Sum frequency generation (SFG) study of the pH-dependent water structure on a fused quartz surface modified by an octadecyltrichlorosilane (OTS) monolayer

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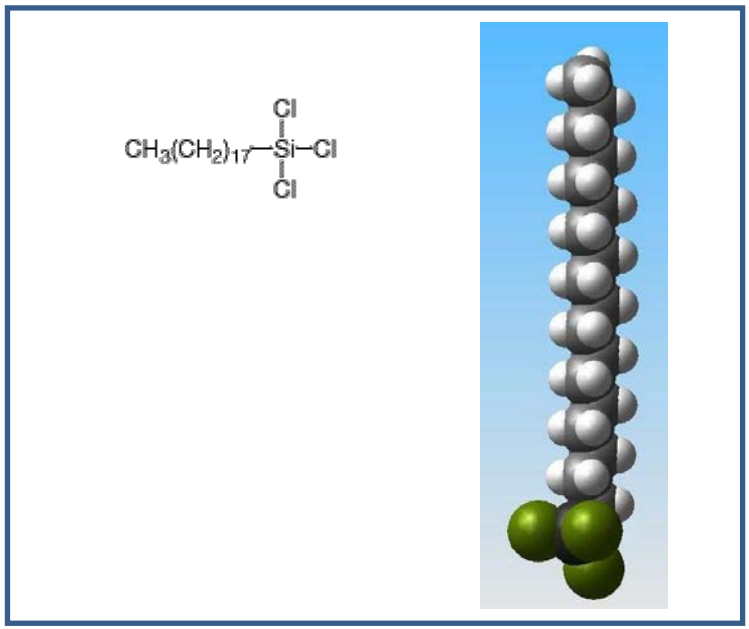
Abstract

The interface-sensitive spectroscopic method, sum frequency generation (SFG), has been used to investigate the interfacial water structure on a fused quartz surface modified by an octadecyltrichlorosilane (OTS) self-assembled monolayer in phosphate buffered solutions at various pHs. The experimental results demonstrate that the water molecules at the quartz/OTS surface flip while the water molecules at the OTS surface maintain their orientation when the solution pH is changed from neutral to acidic. The results show that most of the silanol groups still exist on the fused quartz surface even after a silane coupling reaction of OTS under the reported experimental conditions.

