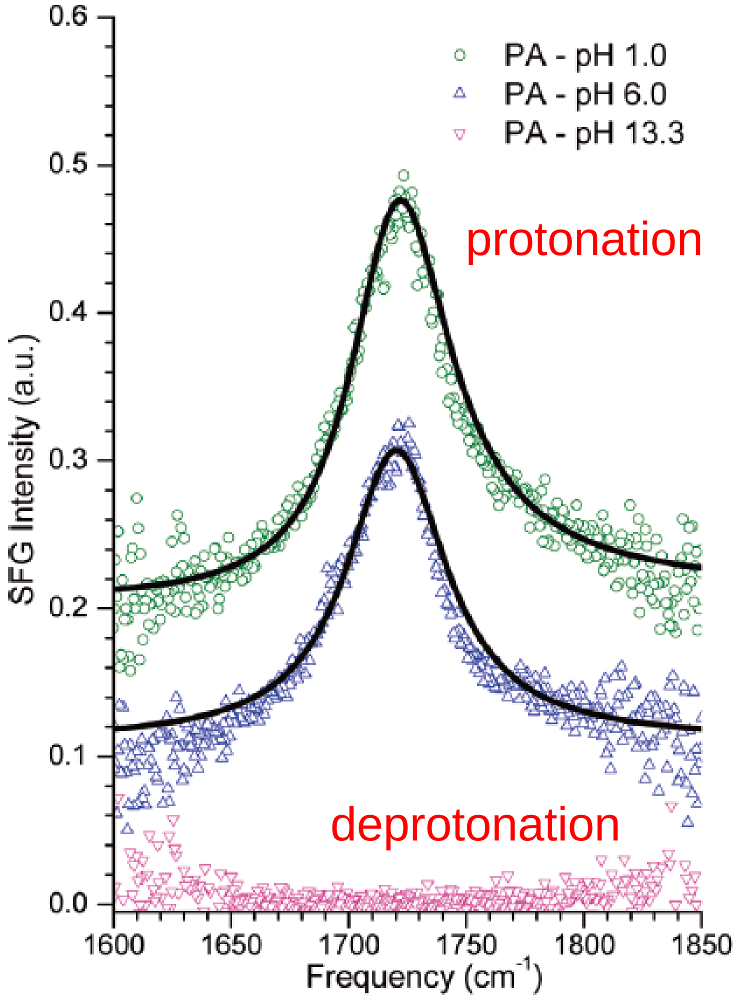
3. Time evolution study

0.3M Ca^{2+}



VSFG (1700-1800 cm^{-1}) vC=O Region

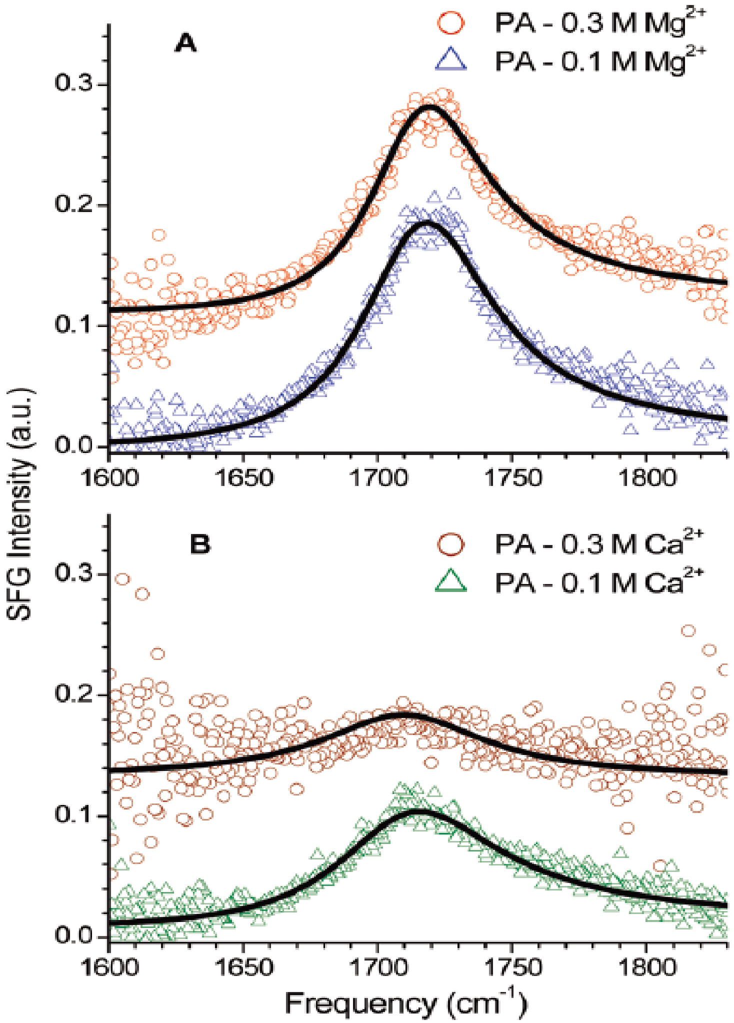
1. pH Control Study



1720 cm^{-1} hydrated C=O group in the COOH headgroup

VSFG (1700-1800 cm^{-1})
vC=O Region

2. Mg^{2+} vs Ca^{2+}



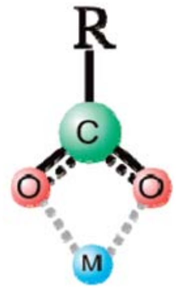
In presence of Ca^{2+}, COOH is more deprotonation

At higher Ca^{2+} concentration, COOH is more deprotonation

Conclusion

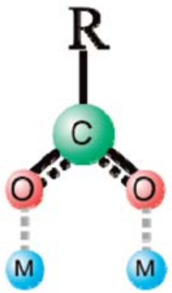
- At 0.1 and 0.3 M Mg^{2+} (aq)

hydrated form of COO^- + smaller fraction



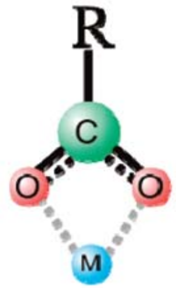
($1Mg^{2+}:1COO^-$)

- At 0.1 M Ca^{2+} (aq)



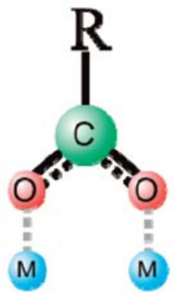
($2Ca^{2+}:1COO^-$)

time increases →



($1Ca^{2+}:1COO^-$)

- At 0.3 M Ca^{2+} (aq) →



($2Ca^{2+}:1COO^-$)