

## Unveiling Microscopic Structures of Charged Water Interfaces by Surface-Specific Vibrational Spectroscopy

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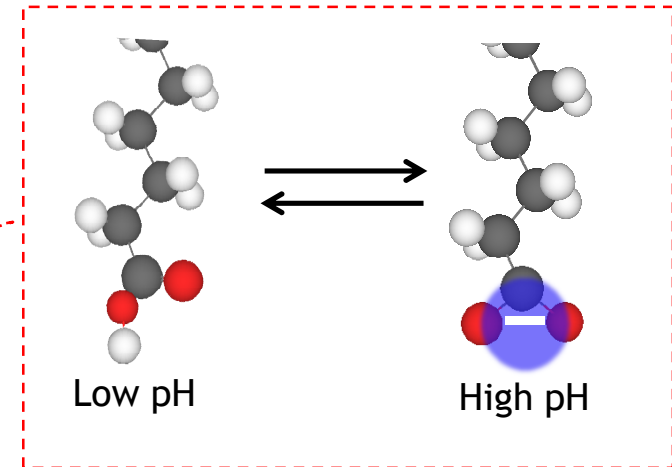
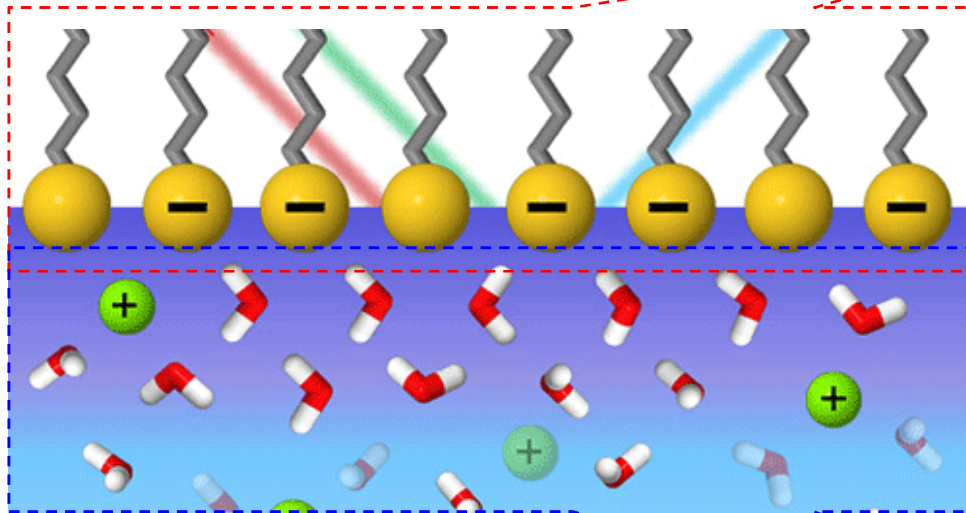
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A sum-frequency spectroscopy scheme is developed that allows the measurement of vibrational spectra of the interfacial molecular structure of charged water interfaces. The application of this scheme to a prototype lipid-aqueous interface as a demonstration reveals an interfacial hydrogen-bonding water layer structure that responds sensitively to the charge state of the lipid headgroup and its interaction with specific ions. This novel technique provides unique opportunities to search for better understanding of electrochemistry and biological aqueous interfaces at a deeper molecular level.

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# System - Charges on air/water interface

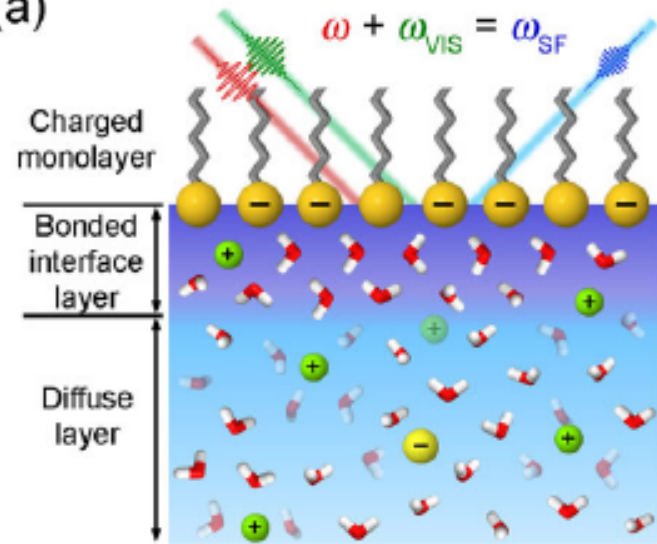
Lignoceric acid ( $\text{C}_{23}\text{H}_{47}\text{COOH}$ )  
Langmuir monolayer



Salts (NaCl), acids (HCl),  
and bases (NaOH)

# Interfacial structure model: BIL and DL

(a)



Water molecules strongly interacting with charged headgroups and counter cations.

Water molecules reoriented by surface electric field.

$$\chi_{S,\text{eff}}^{(2)} = \chi_S^{(2)} + \int_{0^+}^{\infty} [\chi_B^{(2)} + \chi_B^{(3)} \cdot \hat{z} E_0(z')] e^{i\Delta k_z z'} dz' \quad (1)$$

$\chi_S^{(2)}$  : Second-order susceptibility of bonded interface layer

$\chi_B^{(2)}$  : Second-order electric quadrupole bulk susceptibility

$\chi_B^{(3)}$  : Third-order bulk susceptibility

$\Delta k_z$  : Phase mismatch in reflection geometry ( $\Delta k_z = k_{\text{SF},z} - k_{\text{Vis},z} - k_{\text{IR},z}$ )

## Second order susceptibilities from BIL and DL

$$\chi_{S,\text{eff}}^{(2)} = \boxed{\chi_S^{(2)}} + \boxed{\int_{0^+}^{\infty} [\cancel{\chi_B^{(2)}} + \chi_B^{(3)} \cdot \hat{z} E_0(z')] e^{i\Delta k_z z'} dz'} \quad (1)$$

