

# Vibrational spectra of water at water/ $\alpha$ -quartz (0 0 0 1) interface

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- Selected beam geometry allows to suppress the bulk contribution to SFG from crystalline quartz and use SFVS to study water/ $\alpha$ -quartz interfaces with different bulk pH values.
- The spectra are qualitatively similar to those of water/fused-quartz interfaces, but display an ice-like peak that resembles very closely that of a real ice surface, providing the first evidence to the belief that water molecules at a crystalline oxide surface form a more ordered hydrogen bonding network.

## Theoretical background

- The two input pulses overlap in time and space at the interface and generate at  $\omega = \omega_1 + \omega_2$ .
- The output signal is proportional to the absolute square of an effective surface nonlinear susceptibility

$$S(\omega; \hat{e}, \hat{e}_1, \hat{e}_2) \propto \left| \chi_{\text{eff}}^{(2)} \right|^2 I(\omega_1) I(\omega_2)$$
$$\chi_{\text{eff}}^{(2)} = L \hat{e} \cdot \left( \overleftrightarrow{\chi}_S^{(2)} + \frac{\overleftrightarrow{\chi}_B^{(2)}}{i \Delta k} \right) : (\hat{e}_1 L_1)(\hat{e}_2 L_2)$$



$\hat{e}_i$  - the polarization unit vector  
 $L_i$  - transmission Fresnel coefficient at  $\omega_i$   
 $\overleftrightarrow{\chi}_S^{(2)}$  - the surface nonlinear susceptibility  
 $\overleftrightarrow{\chi}_B^{(2)}$  - the bulk nonlinear susceptibility  
 $\Delta k = |\vec{k} - \vec{k}_1 - \vec{k}_2|$  - the wavevector mismatch of the output and input

- The nonvanishing  $\tilde{\chi}_B^{(2)}$  elements for  $\alpha$ -quartz are

$$\chi_{xxx}^{(2)} = -\chi_{xyy}^{(2)} = -\chi_{yxy}^{(2)} = -\chi_{yyx}^{(2)},$$

$$\chi_{xyz}^{(2)} = -\chi_{yxz}^{(2)}, \chi_{yzx}^{(2)} = -\chi_{zyx}^{(2)}, \chi_{zxy}^{(2)} = -\chi_{xzy}^{(2)}$$

- The incidence or exit angle for the beam at  $\omega_i$  is  $\theta_i$ .
- Then find for

$$\chi_B^{(2)}(\hat{e}, \hat{e}_1, \hat{e}_2) \equiv \hat{e} \cdot \tilde{\chi}^{(2)} : \hat{e}_1 \hat{e}_2$$

the expressions with various input/output polarization combinations



## Theoretical background

$$\chi_{B,\text{eff}}^{(2)}(\text{PPP}) \propto \chi_{xxx}^{(2)} \cos \theta \cos \theta_1 \cos \theta_2 \cos 3\phi,$$

$$\chi_{B,\text{eff}}^{(2)}(\text{SSP}) \propto \chi_{xxx}^{(2)} \cos \theta_2 \cos 3\phi,$$

$$\chi_{B,\text{eff}}^{(2)}(\text{SPS}) \propto \chi_{xxx}^{(2)} \cos \theta_1 \cos 3\phi,$$

$$\chi_{B,\text{eff}}^{(2)}(\text{PSS}) \propto \chi_{xxx}^{(2)} \cos \theta \cos 3\phi,$$

$$\begin{aligned} \chi_{B,\text{eff}}^{(2)}(\text{PPS}) \propto & \chi_{xxx}^{(2)} \cos \theta \cos \theta_1 \sin 3\phi + \chi_{yzx}^{(2)} \cos \theta \sin \theta_1 \\ & - \chi_{zxy}^{(2)} \sin \theta \cos \theta_1, \end{aligned}$$

$$\begin{aligned} \chi_{B,\text{eff}}^{(2)}(\text{PSP}) \propto & \chi_{xxx}^{(2)} \cos \theta \cos \theta_2 \sin 3\phi + \chi_{zxy}^{(2)} \sin \theta \cos \theta_2 \\ & - \chi_{xyz}^{(2)} \cos \theta \sin \theta_2, \end{aligned}$$