OTS molecule from the wikipedia



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SFG Spectra main idea

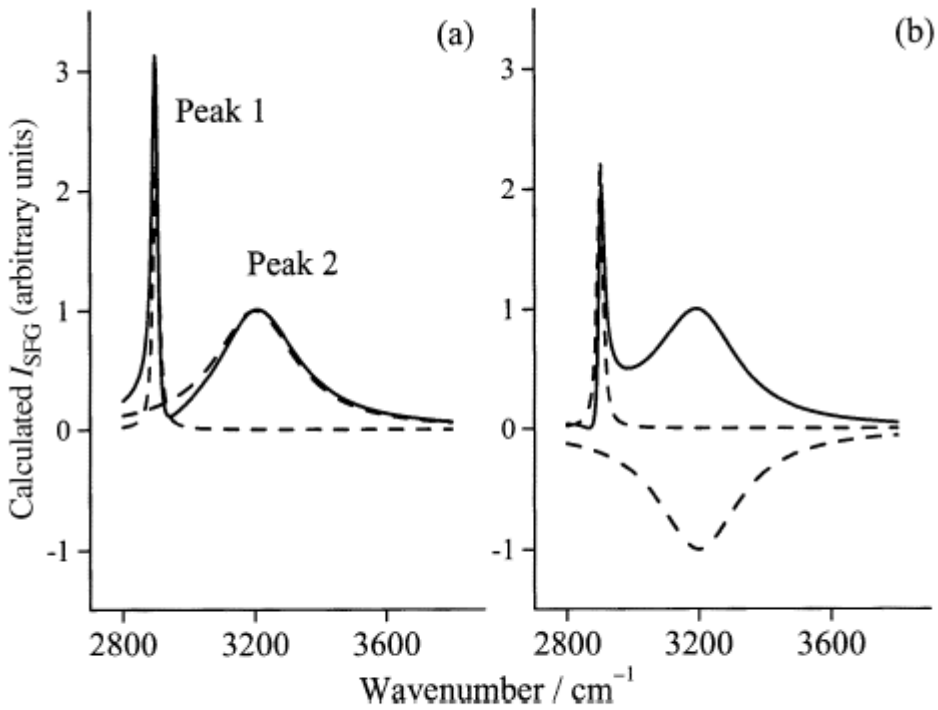

Fig. 1 Simulation of SFG spectra using eqn. (1) with two resonance modes under the following conditions: (a) $A_1 = 15$, $\omega_1 = 2900$, $\Gamma_1 = 10$, $A_2 = 150$, $\omega_2 = 3200$, $\Gamma_2 = 150$, $\chi_{NR} = 0$, $\phi_1 = \phi_2 = 0$; (b) same as (a) except $\phi_2 = \pi$.

Fig. 1 shows a simulated example of the interference effect between the two resonance peaks.

Sample preparation

Substrate : a fused quartz with a hemi-cylindrical shape (IR grade, d=25mm, l=25mm)

Self-assembled monolayer sample : octadecyltrichlorosilane (OTS)

The OTS monolayer was constructed by…

1. immersing the quartz substrate in a 0.1% OTS hexadecane/carbon tetrachloride/chloroform = 80 : 12 : 8 solution for 15 min.
2. after being rinsed in a sonication bath chloroform, the sample was baked at 110°C for 1 h.

SFG measure the OTS sample in electrolyte solution using by visible and IR light angle 70° and 50°.

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Result and discussion

1. Structure of OTS monolayer in air

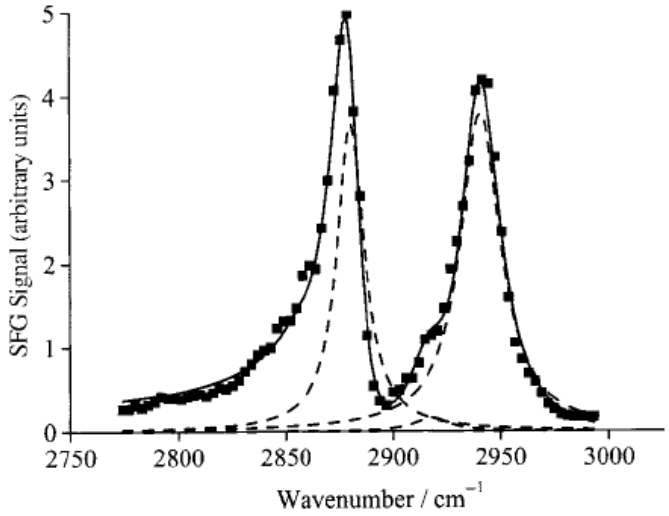


Fig. 2 SFG spectrum of a fused quartz surface modified by an OTS monolayer with full coverage, in the C–H stretching region observed in air.

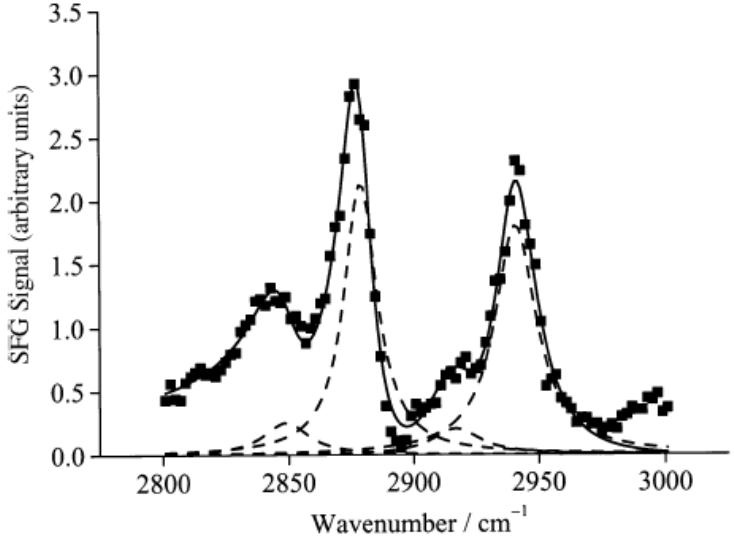


Fig. 3 SFG spectrum of a fused quartz surface modified by OTS with lower coverage measured in air.