$\chi_S^{(2)}$  : Second-order susceptibility of bonded interface layer

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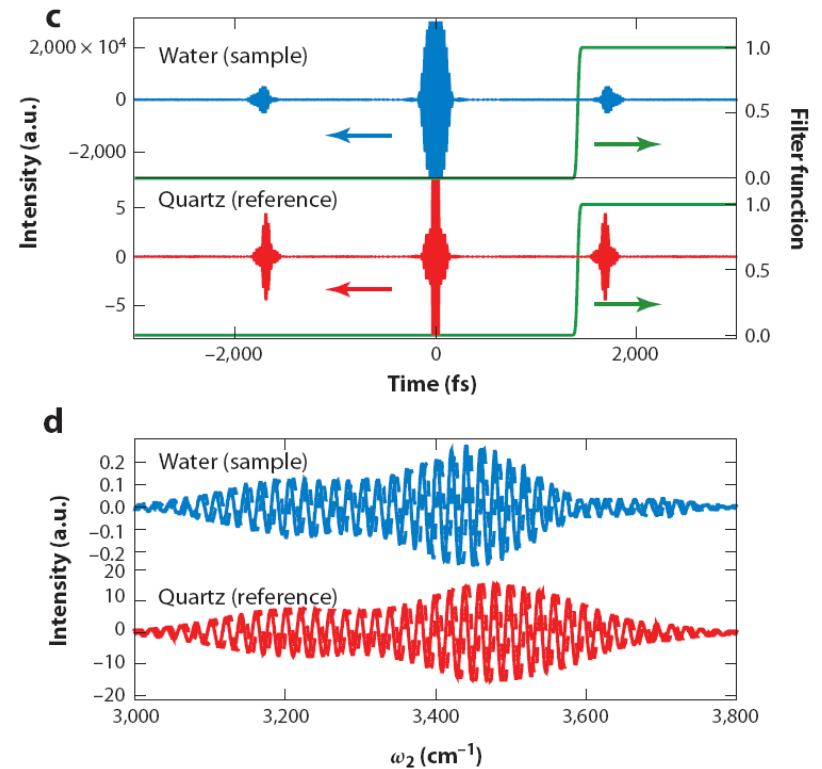
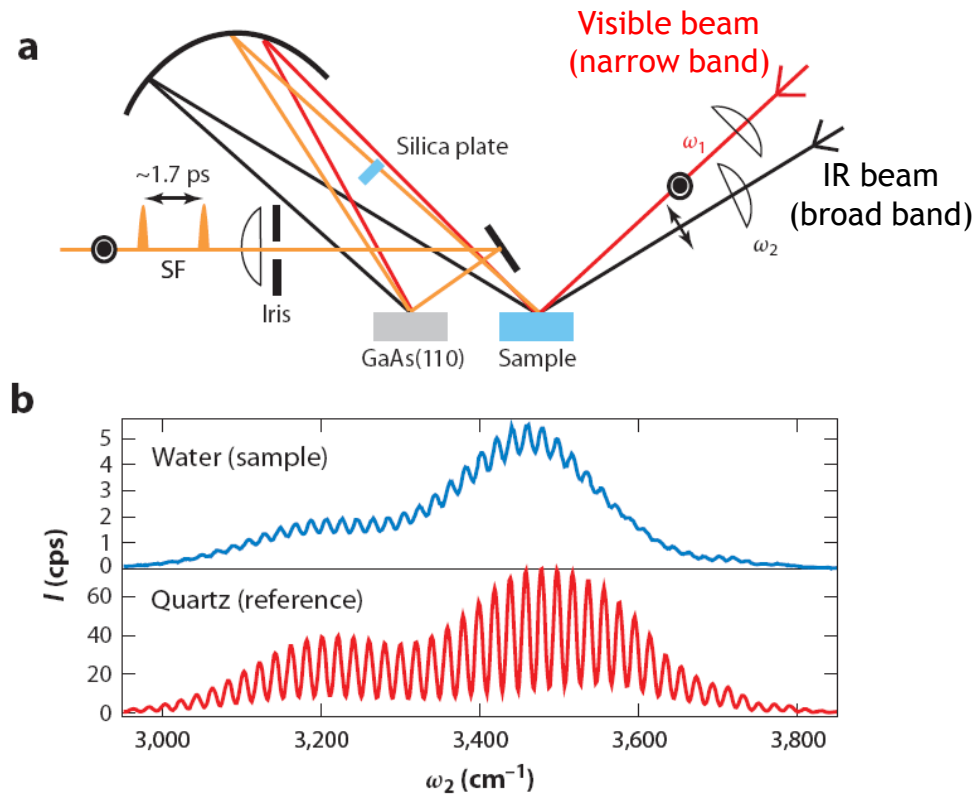
$\Delta k_z$  : Phase mismatch in reflection geometry ( $\Delta k_z = k_{\text{SF},z} - k_{\text{Vis},z} - k_{\text{IR},z}$ )

$$\chi_{S,\text{eff}}^{(2)} = \chi_S^{(2)} + \chi_{S,\text{DL}}^{(2)},$$

$$\chi_{S,\text{DL}}^{(2)} \equiv \int_{0^+}^{\infty} \chi_B^{(3)} \cdot \hat{z} E_0(z') e^{i\Delta k_z z'} dz' \equiv \chi_B^{(3)} \cdot \hat{z} \Psi,$$

$$\text{with } \Psi \equiv \int_{0^+}^{\infty} E_0(z') e^{i\Delta k_z z'} dz'. \quad (2)$$

# Experimental Setup - Same as HD-SFVS in Tahara group



$$\left| E_{sample} + E_{LO} e^{i\Delta\phi} \right|^2 =$$

$$\left| E_{sample} \right|^2 + \left| E_{LO} \right|^2 + E_{LO} E_{sample}^* e^{+i\Delta\phi} + E_{LO}^* E_{sample} e^{-i\Delta\phi}$$

$$\text{where, } \Delta\phi = \frac{2\pi}{\lambda} (n_{FS} - 1)d$$

**F.T.**



$$I(t) = \int I(\omega) e^{-i\omega t} d\omega = \begin{cases} \int \left| E_{ref}(\omega) \right|^2 + \left| E_{LO(\omega)}(\omega) \right|^2 e^{-i\omega t} d\omega \\ \int E_{LO}(\omega) E_{ref}(\omega)^* e^{+i\omega(\Delta T - t)} d\omega \\ \int E_{LO}^*(\omega) E_{ref}(\omega) e^{-i\omega(\Delta T + t)} d\omega \end{cases}$$

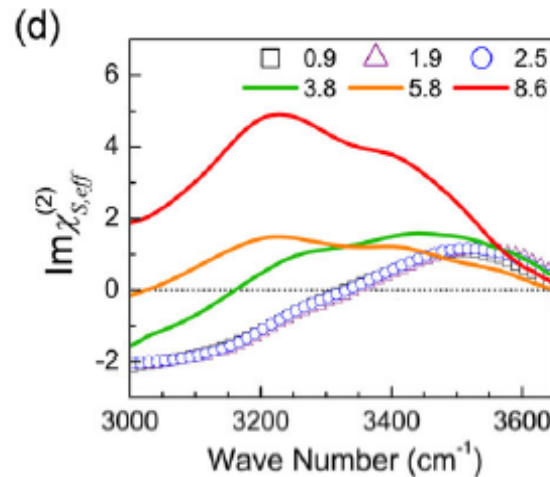
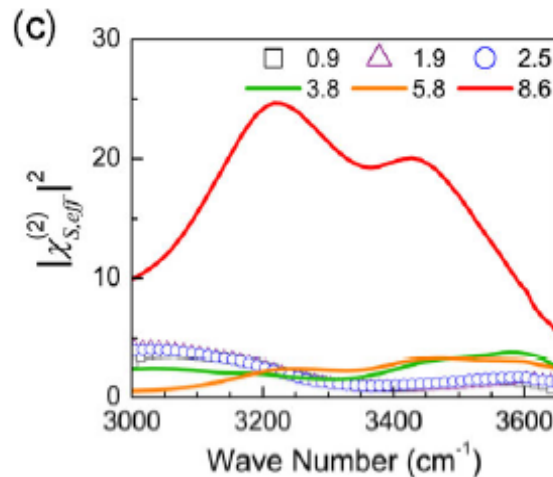
\*Pulse duration of Ti:Sa Amplifier ~ 100 fs

