Phase-Sensitive Sum Frequency Revealing Accommodation of Bicarbonate Ions, and Charge Separation of Sodium and Carbonate Ions within the Air/Water Interface

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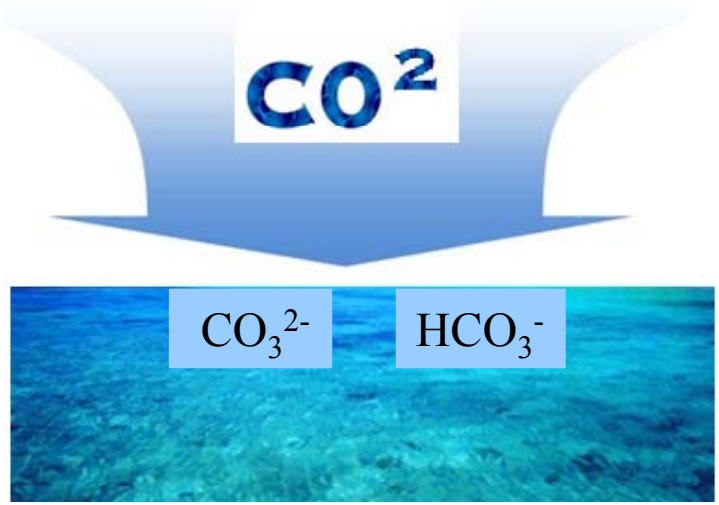
Natural ocean



CO^2 is absorbed into the ocean

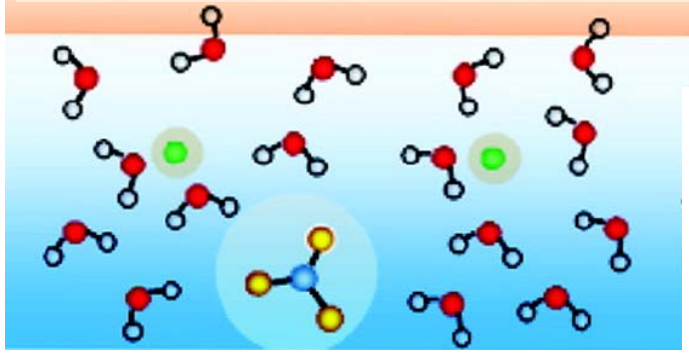
Creation of HCO_3^- ions and CO_3^{2-} ions

Change of water surface organization
(air/ocean interface & air/atmospheric aerosol interfaces)

Artificial ocean

Materials and Salts Solutions

Air/ Na_2CO_3 solution interface

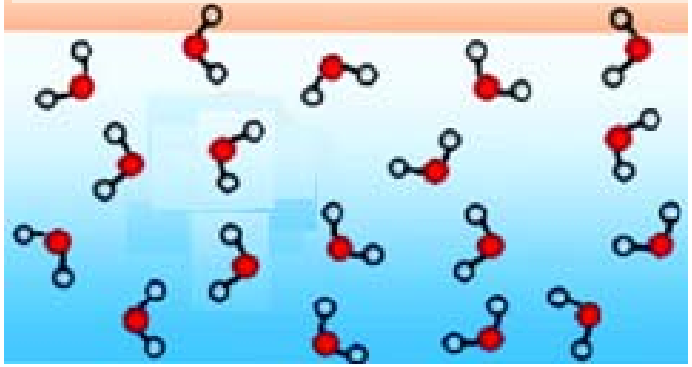


1.1 M Na_2CO_3 solutions

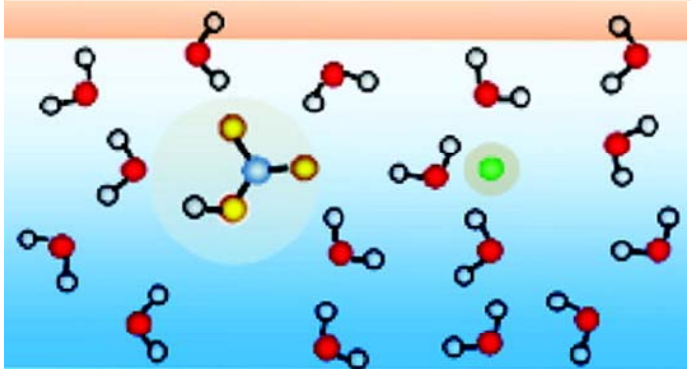
OH^- ions : 0.005 M

pH : 11.7

air/neat water interface
(including isotopic dilution by D_2O)



