



# Effect of Cations on the Dissociation of Arachidic Acid Monolayers on Water Studied by Polarization-Modulated Infrared Reflection-Absorption Spectroscopy

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*Present by Sam Sokhuoy*

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# Effect of Cations on the Dissociation of Arachidic Acid Monolayers on Water Studied by Polarization-Modulated Infrared Reflection–Absorption Spectroscopy

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We report on the variation of the dissociation of a Langmuir monolayer of arachidic acid at the air/water interface as a function of the subphase pH and for several cations ( $\text{Cd}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^{+}$ ) with the help of the polarization-modulated infrared reflection–absorption spectroscopy (PM-IRRAS) method. The infrared spectra give access to the relative concentration of acid and salt molecules and allow us to determine the influence of the subphase pH on the acid dissociation reaction for each cation. It is shown that  $\text{Na}^{+}$  obeys the purely electrostatic Gouy–Chapman theory quite well, whereas the behavior of  $\text{Mg}^{2+}$ , and even more so that of  $\text{Ca}^{2+}$  and  $\text{Cd}^{2+}$ , requires the introduction of some complexation constant to be understood.

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## Sodium–carboxylate contact ion pair formation induces stabilization of palmitic acid monolayers at high pH†

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Sea spray aerosols (SSA) are known to have an organic coating that is mainly composed of fatty acids. In this study, the effect of pH and salt on the stability and organization of a palmitic acid (PA) monolayer is investigated by surface vibrational spectroscopy and molecular dynamics simulations. Results indicate that alkyl chain packing becomes more disordered as the carboxylic headgroup becomes deprotonated. This is associated with packing mismatch of charged and neutral species as charged headgroups penetrate deeper into the solution phase. At pH 10.7, when the monolayer is ~99% deprotonated, palmitate (PA<sup>−</sup>) molecules desorb and solubilize into the bulk solution where there is spectroscopic evidence for aggregate formation. Yet, addition of 100 mM NaCl to the bulk solution is found to drive PA<sup>−</sup> molecules to the aqueous surface. Free energy calculations show that PA<sup>−</sup> molecules become stabilized within the interface with increasing NaCl concentration. Formation of contact −COO<sup>−</sup>:Na<sup>+</sup> pairs alters the hydration state of PA<sup>−</sup> headgroups, thus increasing the surface propensity. As salts are highly concentrated in SSA, these results suggest that deprotonated fatty acids may be found at the air–aqueous interface of aerosol particles due to sea salt's role in surface stabilization.

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## ❖ Motivation of previous study

have been investigated by a multitude of techniques.<sup>29–34</sup> Surprisingly, studies on the influence of pH on the surface properties of fatty acids are sparse in literature,<sup>35–39</sup> and the majority of these studies focus on fatty acids with a chain length of 20 or more carbons.<sup>35–37</sup> Solubility of fatty acids increase with decreasing chain length, and as most fatty acids in SSA have chain lengths in the range of  $C_{14}$ – $C_{18}$ ,<sup>27,28</sup> it is likely that stability and surface activity of these shorter chain fatty acids decrease upon dissociation of the carboxylic acid proton.

# ❖ SFG results

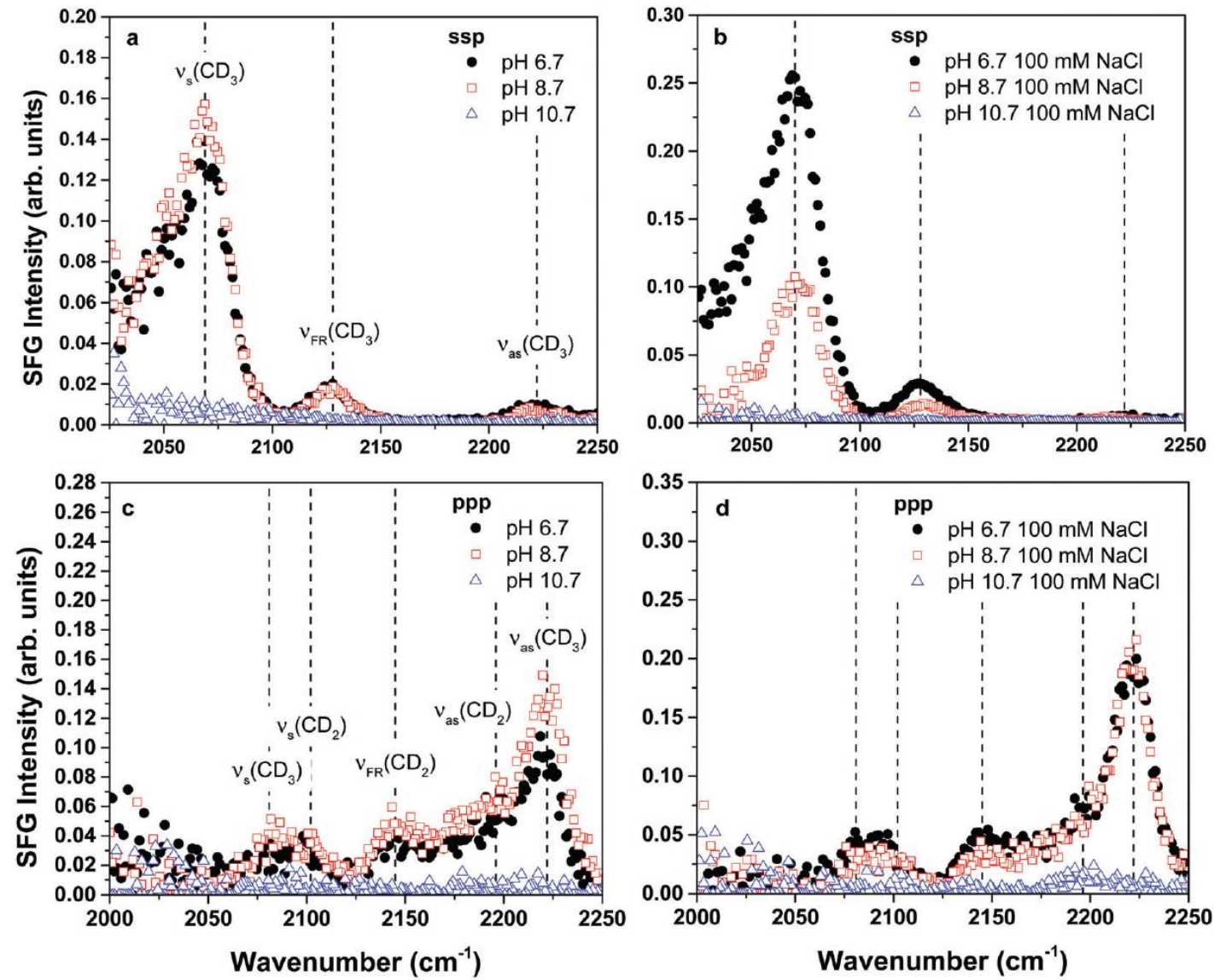


Fig. 5 VSFG spectra of the CD stretching region of  $d_{31}$ -PA monolayers in the UC phase ( $20.5 \text{ \AA}^2$  per molecule) on various pH solutions in (a and c) *ssp* and (b and d) *ppp* polarizations.