## Strategy - How to deduced $\chi_{S,DL}^{(2)}$ from $\chi_{eff}^{(2)}$

- 1) Take SF spectra of the LA monolayer/water interface in the pH range far below the half ionization point of carboxyl headgroup (pH < 9)

➡  $\chi_S^{(2)} \sim \chi_{S,0}^{(2)}$ : Second-order susceptibility of **charge neutral interface**

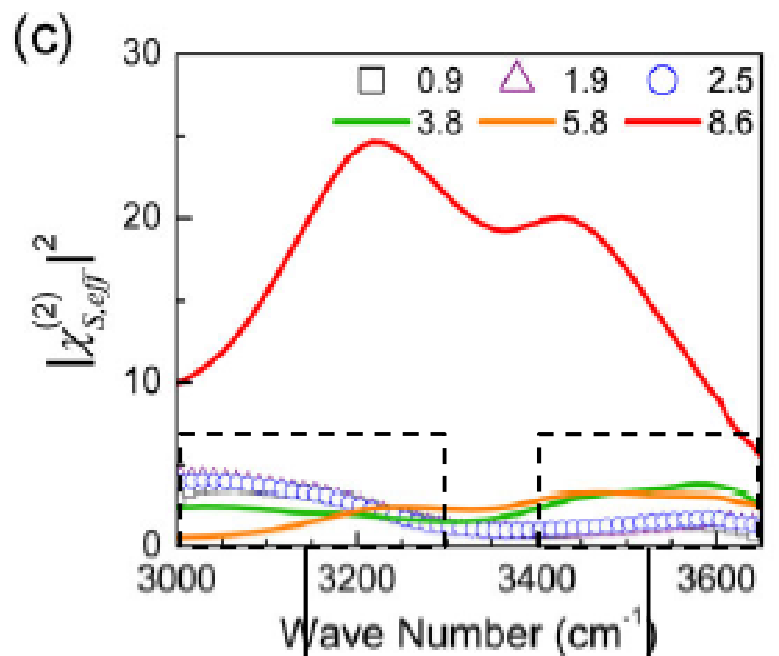
➡  $\chi_{S,eff}^{(2)} = \boxed{\chi_S^{(2)}} + \int_{0+}^{\infty} [\chi_B^{(2)} + \chi_B^{(3)} \cdot \hat{z} E_0(z')] e^{i\Delta k_z z'} dz', \quad (1)$



$\chi_S^{(2)} \sim \chi_{S,0}^{(2)}$  at pH < 2.5

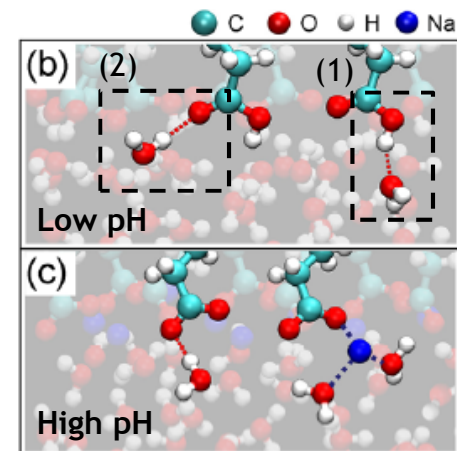
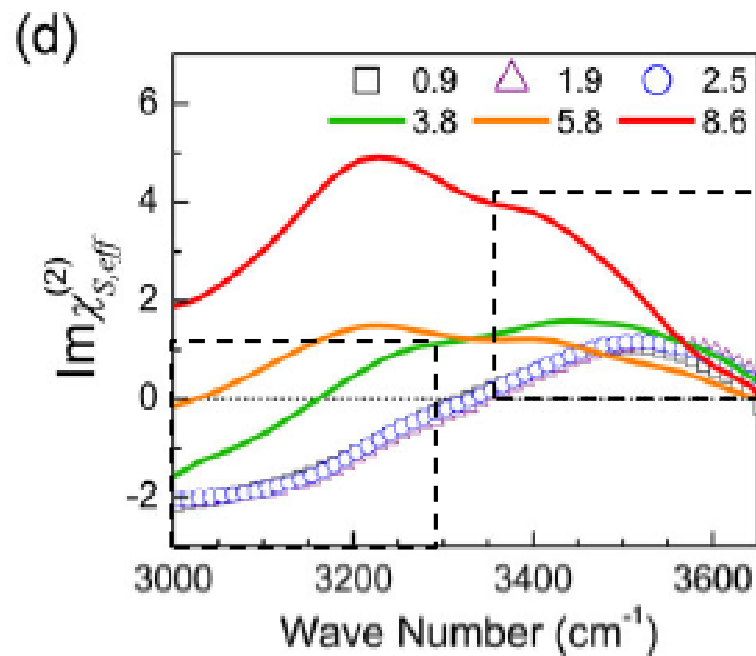
# Strategy - How to deduced $\chi^{(2)}_{S,DL}$ from $\chi^{(2)}_{eff}$