Air/ Na_2HCO_3 solution interface



0.8 M NaHCO3 solutions

OH^- ions : ~10^{-5} M

pH : 8.8

Carbon ions : bluish-gray
Oxyge ions : nyellow spheres
Sodium ions : green

VSFG method

Conventional VSFG method :

$$I_{SFG} \propto \left|\chi^{(2)}\right|^2 I_{vis} I_{IR} \propto \left|\chi_{NR}{}^{(2)} + \sum_{\nu} \chi_{\nu}{}^{(2)}\right|^2 I_{vis} I_{IR}$$

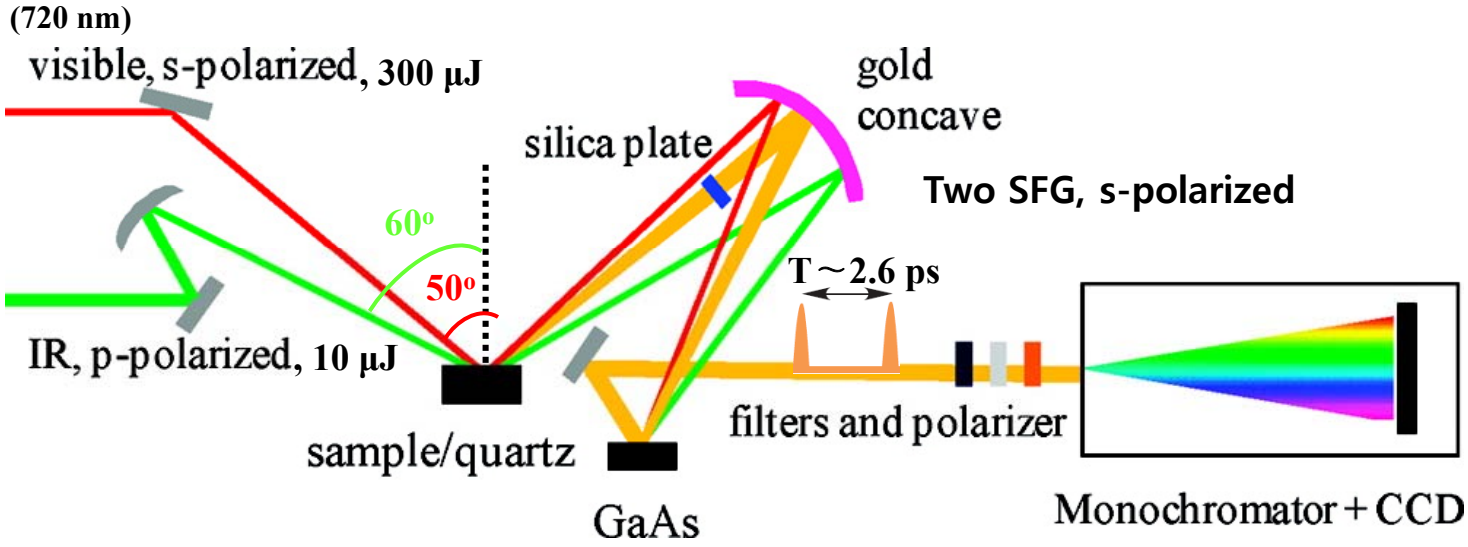
➡ Intensity provides strength of the hydrogen bonds of surface species

Phase-sensitive SFG method :