## ❖ Infrared reflection-absorption spectroscopy (IRRAS) results

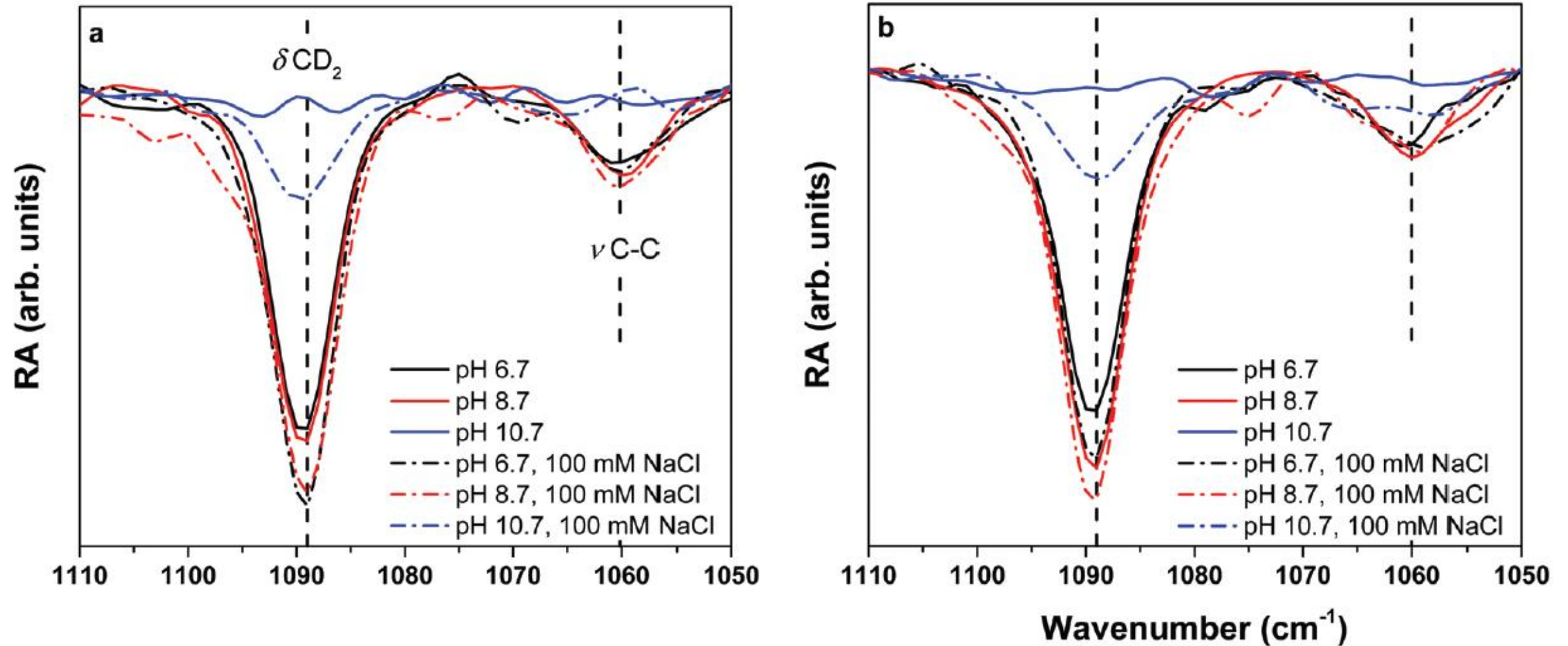
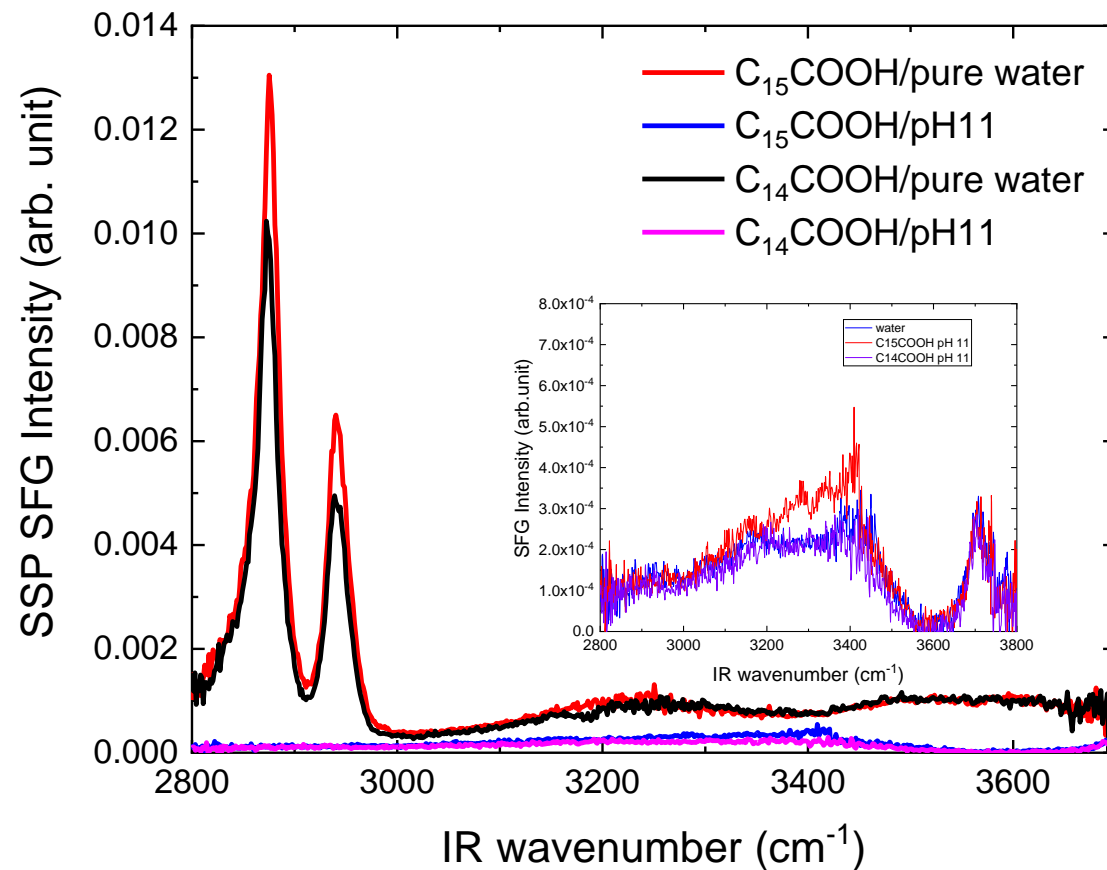
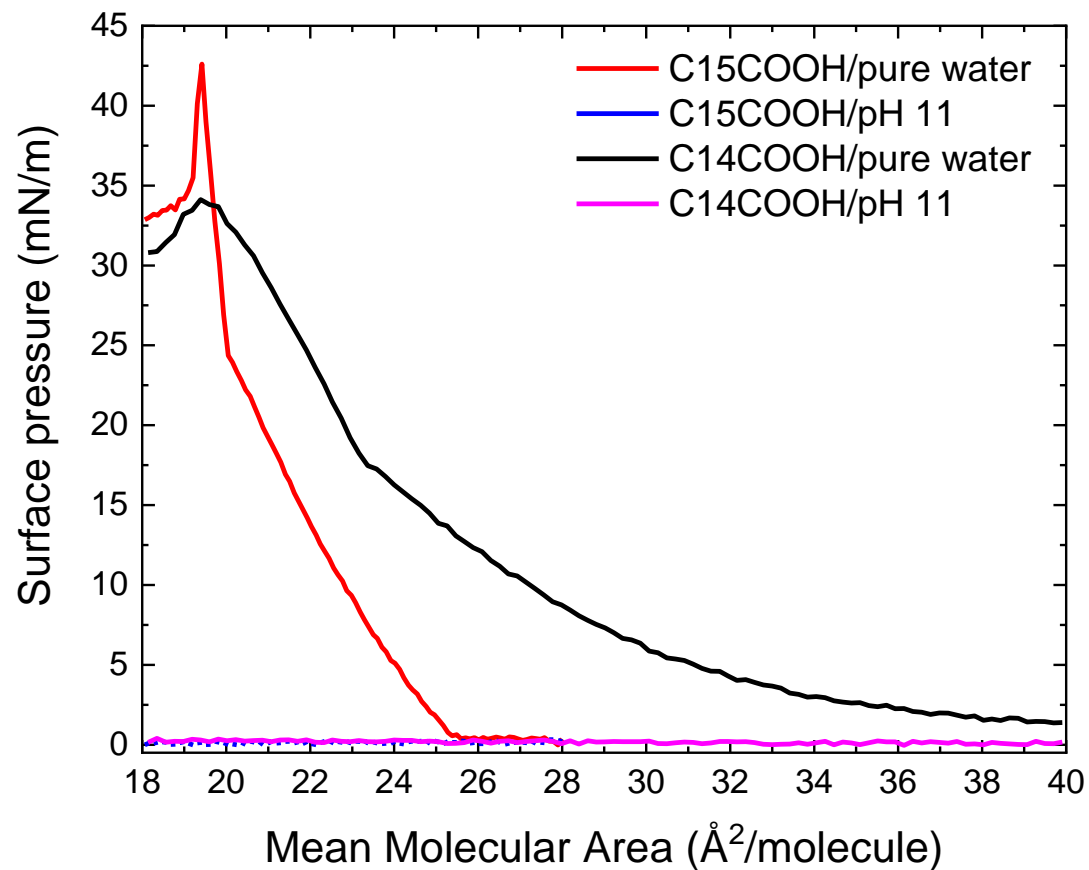
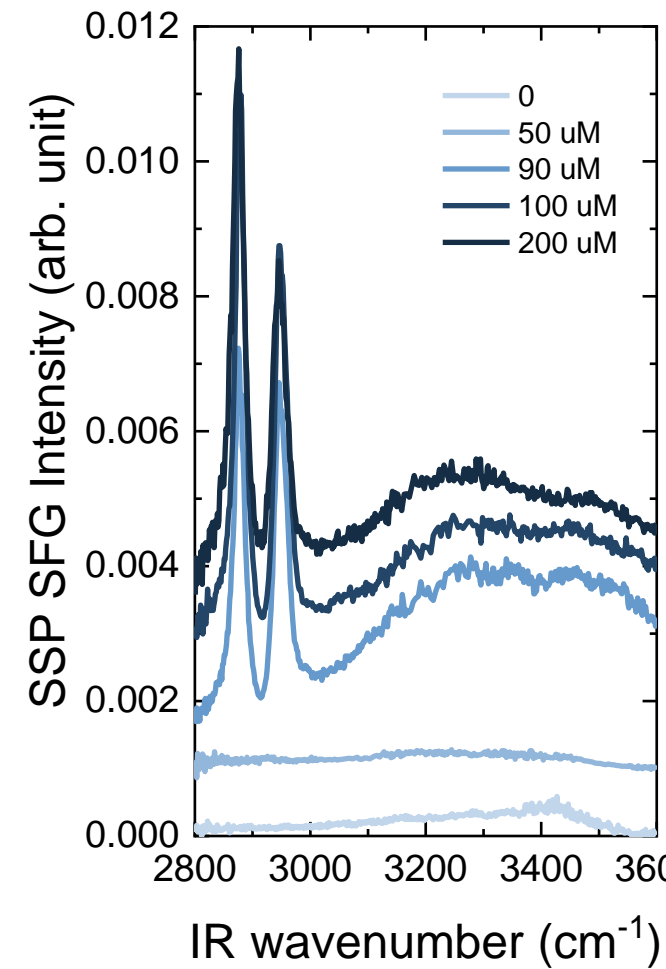