$$\begin{aligned} \chi_{B,\text{eff}}^{(2)}(\text{SPP}) \propto & \chi_{xxx}^{(2)} \cos \theta_1 \cos \theta_2 \sin 3\phi + \chi_{xyz}^{(2)} \cos \theta_1 \sin \theta_2 \\ & - \chi_{yzx}^{(2)} \sin \theta_1 \cos \theta_2, \end{aligned}$$

$$\chi_{B,\text{eff}}^{(2)}(\text{SSS}) \propto \chi_{xxx}^{(2)} \sin 3\phi.$$



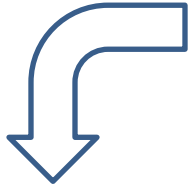
For  $\phi$  equal to  $30^\circ$  or  $90^\circ$ ,  $\chi_B^{(2)}$  vanishes for all the polarization combinations

## Theoretical background

- For the interfacial water layer, the nonvanishing elements are

$$\chi_{S,zzz}^{(2)}, \chi_{S,xxz}^{(2)} = \chi_{S,yyz}^{(2)},$$

$$\chi_{S,xzx}^{(2)} = \chi_{S,yzy}^{(2)}, \chi_{S,zxx}^{(2)} = \chi_{S,zyy}^{(2)}$$

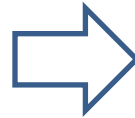


$$\chi_{S,\text{eff}}^{(2)}(\text{PPP}) \propto \chi_{S,zzz}^{(2)} \sin \theta \sin \theta_1 \sin \theta_2 + \dots,$$

$$\chi_{S,\text{eff}}^{(2)}(\text{SSP}) \propto \chi_{S,yyz}^{(2)} \sin \theta_2,$$

$$\chi_{S,\text{eff}}^{(2)}(\text{SPS}) \propto \chi_{S,yzy}^{(2)} \sin \theta_1,$$

$$\chi_{S,\text{eff}}^{(2)}(\text{PSS}) \propto \chi_{S,zyy}^{(2)} \sin \theta,$$



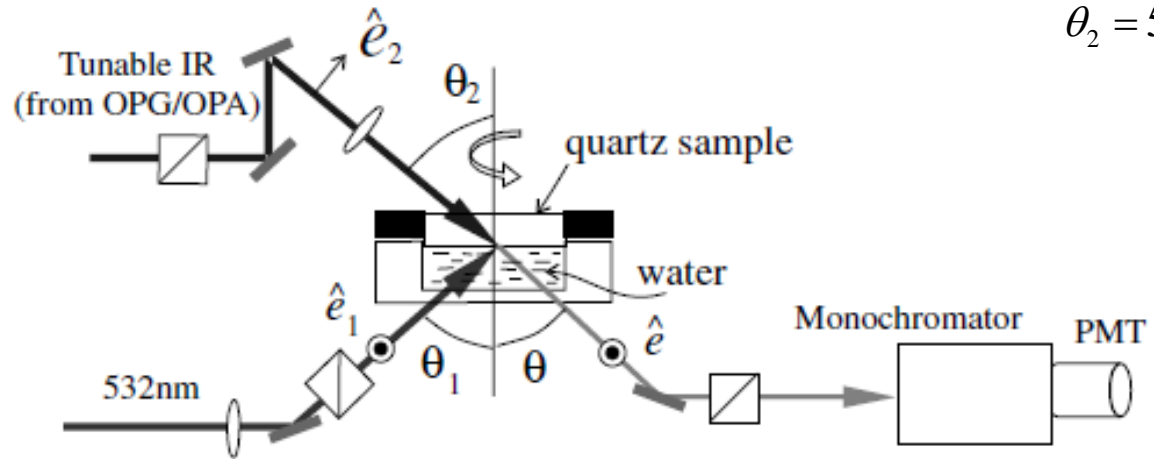
Summary :

we can suppress the bulk nonlinear susceptibility contribution from  $\alpha$ -quartz with the PPP, SSP, SPS, and PSS polarization combinations and deduce all the nonvanishing elements of the surface nonlinear susceptibility for the interfacial water layer from the measurements