@ 2879 cm^{-1} (CH_3 symmetric stretch)
@ 2940 cm^{-1} (CH_3 Fermi resonance)
@ 2859 cm^{-1} (CH_2 symmetric stretch)
@ 2917 cm^{-1} (CH_2 asymmetric stretch)

Result and discussion – pH dependence of water structure at the qz/OTS/solution inter

2.1 Neutral pH solution – in neutral phosphate buffer pH 7

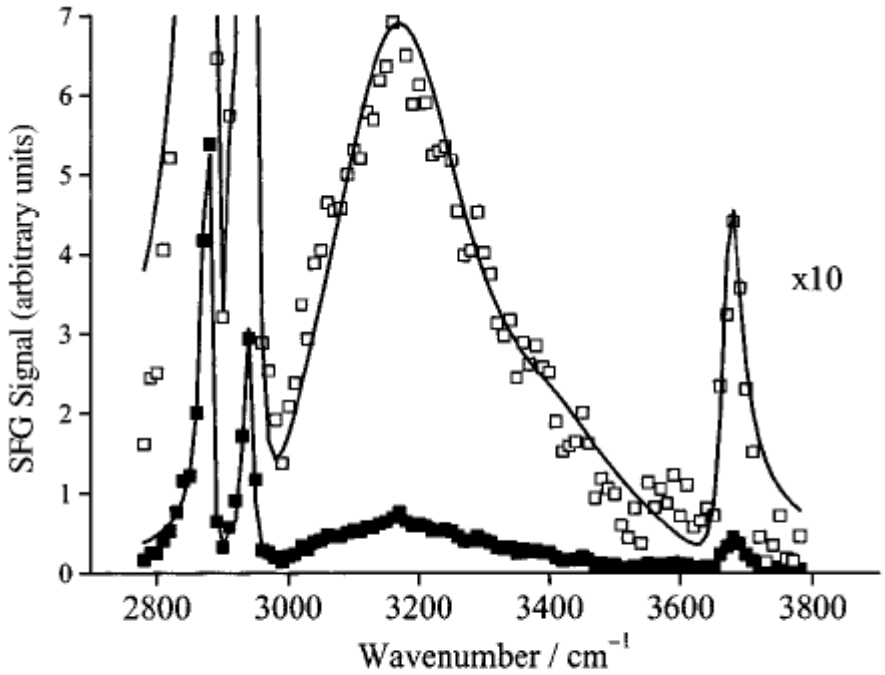


Fig. 4 SFG spectrum of a fused quartz surface modified by an OTS monolayer with full coverage in a neutral phosphate buffered solution of pH 7, in the region of 2800 to 3800 cm^{-1}. Also shown is the same spectrum at an enlarged scale (10 times) in the OH region.

Result and discussion – pH dependence of water structure at the qz/OTS/solution inter