Fig. 4 IRRAS spectra of the CD<sub>2</sub> scissoring region for d31-PA monolayers on various pH solutions in (a) TC phase (24 Å<sup>2</sup> per molecule) and (b) UC phase (20.5 Å<sup>2</sup> per molecule).

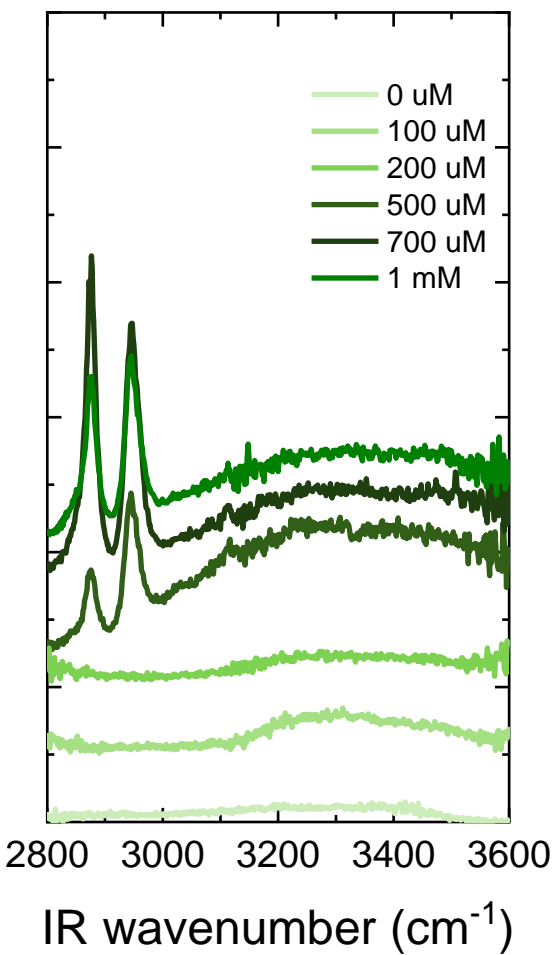
## ❖ My current work



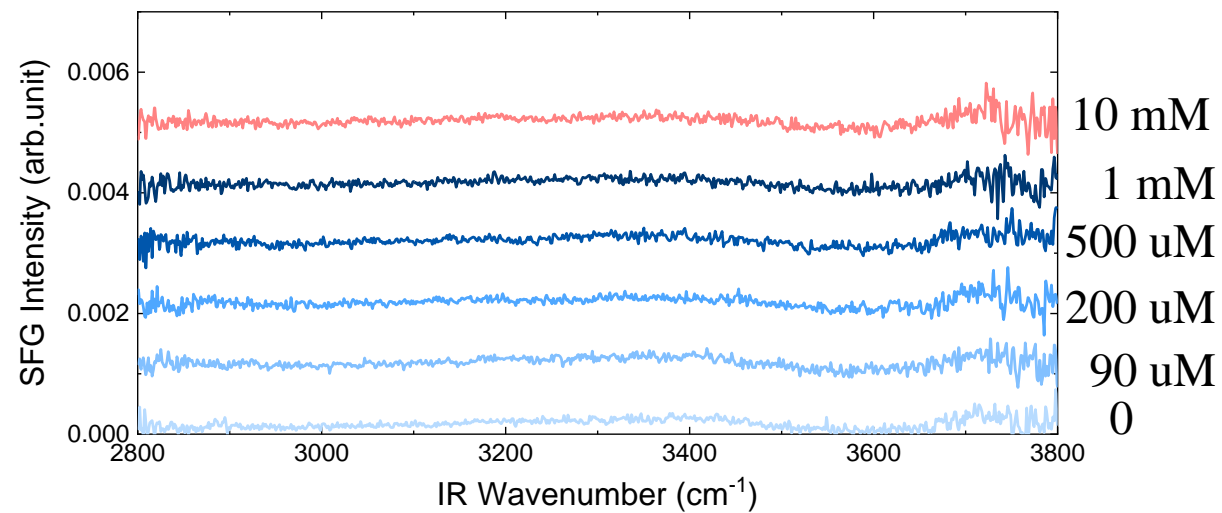
$C_{15}COOH$  pH 11 +  $MgCl_2$



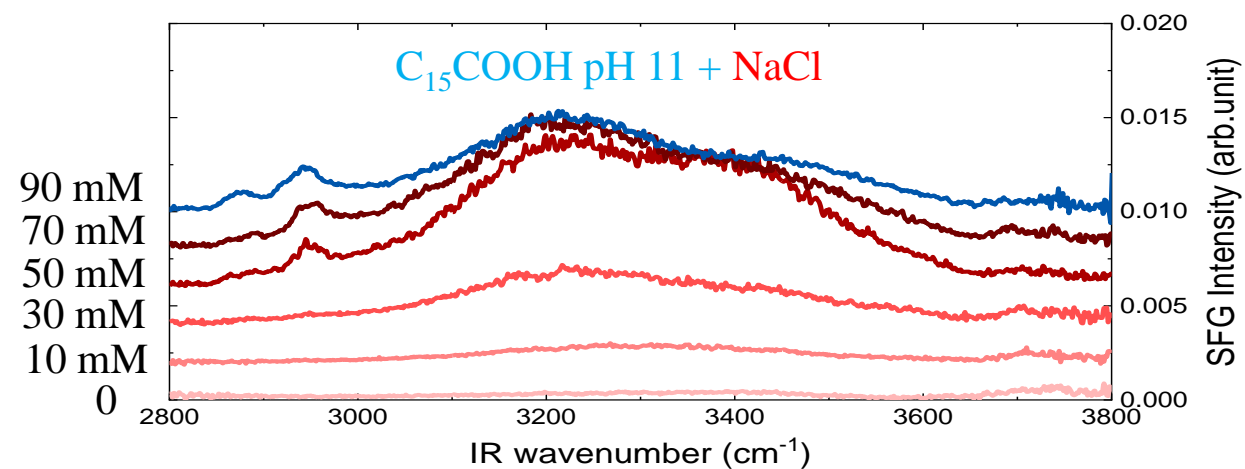
$C_{14}COOH$  pH 11 +  $MgCl_2$



$C_{15}COOH$  pH 11 +  $CaCl_2$



$C_{15}COOH$  pH 11 +  $NaCl$





## ❖ Experimental section

- ❑ Deuterated arachidic acid (CENSaclay, France) was dissolved in chloroform at a concentration of  $5 \times 10^{-3}$  M and spread onto a subphase of ultrapure water (MilliQ from Millipore) containing either  $\text{CaCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{MgCl}_2$ , or  $\text{NaCl}$ .