- Discrete $\chi_{\nu}^{(2)} = \dfrac{A_{\nu}}{\omega_{IR} - \omega_{v} + i\Gamma_{v}}$ and $\mathrm{Im}\,\chi^{(2)} = -\sum_{\nu} \dfrac{A_{\nu}\Gamma_{v}}{(\omega_{IR} - \omega_{v})^2 + \Gamma_{v}{}^2}$

➡ Im $\chi^{(2)}$ provides the net water dipole orientation of surface species

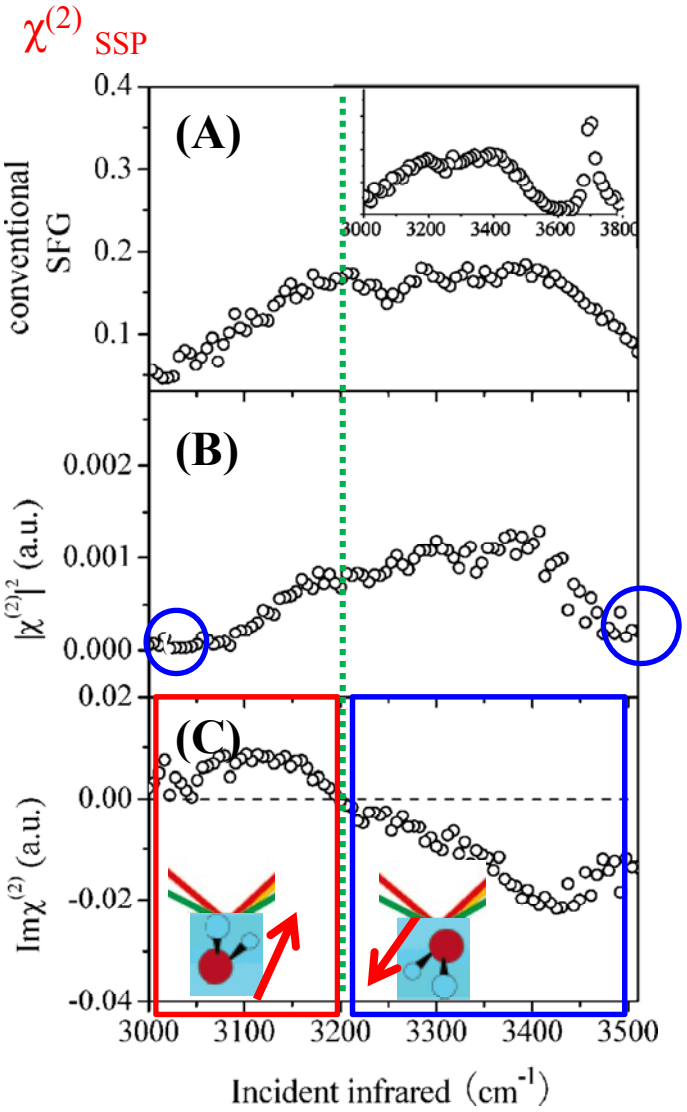
The broad-bandwidth VSFG spectrometer setup