# Experiment

the tunable infrared light  
( $2700\text{--}3900\text{ cm}^{-1}$ )

10-Hz, 20-ps Nd:YAG  
generate the green visible light



$$\theta \cong 46^\circ$$

$$\theta_1 = 45^\circ$$

$$\theta_2 = 55^\circ$$

Fig. 1. SFG experimental geometry.

# Sample

## ■ The sample

- was a synthetically grown quartz plate of 5 mm thickness
- cut along (0 0 0 1) plane
- polished by chemical/mechanical etching to near atomic-scale flatness

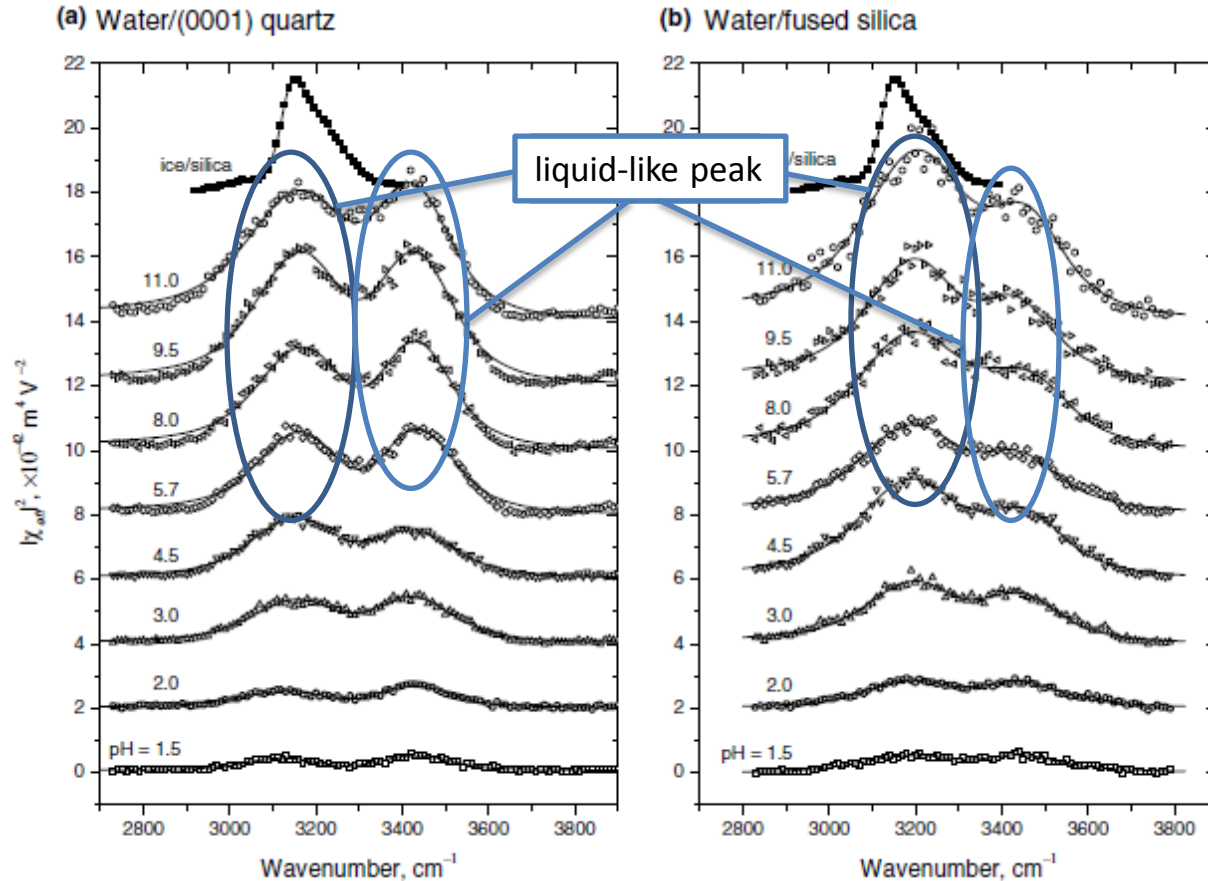
## ■ Before measurements

- it was cleaned in a concentrated sulfuric acid solution mixed with a commercial oxidizing agent for 3 h (to remove contaminants)
- followed by thorough rinsing in distilled water
- blow-drying with nitrogen gas