- ❑ The pH of the subphase was adjusted by addition of  $\text{HCl}$ ,  $\text{NaOH}$ ,  $\text{CaO}$ , or  $\text{MgO}$  and was directly checked in situ during spectrum acquisition. The concentrations of the subphase counterions ( $3.1 \times 10^{-3}$  M  $\text{CaCl}_2$ ,  $3.5 \times 10^{-3}$  M  $\text{CdCl}_2$ ,  $3 \times 10^{-3}$  M  $\text{MgCl}_2$ , and  $10^{-2}$  M  $\text{NaCl}$ ) have been chosen to prevent a significant variation of metallic cation concentration when the pH is increased.

## ❖ Experimental setup

### Polarization-modulated IRRAS (PM-IRRAS)

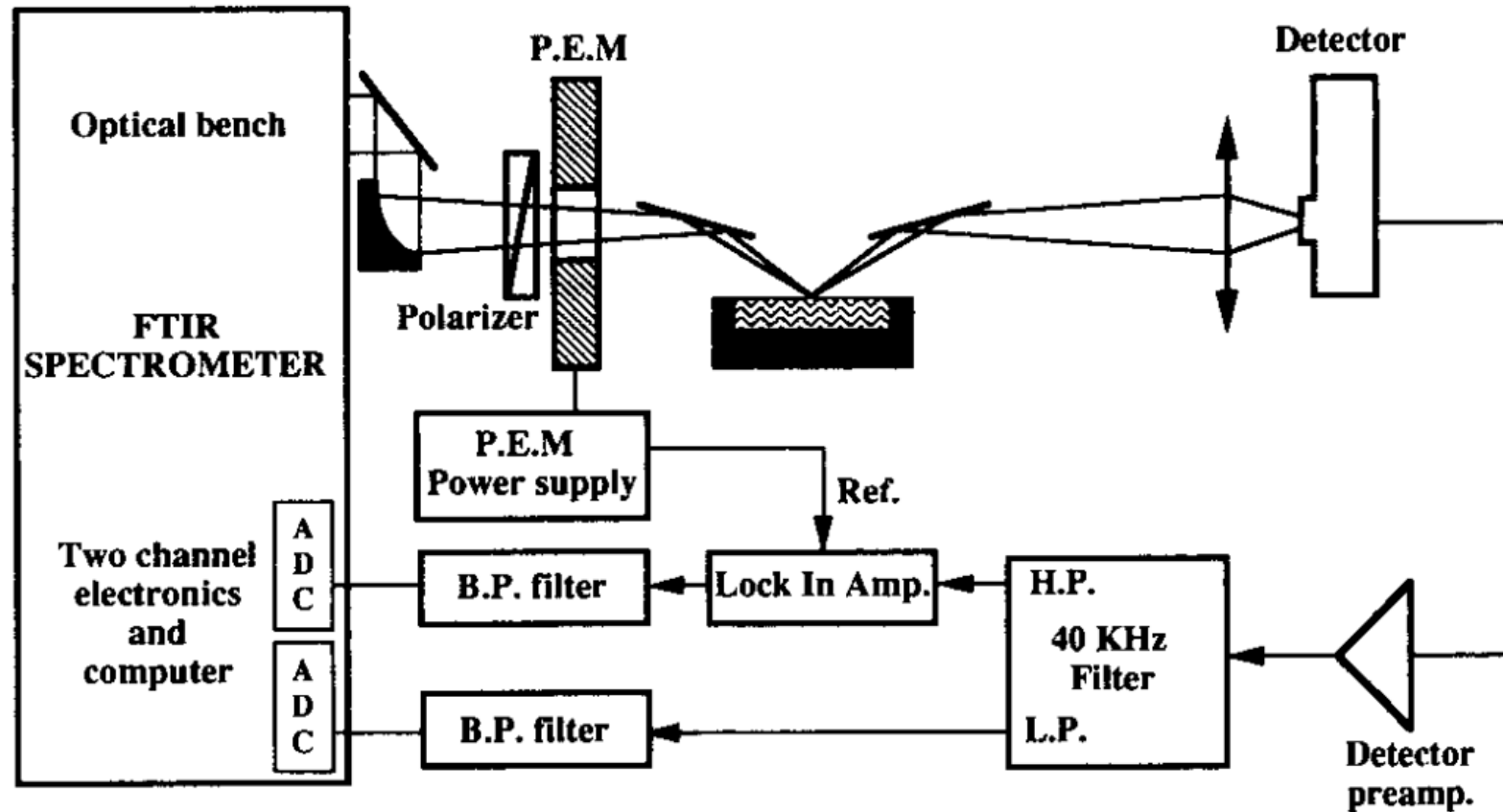
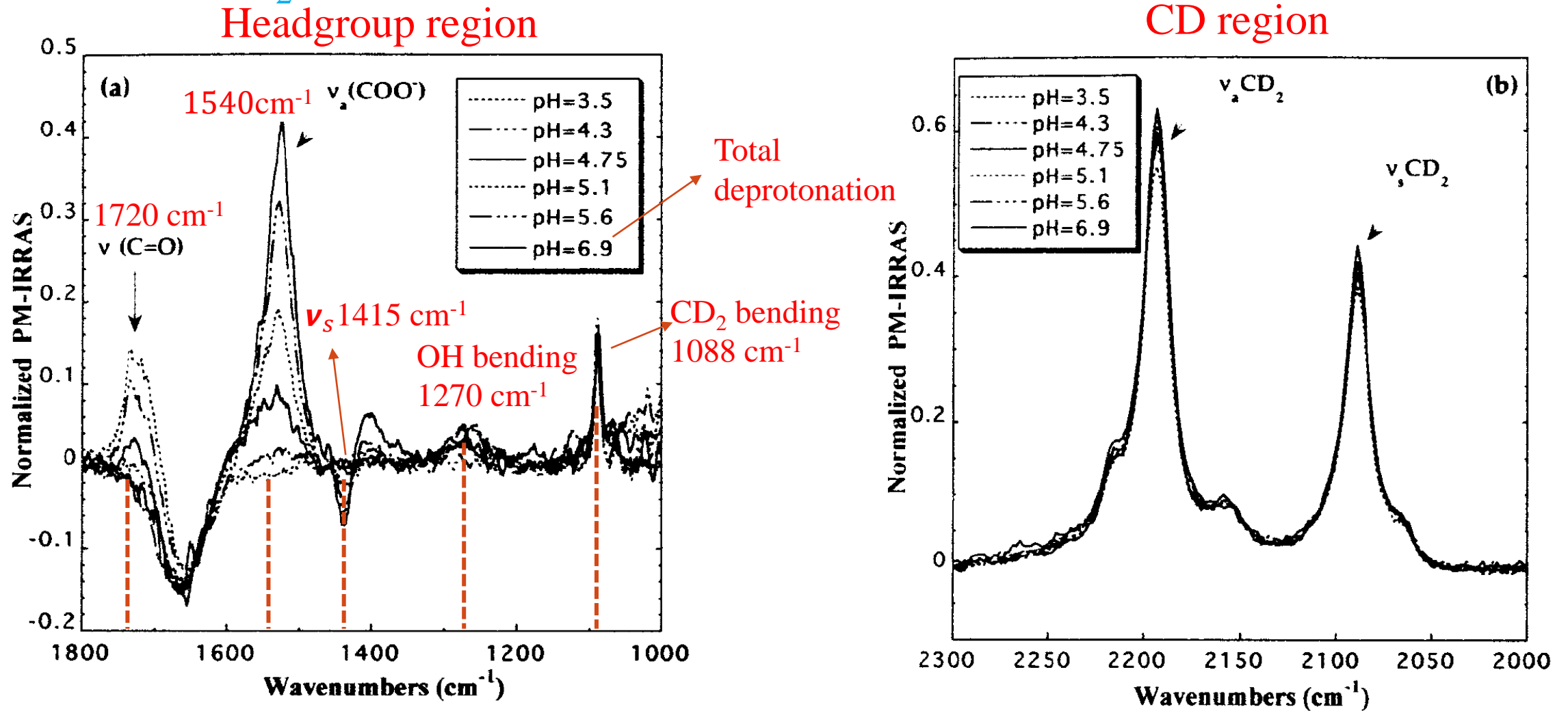