\*Assignment of the OH band



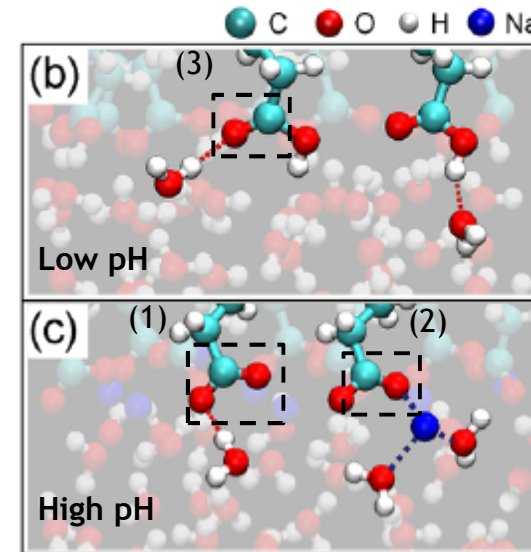
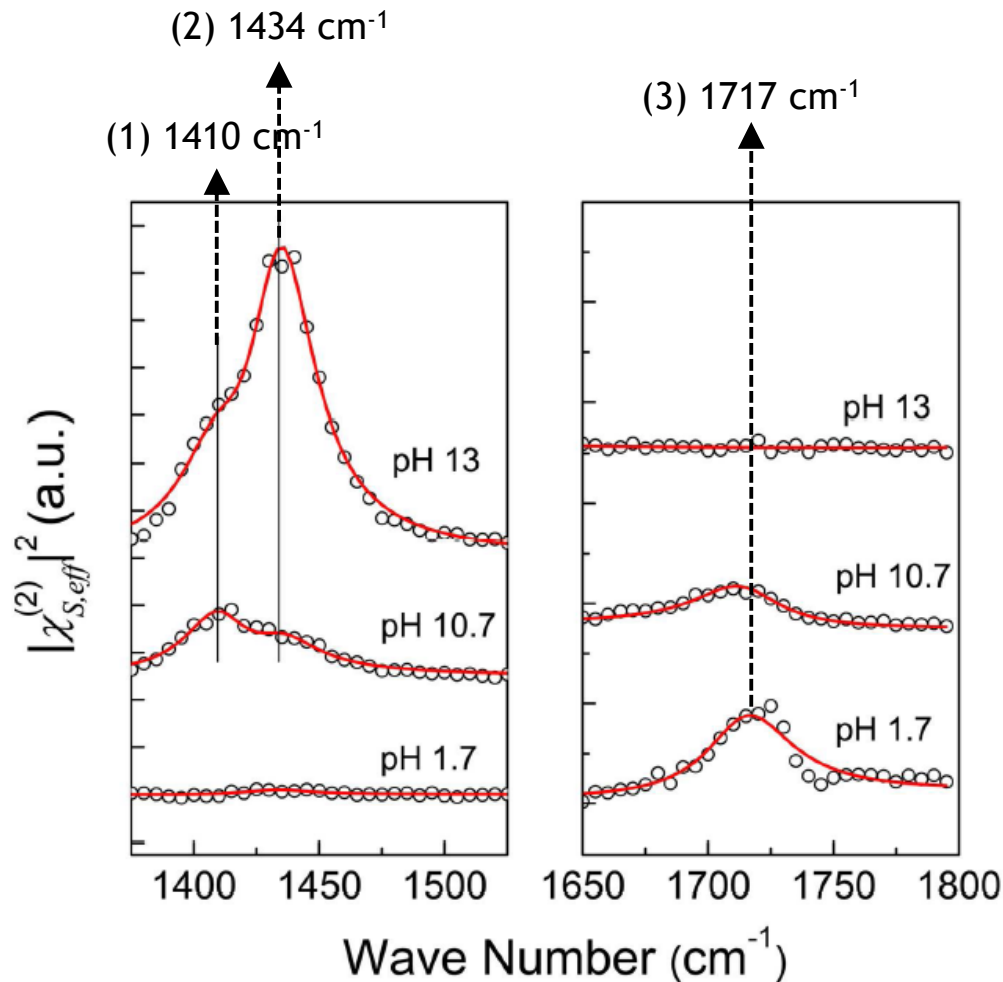
(1) From OH stretch mode of -COOH headgroup (H-bonded)

(2) From OH stretch mode of water molecules Bound to headgroup



## Strategy - How to deduced $\chi^{(2)}_{S,DL}$ from $\chi^{(2)}_{eff}$

- (2) Take SF spectra of the COOH (COO<sup>-</sup>) stretch modes of the LA monolayer/water interface.





## Strategy - How to deduced $\chi^{(2)}_{s,DL}$ from $\chi^{(2)}_{eff}$

- (3) Calculate surface charge density from the fitting result of the low frequency spectra (for the case of pH >9)

$$X_{COOH} + X_{COO^-} + X_{COO^- \cdots Na^+} = 1$$

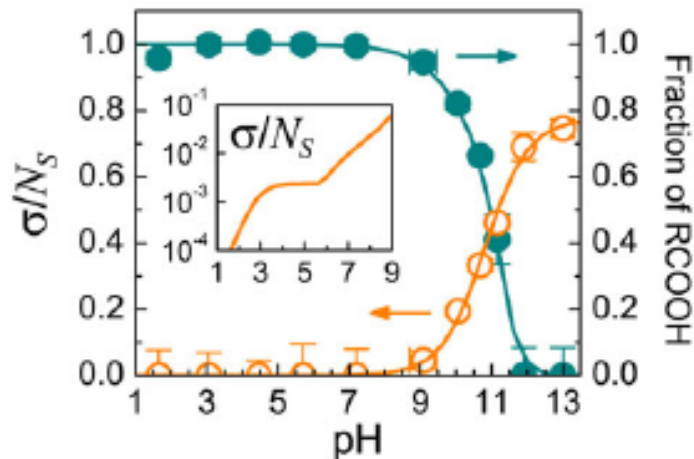
\*From MD simulation → **one Na<sup>+</sup> cation** prefer to bind to **three COO<sup>-</sup> headgroups**

➡  $\sigma = N_s(1 - X_{COOH}) - (1/3) \cdot N_s X_{COO^- \cdots Na^+}$

$\sigma$ : Net surface charge density

$N_s$ : Surface number density of carboxyl headgroup ( $N_s \sim \frac{1}{20 \text{ } \text{\AA}^2}$ )

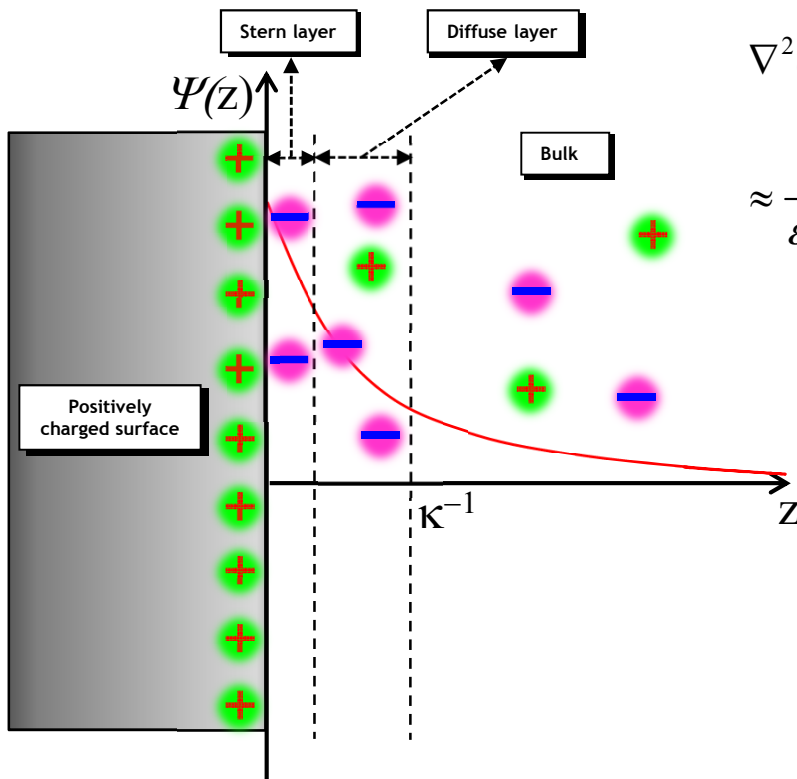
(b)



## Strategy - How to deduced $\chi^{(2)}_{s,DL}$ from $\chi^{(2)}_{eff}$

- (4) Calculate depth-dependent electric field,  $E_0(z)$  from PB theory  
(for the case of pH > 9)