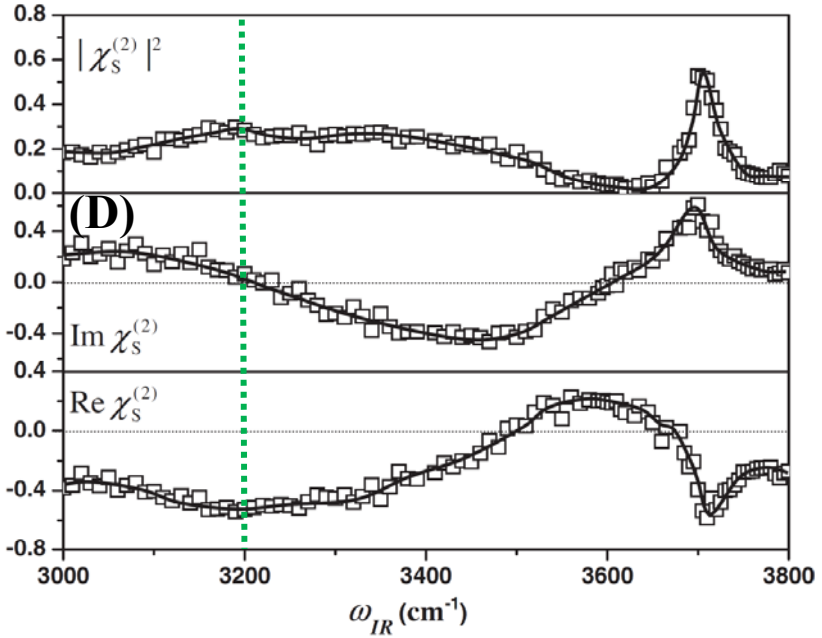


- Spectral bandwidth of the infrared beam : ~ 500 cm^{-1}

Phase-sensitive & conventional VSFG spectra of neat water

OH stretching frequency region





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From SFG spectra of neat water

In the 3000~3200 cm^{-1} region

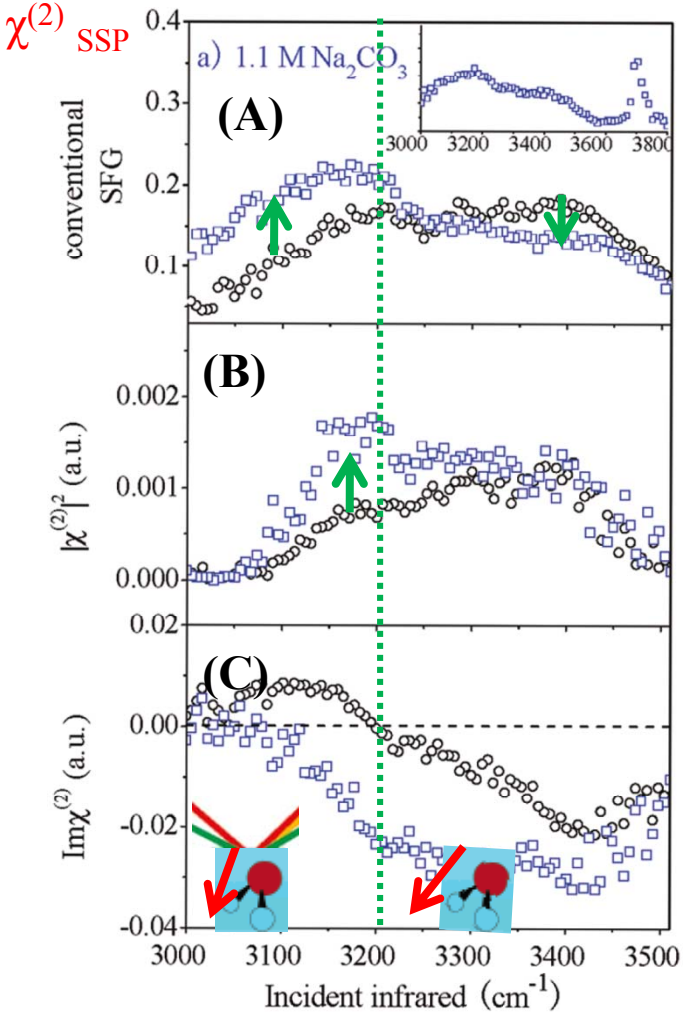
- Net dipole orientation pointing up toward the interface
- the more tightly hydrogen bonded spectral region
- come from the subsequent layers of the top few layers of the water surface

In the 3200 to 3500 cm^{-1} region

- Net dipole orientation pointing down toward the bulk
- the more weakly hydrogen bonded spectral region
- come from the top few layers of the water surface

SFG spectra of water molecules in aqueous Na_2CO_3 solution

OH stretching frequency region



spectra at air/neat water are black circles
spectra at air/aqueous Na_2CO_3 solution are blue circles