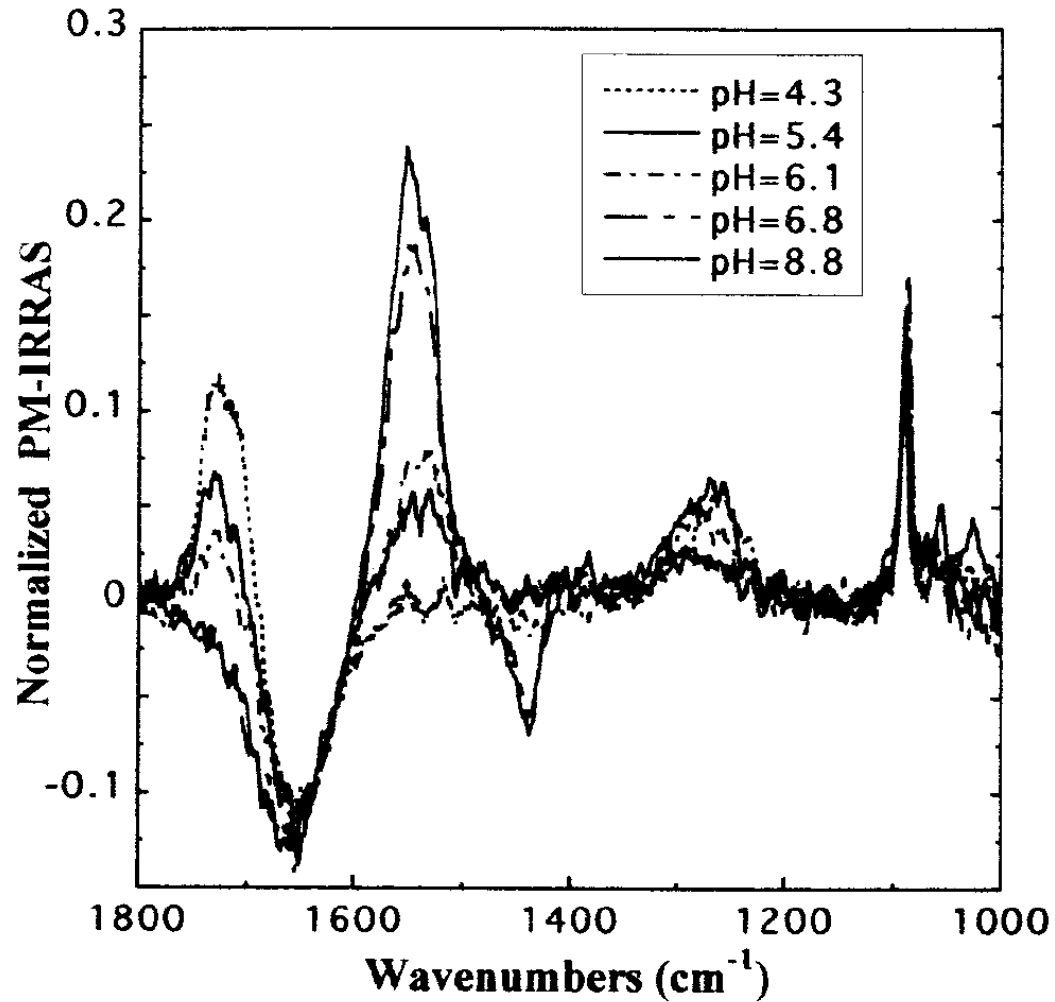
FIG. 2. Schematic of the optical PM-IRRAS setup and of the two-channel electronic processing.

## □ dAA with $\text{CdCl}_2$

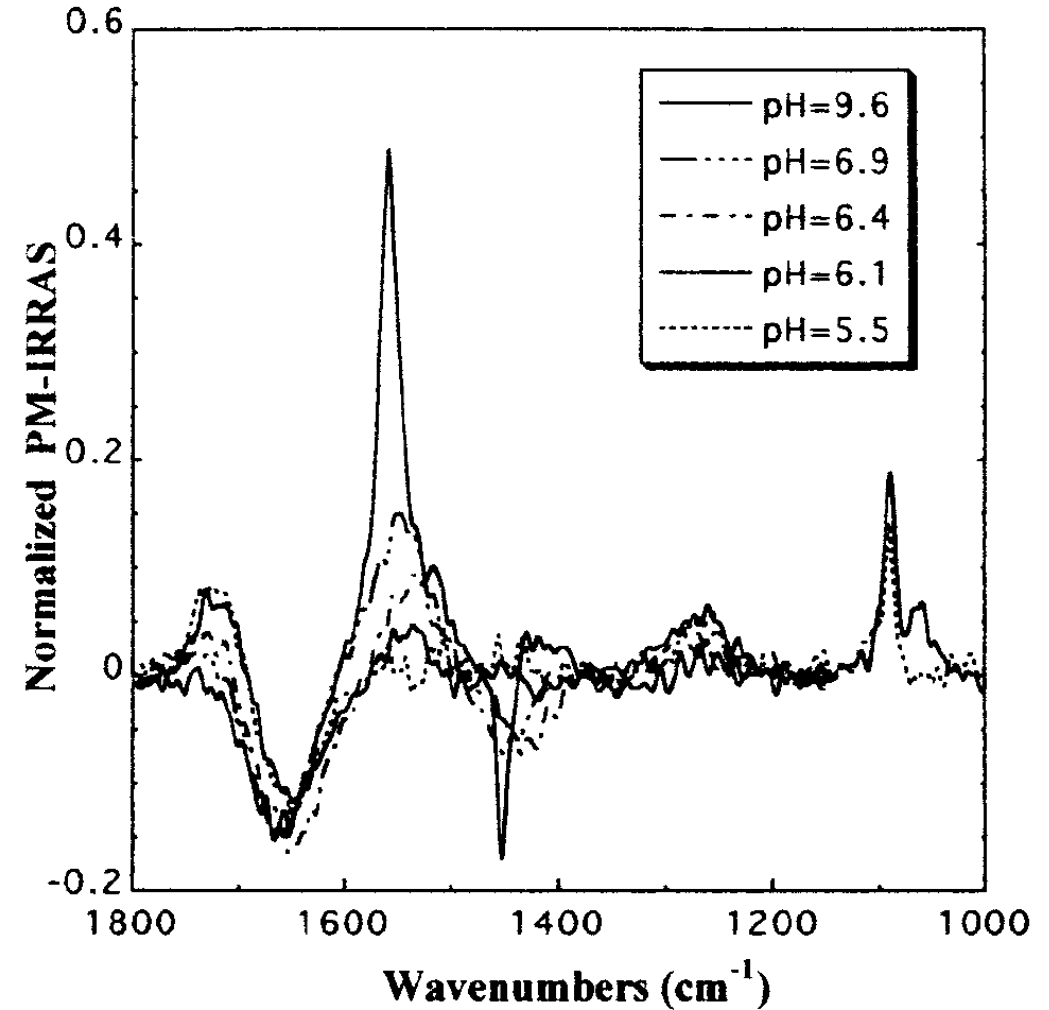


**Figure 1.** Normalized PM-IRRAS spectra of a monolayer of deuterated arachidic acid spread onto a water subphase containing  $3.5 \times 10^{-3} \text{ M}$   $\text{CdCl}_2$  as a function of the subphase pH in the headgroups vibration range (a) and in the alkyl chains vibration range (b).