### < Gouy-Chapman model >



(PB theory)

$$\nabla^2 \psi = -\frac{\rho_+(z) + \rho_-(z)}{\epsilon_r \epsilon_0} = -\left( \frac{c_0(+e)}{\epsilon_r \epsilon_0} e^{-\frac{(+e)\psi(z)}{kT}} + \frac{c_0(-e)}{\epsilon_r \epsilon_0} e^{-\frac{(-e)\psi(z)}{kT}} \right)$$

$$\approx \frac{2c_0 e^2}{\epsilon_r \epsilon_0 kT} \psi(z) \text{ for } \frac{e\psi(z)}{kT} \ll 1$$

$$\psi(z) = \psi_0 e^{-\kappa z}, \kappa = \sqrt{\frac{2c_0 e^2}{\epsilon_r \epsilon_0 kT}}$$

$\frac{e\psi(z)}{kT} \geq 1$  for highly charged surface  
( $\psi(0) > 100$  mV)

## Strategy - How to deduced $\chi^{(2)}_{s,DL}$ from $\chi^{(2)}_{eff}$

\*Explicit solution of PB equation for 1:1 electrolyte solution surface

$$\frac{d^2 y}{dz^2} = \frac{c_0 e^2}{\varepsilon_r \varepsilon_0 k_B T} (e^y - e^{-y}) = \frac{2c_0 e^2}{\varepsilon_r \varepsilon_0 k_B T} \sinh y = \kappa^2 \sinh y \cdots (1)^*$$

$$\text{where, } y = \frac{e\psi(z)}{k_B T}, \text{ and } \kappa = \sqrt{\frac{2c_0 e^2}{\varepsilon_r \varepsilon_0 k_B T}}$$



$$2 \frac{dy}{dz} \cdot \frac{d^2 y}{dz^2} = 2 \frac{dy}{dz} \cdot \kappa^2 \sinh y \cdots (2)^*$$



$$\int \frac{d}{dz'} \left( \frac{dy}{dz'} \right)^2 dz' = \left( \frac{dy}{dz} \right)^2 = 2\kappa^2 \int \frac{dy}{dz'} \cdot \sinh y dz' = 2\kappa^2 \int \sinh y dy' = 2\kappa^2 \cosh y + C_1 \cdots (3)^*$$

$$C_1 = -2\kappa^2$$

From M.S. dissertation of W. M. Sung

Strategy - How to deduced  $\chi^{(2)}_{s,DL}$  from  $\chi^{(2)}_{eff}$

$$\frac{dy}{dz} = \pm \kappa \sqrt{2 \cosh y - 2} = \pm 2\kappa \sinh\left(\frac{y}{2}\right) \cdots (4)^*$$

+ for negatively charged surface

- for positively charged surface



$$\int \frac{1}{\sinh \frac{y'}{2}} dy' = 2\kappa \int dz' \Rightarrow 2 \ln(\tanh \frac{y}{4}) = 2\kappa z + 2C_2 \cdots (5)^*$$

$$C_2 = \ln\left(\frac{e^{y_0/2} - 1}{e^{y_0/2} + 1}\right), y_0 = \frac{e\psi(0)}{k_B T}$$

From M.S. dissertation of W. M. Sung

Strategy - How to deduced  $\chi^{(2)}_{s,DL}$  from  $\chi^{(2)}_{eff}$

$$\ln\left(\frac{e^{y/4} - e^{-y/4}}{e^{y/4} + e^{-y/4}}\right) = \ln\left(\frac{e^{y/2} - 1}{e^{y/2} + 1}\right) = -\kappa z + C_2 \cdots (6)^*$$

$$C_2 = \ln\left(\frac{e^{y_0/2} - 1}{e^{y_0/2} + 1}\right), y_0 = \frac{e\psi(0)}{k_B T}$$

From M.S. dissertation of W. M. Sung



$$\phi(z) = \frac{4k_B T}{e} \tanh^{-1} \left\{ \tanh\left(\frac{e\phi_0}{4kT}\right) \exp(-\kappa z) \right\}, \quad (S3)$$

$$\kappa = \left( \frac{2Ce^2}{\epsilon kT} \right)^{1/2}, \quad (S4)$$

## Strategy - How to deduced $\chi^{(2)}_{s,DL}$ from $\chi^{(2)}_{eff}$

\*Grahame equation for charge neutrality

$$\sigma = -\varepsilon_0 \varepsilon_r \int_0^\infty \rho_e dz = -\varepsilon_0 \varepsilon_r \left. \frac{d\psi}{dz} \right|_{z=0} \dots (7)$$

$$\sigma = \sqrt{8C_0 \varepsilon_0 \varepsilon_r k_B T} \cdot \sinh\left(\frac{e\psi_0}{2k_B T}\right) \dots (8)$$