Spectra A and B show
there is a strengthening of the hydrogen bonds

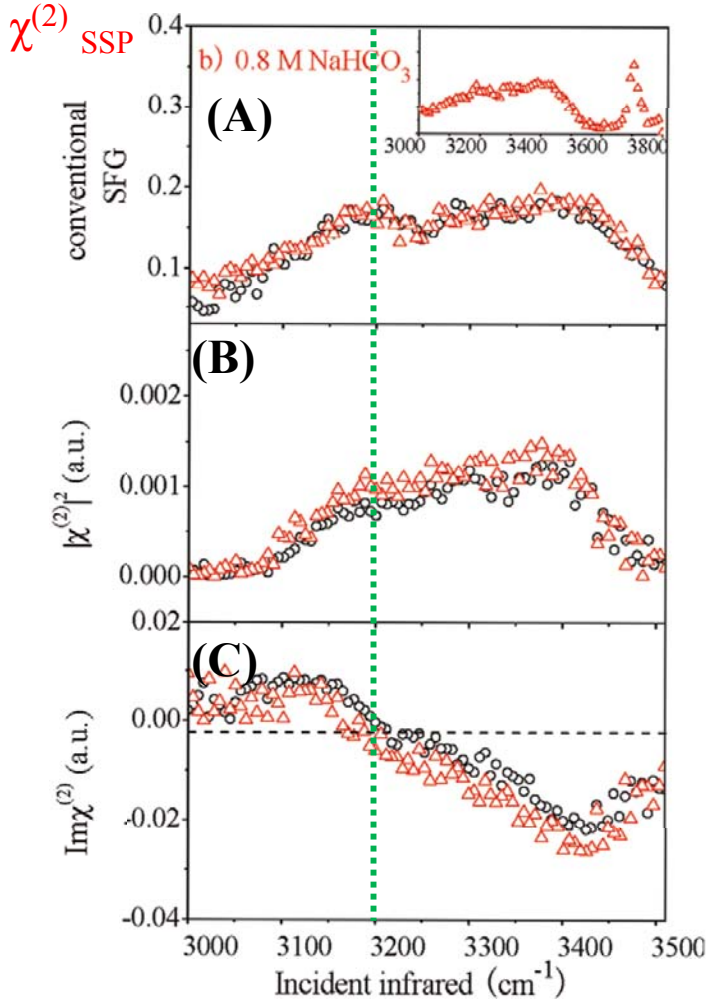
In spectrum C
The strong negative band talk a large fraction dipole of interfacial water molecules pointing toward the bulk

The sodium cations and the carbonate anions provide the field to align the water dipole

The sodium cations are above the carbonate anions in the interfacial region

SFG spectra of water molecules in aqueous $NaHCO_3$solution

OH stretching frequency region



The net polar orientation and structure of water molecules in the interface is unchanged.

The HCO_3^- and Na^+ are dispersed in the hydrogen bonding network

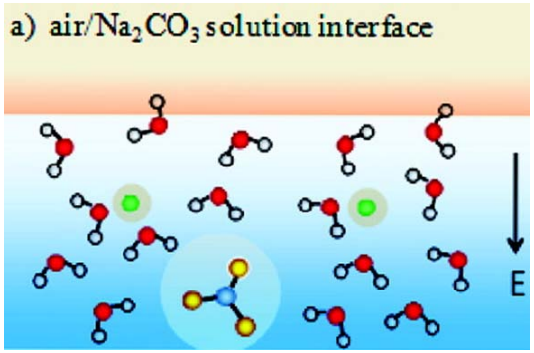
Water spectra are shown as a reference (black circles).

Conclusion

In aqueous Na_2CO_3 solution

- The sodium cations are above the carbonate anions in the interfacial region

-The water molecules orientation arises from charge separation in the interfacial region



In aqueous $NaHCO_3$solution

-The bicarbonate anions incorporate into the hydrogen bonding structure of water molecules in the interfacial region

- The sodium cations reside near to the same depth as the bicarbonate anions