## □ dAA with $\text{MgCl}_2$ and $\text{CaCl}_2$

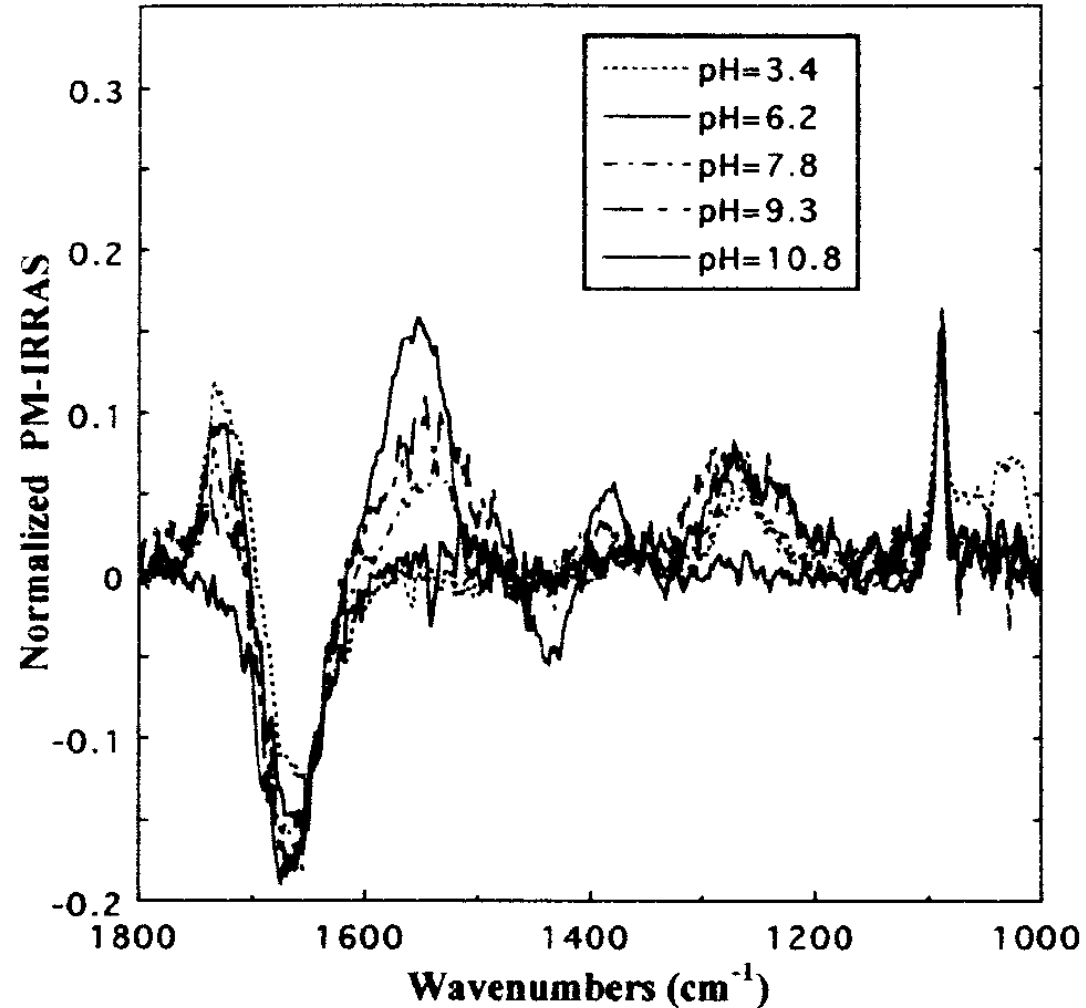


**Figure 2.** Normalized PM-IRRAS spectra of a monolayer of deuterated arachidic acid spread onto a water subphase containing  $3.1 \times 10^{-3} \text{ M}$   $\text{CaCl}_2$  as a function of the subphase pH.



**Figure 3.** Normalized PM-IRRAS spectra of a monolayer of deuterated arachidic acid spread onto a water subphase containing  $3 \times 10^{-3} \text{ M}$   $\text{MgCl}_2$  as a function of the subphase pH.

## □ dAA with NaCl

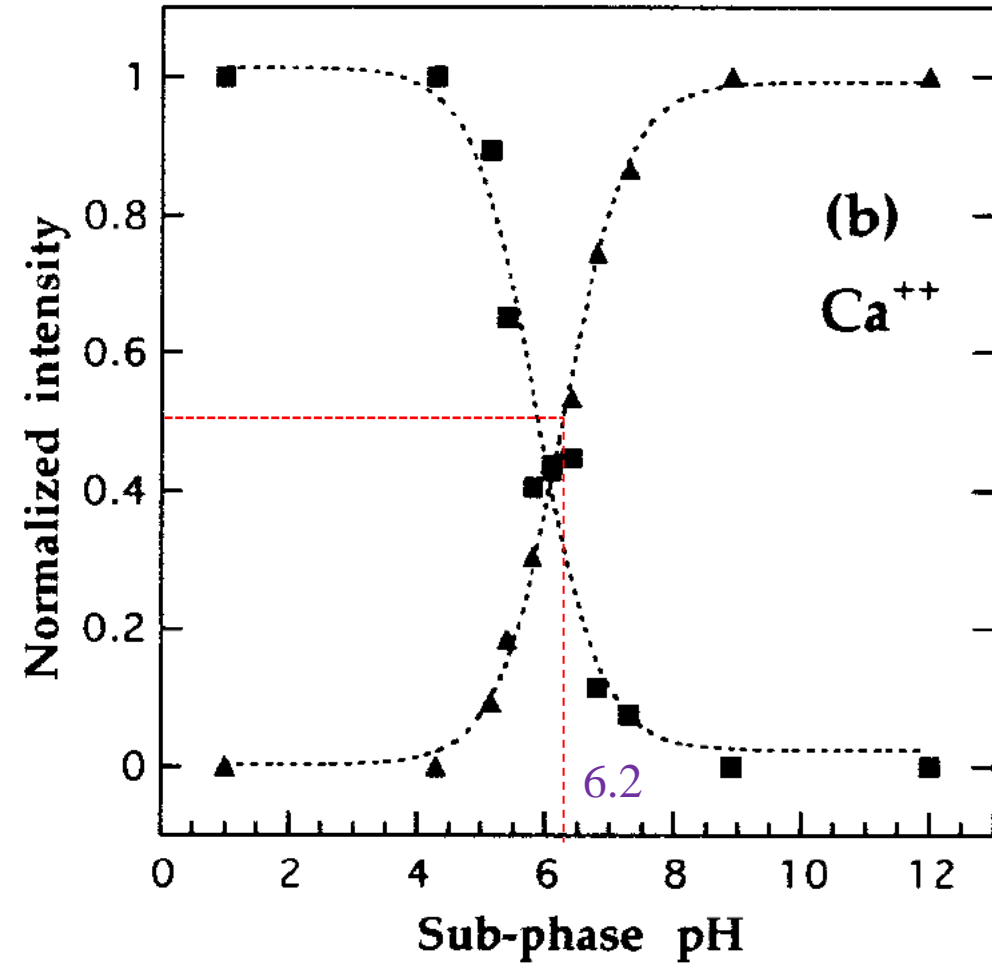
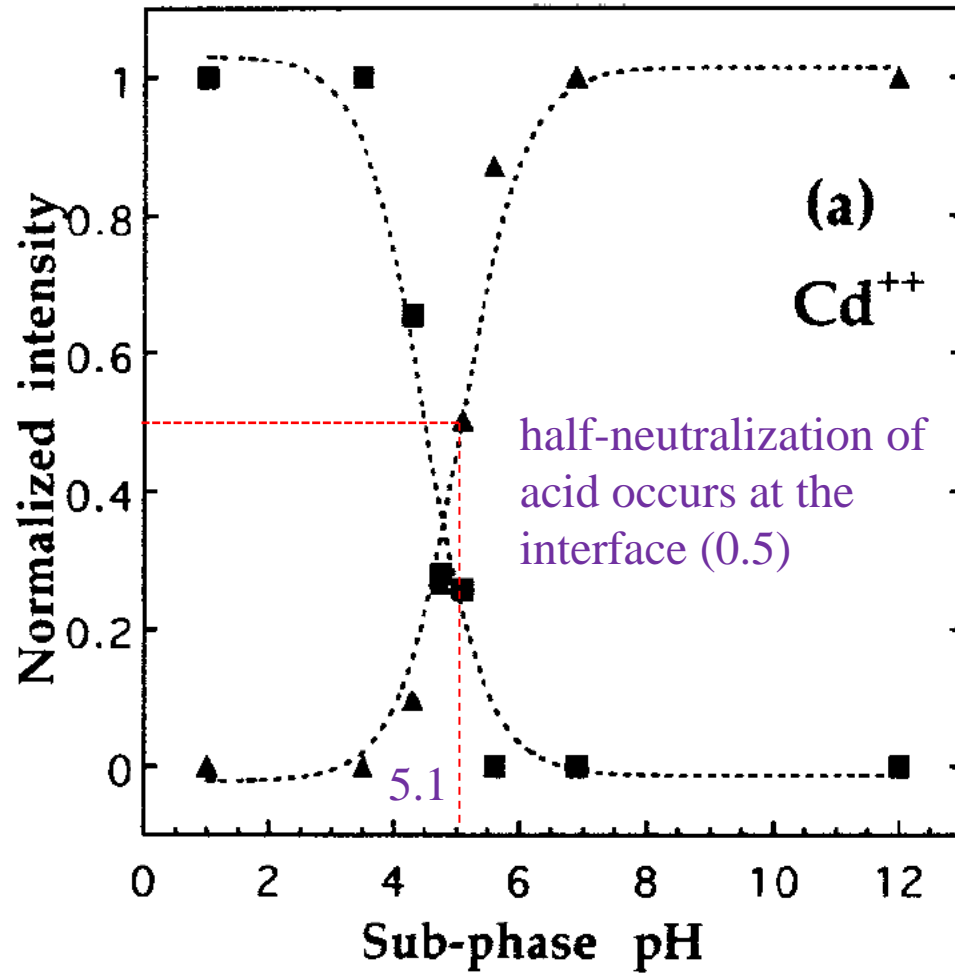