- The sample was then placed on top of water as shown in Fig. 1.



# Result



- 3100–3200  $\text{cm}^{-1}$  is ice-like peak
  - the former represents OH in a more ordered ice-like hydrogen-bonding network
- ~ 3400–3450  $\text{cm}^{-1}$  is liquid-like
  - the former represents in a less ordered liquid-like hydrogen-bonding structure
- Differences:
  - a downshift and narrowing of the ice-like peak in the water/ $\alpha$ -quartz case make it more closely resemble the real ice peak at 3150  $\text{cm}^{-1}$
  - the liquid-like peaks of the two cases appear nearly the same for all pH values

# Result

- A more quantitative description of the results can be obtained by fitting the spectra

$$\hat{e} \cdot \chi^{(2)} : \hat{e}_1 \hat{e}_2 = \chi_{\text{NR}} + \sum_q \int_{-\infty}^{\infty} \frac{A_q(\hat{e}, \hat{e}_1, \hat{e}_2)}{\omega_2 - \omega' + i\Gamma_q} \frac{1}{\sqrt{2\pi}\sigma_q} \exp\left(-\frac{(\omega' - \omega_{q,0})^2}{2\sigma_q^2}\right) d\omega',$$

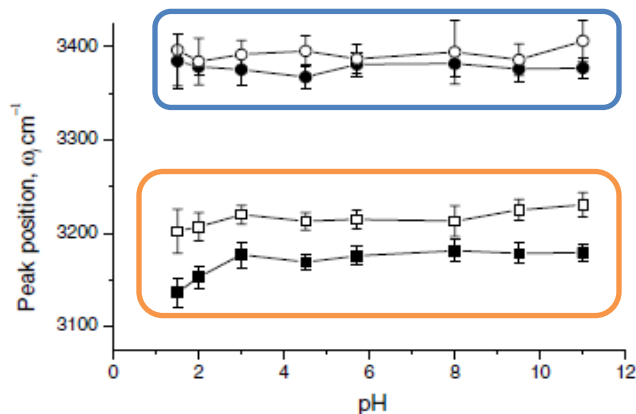
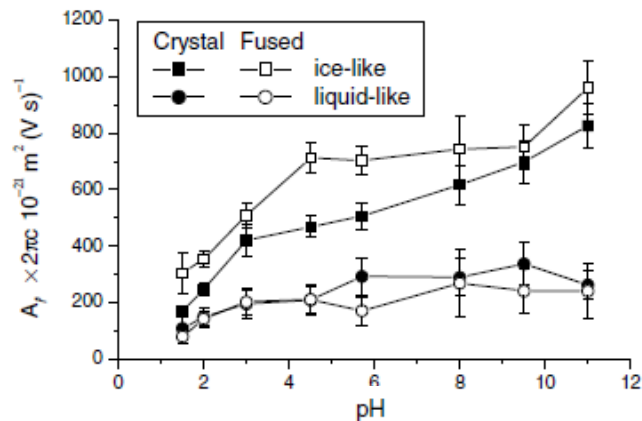
the strength