From M.S. dissertation of W. M. Sung

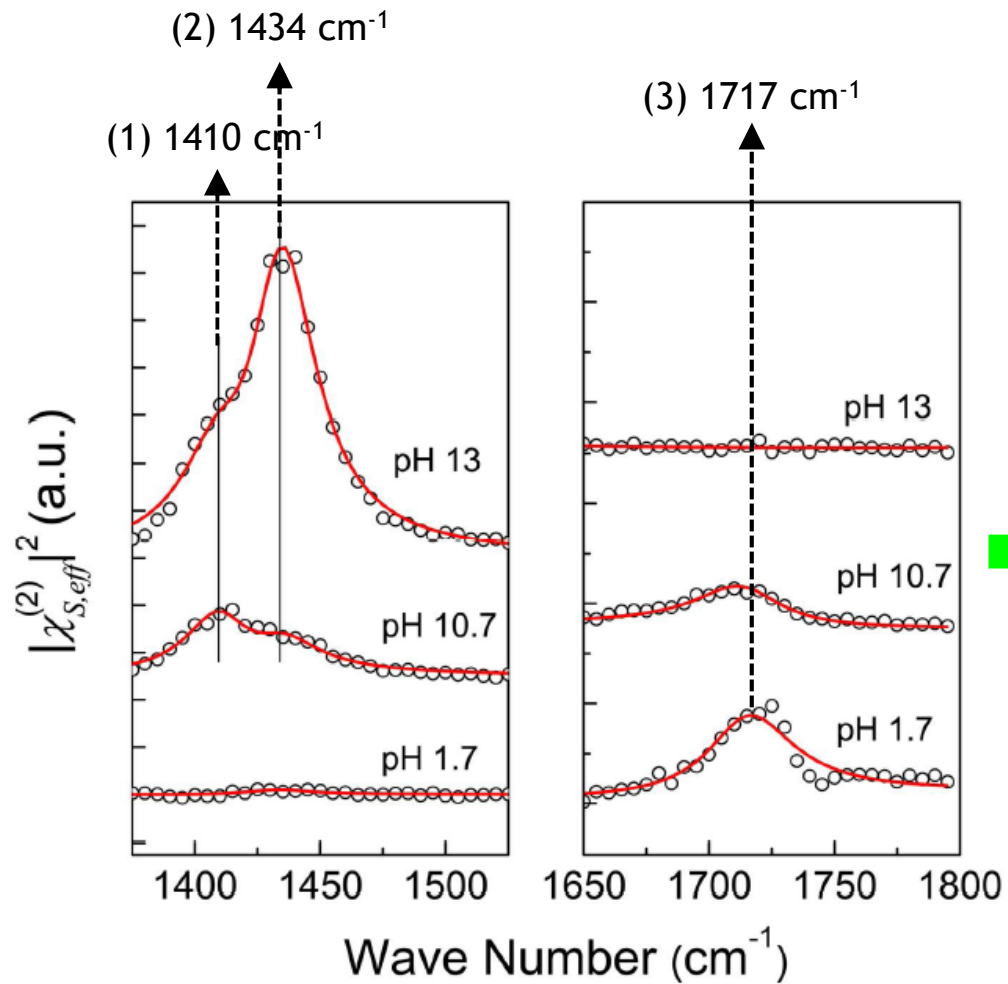


$$\phi_0 = -\frac{2kT}{e} \sinh^{-1} \left\{ \frac{e\sigma}{(8k_B T \varepsilon C)^{1/2}} \right\}, \quad (S5)$$

Once surface charge density,  $\sigma$  and bulk concentration,  $C$  are determined, depth profile of surface electric field is uniquely determined by PB equation (pH > 9)

# Strategy - How to deduced $\chi^{(2)}_{S,DL}$ from $\chi^{(2)}_{eff}$

At neutral and acidic pH (pH <9)



COO<sup>-</sup> and COO<sup>-</sup>Na<sup>+</sup> modes cannot be measured accurately...

# Strategy - How to deduced $\chi^{(2)}_{s,DL}$ from $\chi^{(2)}_{eff}$

By introducing surface pH,  $pH_s$

Known: 5.6

$$pK_a = pH_s - \log\left[\frac{(1 - X_{COOH})}{X_{COOH}}\right] \rightarrow \text{known}$$

$$pH_s = pH_b + \frac{e\phi_0}{2.3k_B T}, \quad (S1)$$

$$[H^+]_s(0) = [H^+]_b e^{-\frac{e\psi(0)}{k_B T}}$$

$$-\log_{10}([H^+]_s(0)) = -\log_{10}([H^+]_b) - \log_{10}\left(e^{-\frac{e\psi(0)}{k_B T}}\right)$$

$$\sigma = \sqrt{8C_0 \epsilon_0 \epsilon_r k_B T} \cdot \sinh\left(\frac{e\psi(0)}{2k_B T}\right) \dots (8)$$



# Strategy - How to deduced $\chi^{(2)}_{S,DL}$ from $\chi^{(2)}_{eff}$

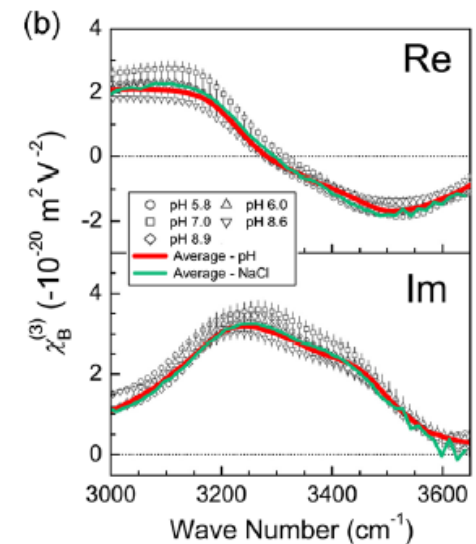
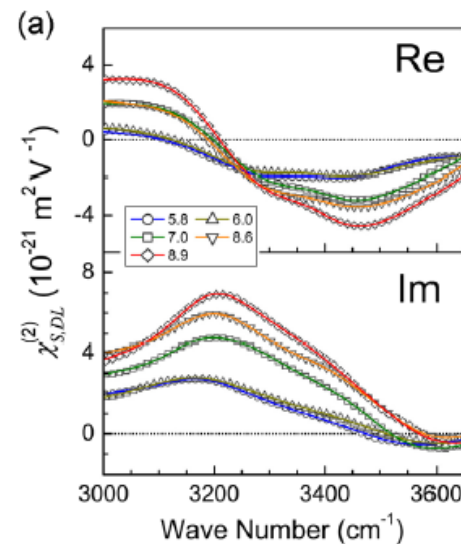
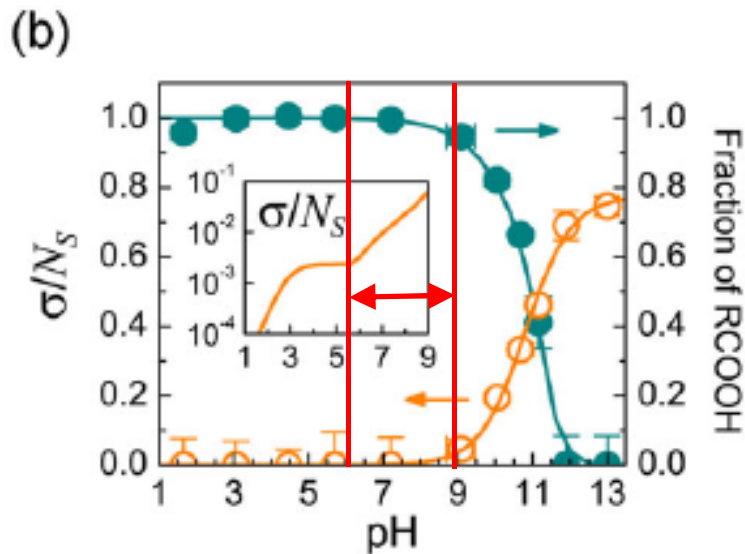
➡  $\chi^{(2)}_S \sim \chi^{(2)}_{S,0}$  : Second-order susceptibility of **charge neutral interface**

Converge to  $\chi^{(2)}_{S,0}$  when deprotonation fraction of COOH is low.