**Figure 4.** Normalized PM-IRRAS spectra of a monolayer of deuterated arachidic acid spread onto a water subphase containing  $10^{-2}$  M NaCl as a function of the subphase pH.

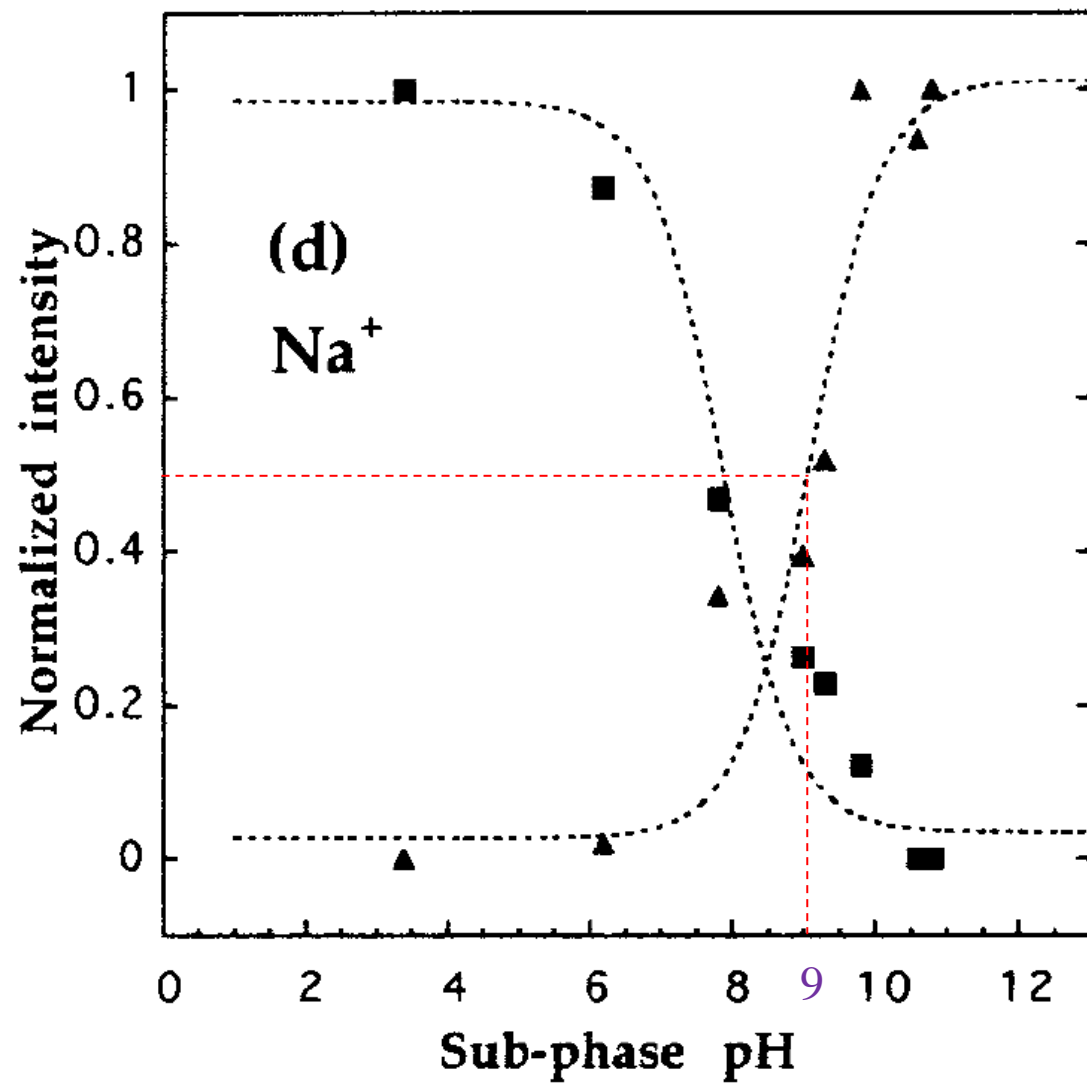
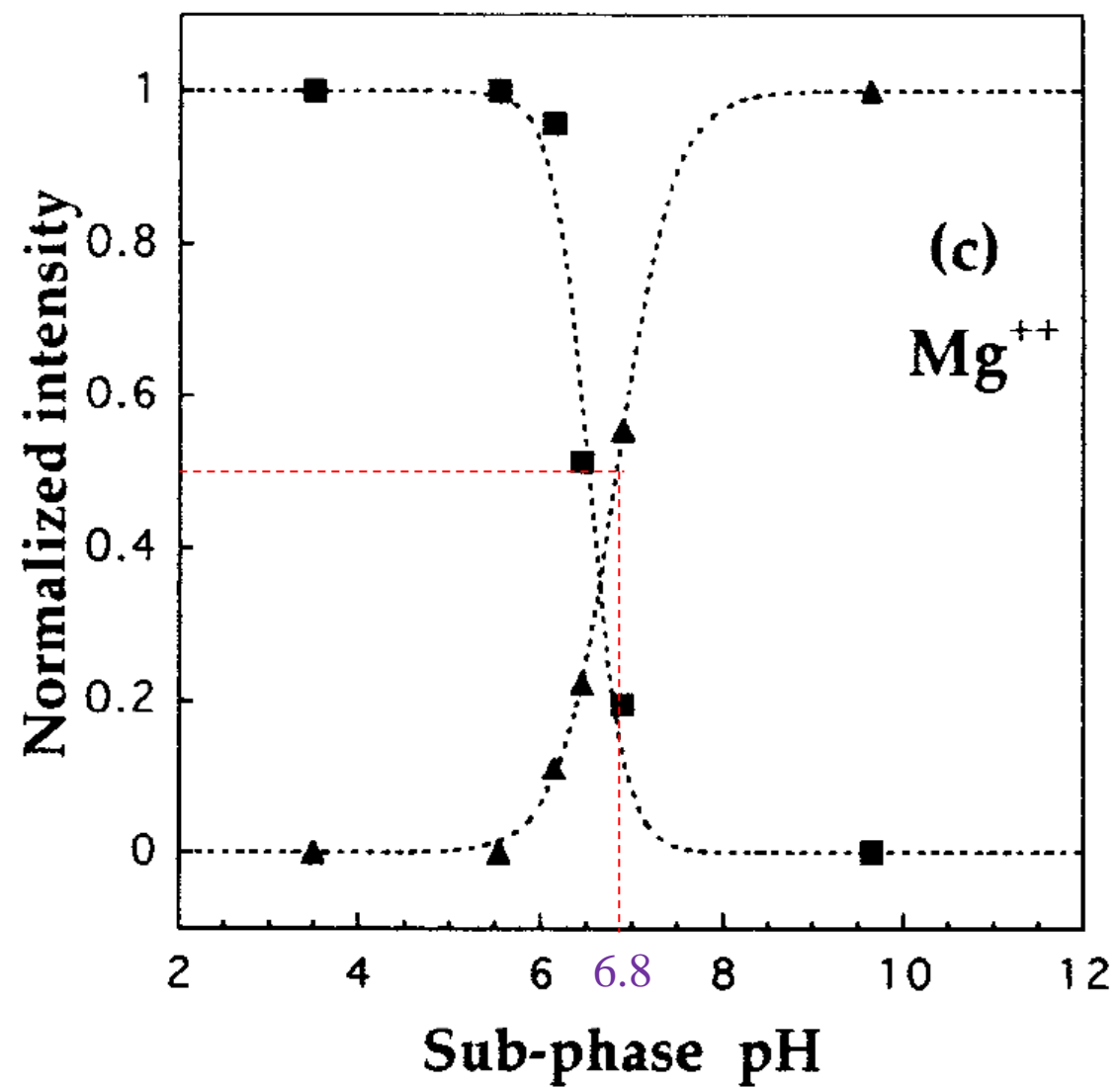
□ Deprotonation is much more difficult to obtain and a pH 10.8 is required to eliminate the acidic form