the resonant frequency

the nonresonant contribution

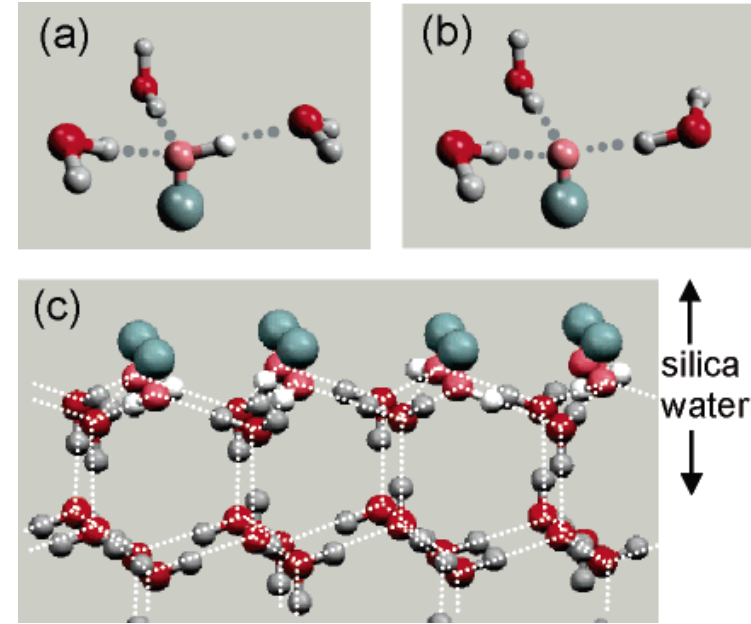
the damping constant of the  $q$ th vibrational mode

Gaussian resonant frequency distribution of width



# Discussion

- When immersed in water, it adjusts to the equilibrium structure dictated by the reaction  $\text{SiOH} \rightleftharpoons \text{SiO}^- + \text{H}^+$ .
- The surface remains as SiOH in the neutral state, if the pH of bulk water is lower than 2, becomes increasingly deprotonated as pH increases, and is completely deprotonated and saturated with negative charges at  $\text{pH} \geq 10$  that produce a surface field of  $\sim 10^{-7} \text{ V/m}$ .
- To both neutral (SiOH) and charged (SiO<sup>-</sup>) surfaces, the water molecules can be bonded via hydrogen bonding.
  - two molecules can bind with H to O and one with O to H on SiOH.
  - three molecules can bind with H to O of SiO<sup>-</sup>.
- The strong surface field at high pH should help orient the water molecules with H bonding to the surface and establish a more ordered hydrogen-bonding network.



Possible hydrogen-bonding configuration of water molecules on hydrophilic silica surface: (a) protonated (SiOH) surface sites, low pH; (b) deprotonated (SiO<sup>-</sup>) surface sites, high pH; (c) structure of water/silica interface at low pH. Red and gray spheres represent O and H atoms of water molecules; large gray green, pink, and white spheres represent Si, O, and H atoms of SiOH groups at silica surface. Dotted lines indicate hydrogen bonds. Chem. Rev. **2006**, **106**, 1140-1154

- In the case of water/ $\alpha$ -quartz interfaces, the phase measurements can be easily carried out by leaking a small amount of SFG from quartz to interfere with the SF signal from water
- The SF output from the interface is now given by

$$S \propto |\pm \chi_{\text{eff}}^{(2)}(\text{quartz}) + \chi_{\text{eff}}^{(2)}(\text{water})|^2 = |\chi^{(2)}(\text{quartz})|^2 + |\chi^{(2)}(\text{water})|^2 \pm 2|\chi^{(2)}(\text{quartz})||\chi^{(2)}(\text{water})|\cos(\Delta\Phi).$$

- The amplitude of the ice-like peak indeed changed sign as the pH value changed from 11 to 1.5.
- Phase measurements of SFVS confirm that water molecules contributing to the ice-like peak are hydrogen-bonded to the quartz surface with oxygen and hydrogen, respectively, at low and high pH values.

## Conclusion

- Ostroverkhov et al. obtained SFVS of water/ $\alpha$ -quartz(0001) interfaces for different pH values and compared them with those of the water/silica interfaces.
- The two sets are qualitatively very similar, but the ice-like peak of the former is shifted by  $\sim 50 \text{ 1/cm}$ , much closer in position to the real ice peak.
  - The frequency shift suggests that the water structure next to  $\alpha$ -quartz is more ordered.