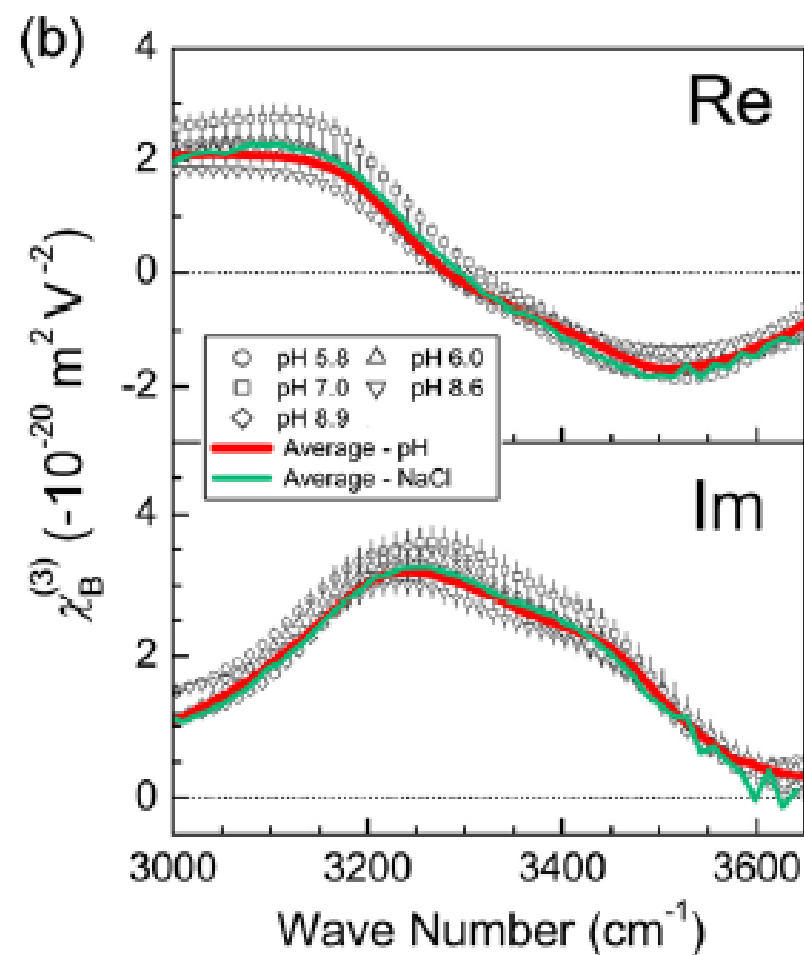
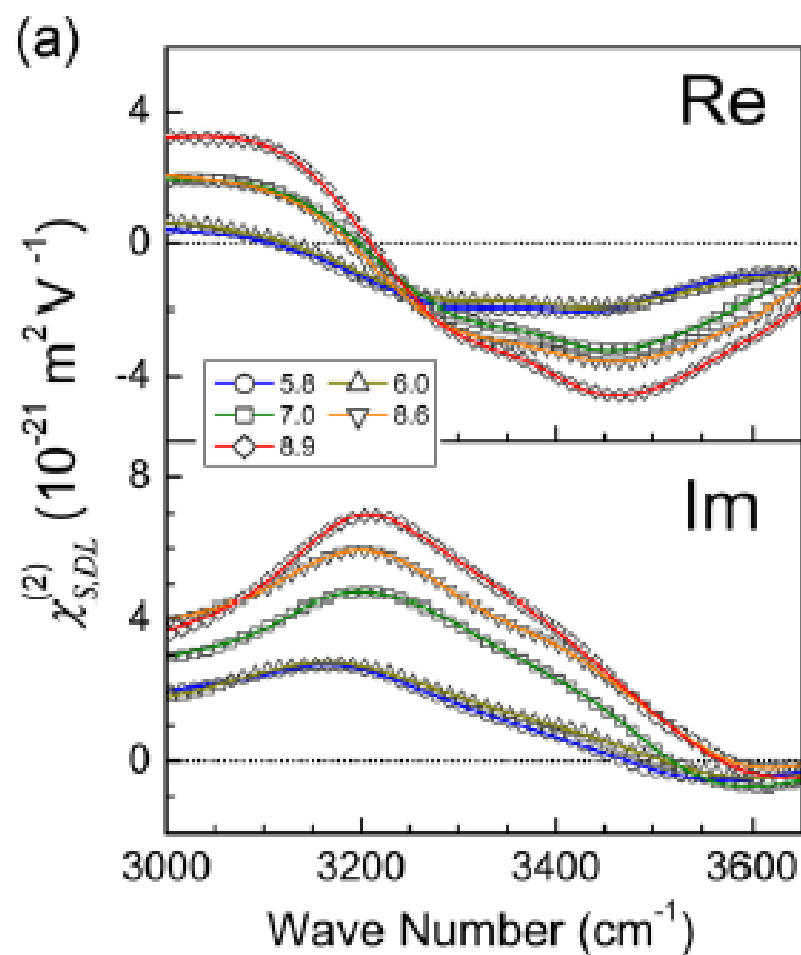
$$\chi^{(2)}_{S,eff} = \chi^{(2)}_S + \chi^{(2)}_{S,DL},$$

➡ 
$$\chi^{(2)}_{S,eff} = \boxed{\chi^{(2)}_S} + \int_{0^+}^{\infty} \left[ \cancel{\chi^{(2)}_B} + \chi^{(3)}_B \cdot \hat{z} E_0(z') \right] e^{i\Delta k_z z'} dz', \quad (1)$$

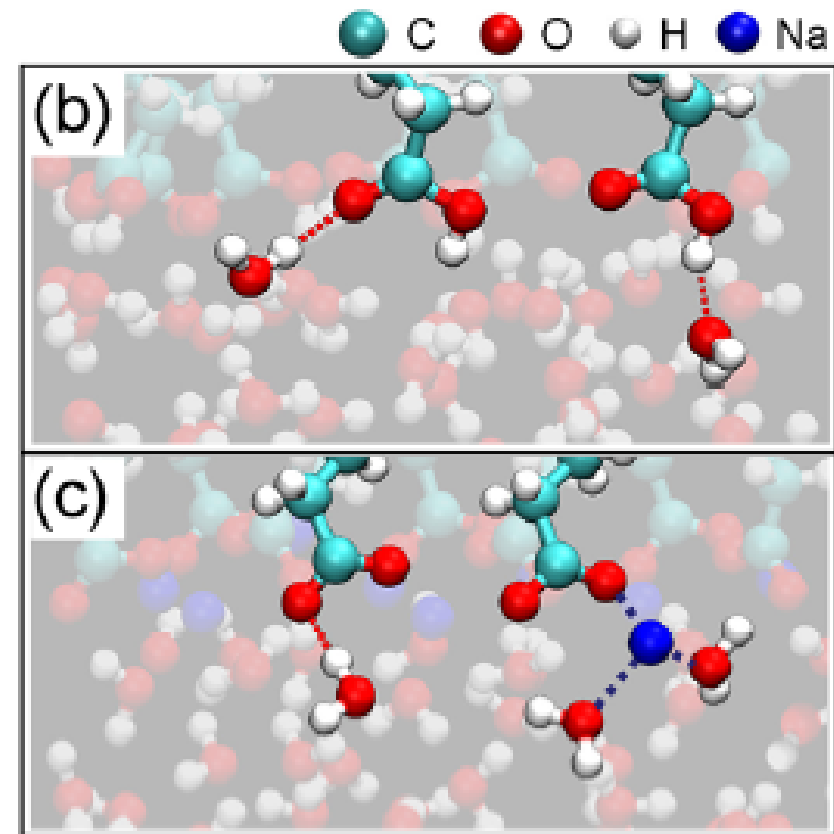
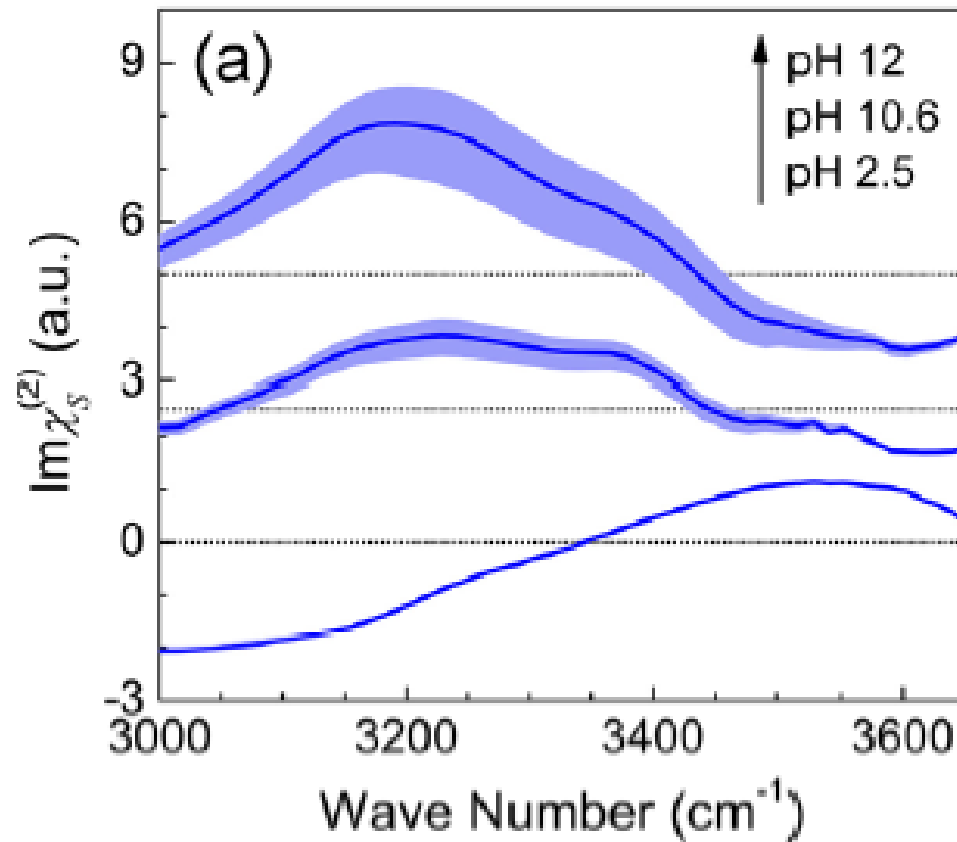
known