□ Normalization (Integrated intensity at highest pH for  $\nu_a$  COO<sup>-</sup> band and the lowest pH for the C=O band)



Normalized integrated PM-IRRAS intensities of the  $\nu_a$  COO<sup>-</sup> band (▲) and of the  $\nu$  C=O band (■)



❖ Determine  $\Delta pH$  (difference between  $pK_a$  at the interface and  $pH_{\text{half-neutral}}$  at the subphase)

## Introduction to $pK_a$

Acid–base equilibrium:

$$\frac{[-COO^-][H^+]_{\text{bulk}}}{[-COOH]} = K_a$$

$$\Rightarrow \log_{10} \frac{[-COO^-]}{[-COOH]} = pH - pK_a$$

**$pK_a$**  is the pH at which **half** of headgroups are protonated/deprotonated.

$$\Delta pH = pka - pH_{\text{half\_neutral}}$$

$pK_a = 5.6$ for arachidic acid		
$pH_{\text{half\_neutral}}$	$Cd^{2+}$	5.1
	$Ca^{2+}$	6.2
	$Mg^{2+}$	6.8
	$Na^+$	9



$\Delta pH$	$Cd^{2+}$	0.5
	$Ca^{2+}$	-0.6
	$Mg^{2+}$	-1.2
	$Na^+$	-3.4

$\Delta pH > 0$  :  $[H_3O^+]$  is smaller at the interface compare to subphase

$\Delta pH < 0$  :  $[H_3O^+]$  is higher at the interface compare to subphase

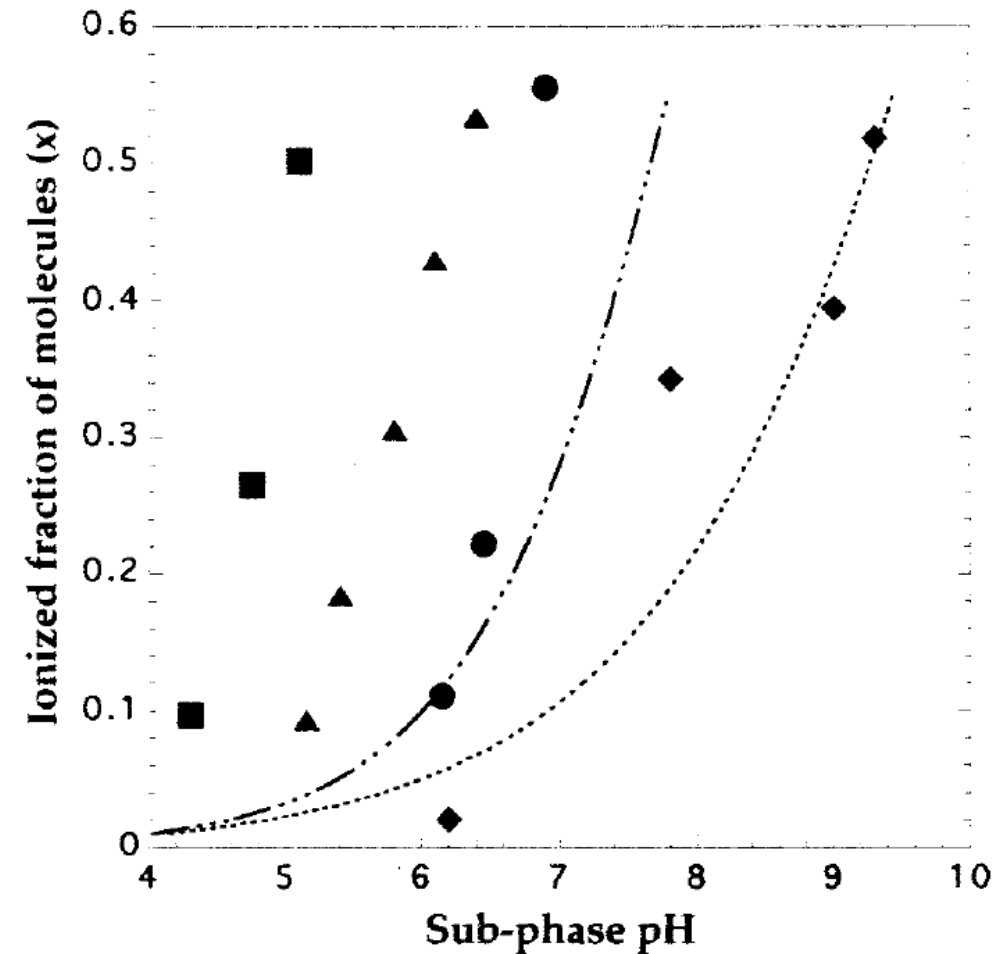
$$[H_3O^+] = 10^{\Delta pH}$$

$[H_3O^+]$	$Cd^{2+}$	3 times smaller
	$Ca^{2+}$	4 times higher
	$Mg^{2+}$	15 times higher
	$Na^+$	Thousand times higher

## Gouy-Chapman theory

$$\text{pH}_{\text{subphase}} = \text{p}K_a + \log\left(\frac{x}{1-x}\right) + \frac{0.87}{z} \sinh^{-1}\left(\frac{1.36x}{A\sqrt{C}}\right)$$

- ❑ Ions having a low number of electrons ( $\text{Na}^+$ ,....) is well adapted with Gouy-Chapman theory.
- ❑ Ions having a high number of electrons ( $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,...) have a specificity and an aptitude to form directed interactions with carboxylate



**Figure 6.** Experimental values of the ionized fraction of molecules as a function of the subphase pH for  $\text{Cd}^{2+}$  (■),  $\text{Ca}^{2+}$  (▲),  $\text{Mg}^{2+}$  (●), and  $\text{Na}^+$  (◆) and theoretical curves obtained from the Gouy-Chapman equation (see text) for a single-charged cation (dotted line) and for a double-charged cation (dotted-dashed line). The experimental values have been obtained from Figure 5.