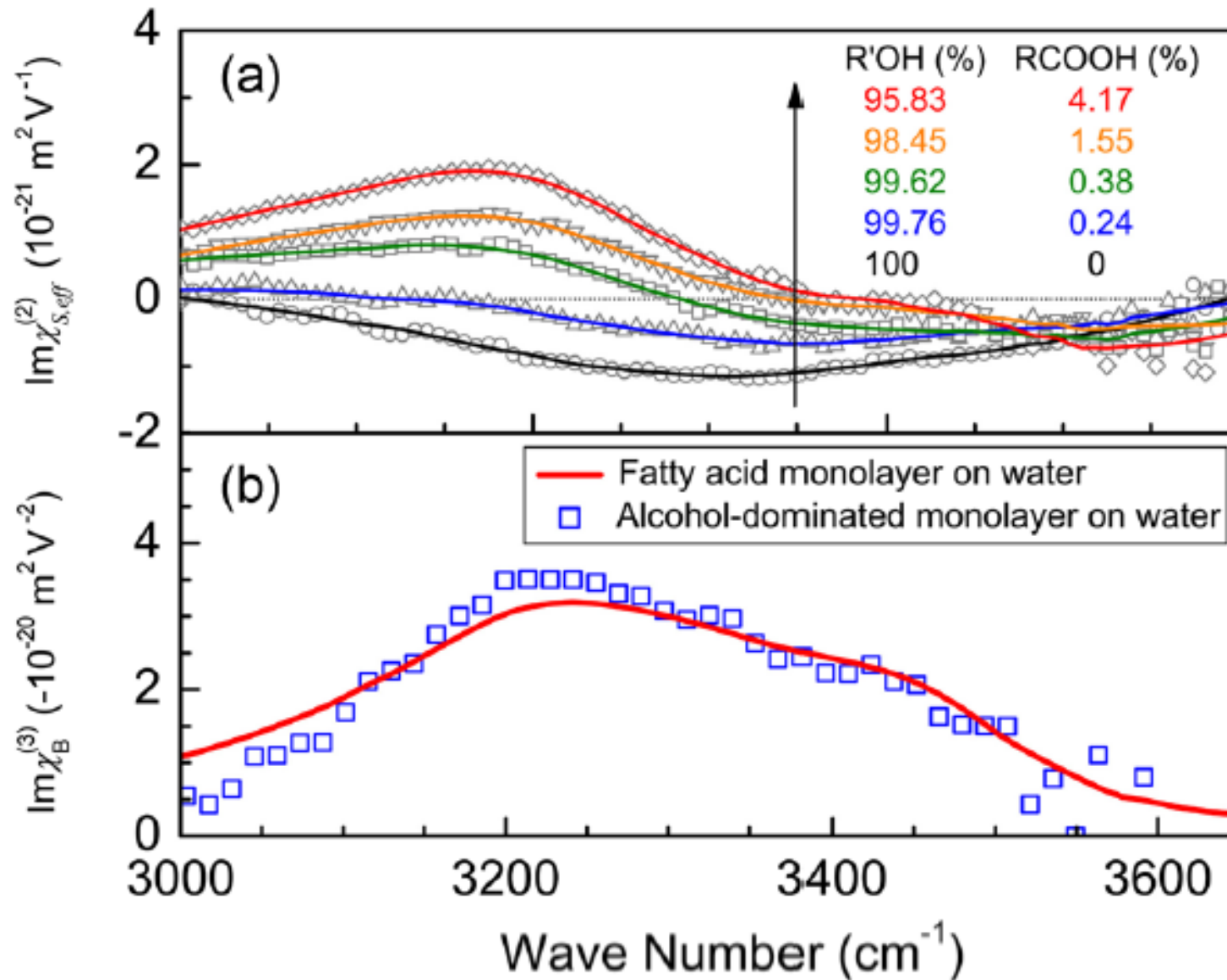
## Deduced $\chi^{(2)}_{S,DL}$ spectra



## Deduced $\chi^{(2)}_s$ spectra



$\chi^{(3)}_B$  does not sensitively depend on interface property



## In summary,

We have demonstrated a scheme using PS-SFVS to separately deduce the vibrational spectra of the BIL and the diffuse layer of a charged water interface.

For any water interface with a given surface charge density  $\sigma$ , it is now possible to find the spectrum of the diffuse layer and, in turn, the spectrum of the BIL from measurement. Even if  $\sigma$  is not known, one can still carry out a measurement with several different phase mismatches  $\Delta k_z$ , and deduce both  $\sigma$  and the spectrum of the BIL, which are intimately related to the microscopic structure of BIL. Such work offers new opportunities to explore various charged water interfaces at a deeper molecular level, providing a base for the understanding and theoretical modeling of such interfaces.