2.1 Neutral pH solution – in neutral phosphate buffer pH 7

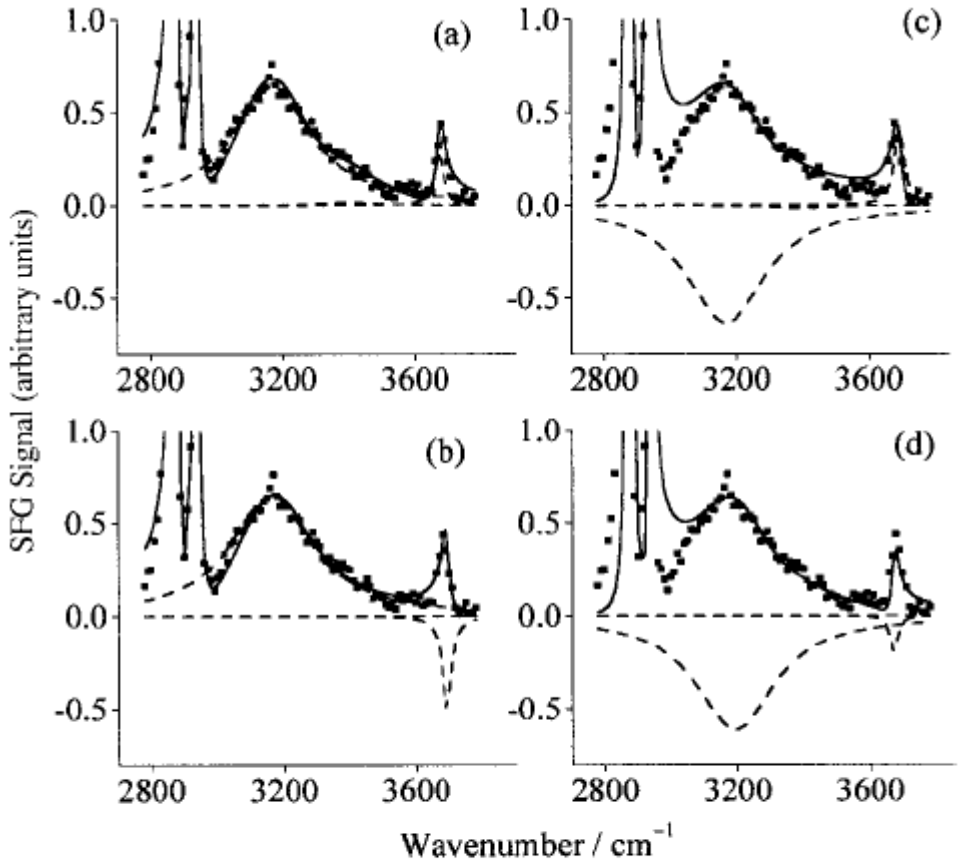


Fig. 5 A set of fitting curves for the SFG spectrum shown in Fig. 4 (solid lines) and deconvoluted OH peaks (dashed lines) under phase conditions of: (a) $\phi_{OH} = \phi_{free\ OH} = 0$; (b) $\phi_{bond\ OH} = 0$, $\phi_{free\ OH} = \pi$; (c) $\phi_{bond\ OH} = \pi$, $\phi_{free\ OH} = 0$; and (d) $\phi_{bond\ OH} = \pi$, $\phi_{free\ OH} = \pi$. The ϕ_{CH} value is assumed to be zero in all cases. The negative peak represents the one for $\phi = \pi$.

Fit to the Fig.4

Result and discussion – pH dependence of water structure at the qz/OTS/solution inter

2.2 Alkaline solution – in an alkaline phosphate solution of pH 11

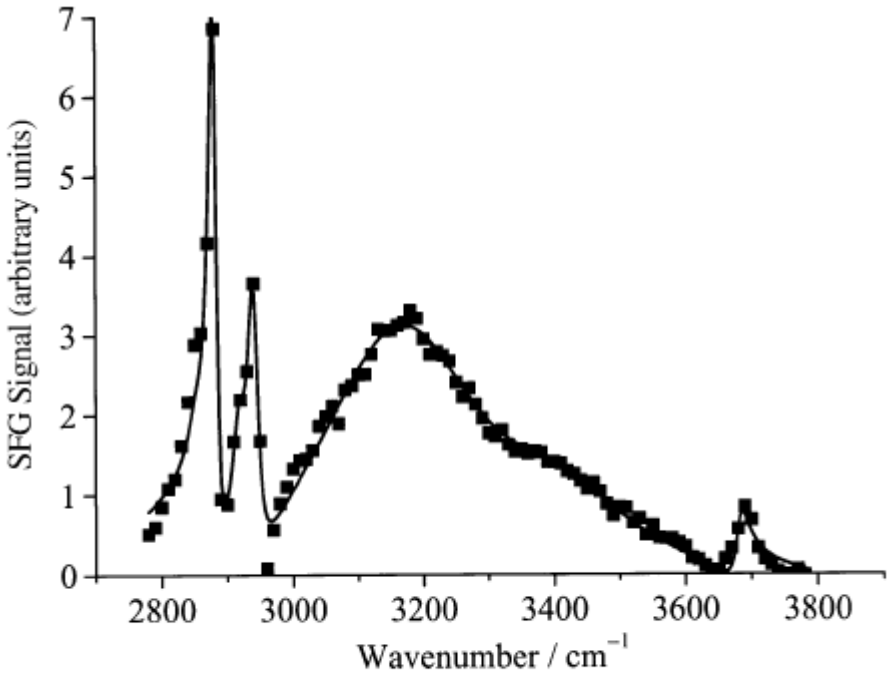


Fig. 6 SFG spectrum of a fused quartz surface modifed by an OTS monolayer with full coverage in an alkaline phosphate buffered solution of pH 11.

Result and discussion – pH dependence of water structure at the qz/OTS/solution inter

2.2 Alkaline solution – in an alkaline phosphate solution of pH 11

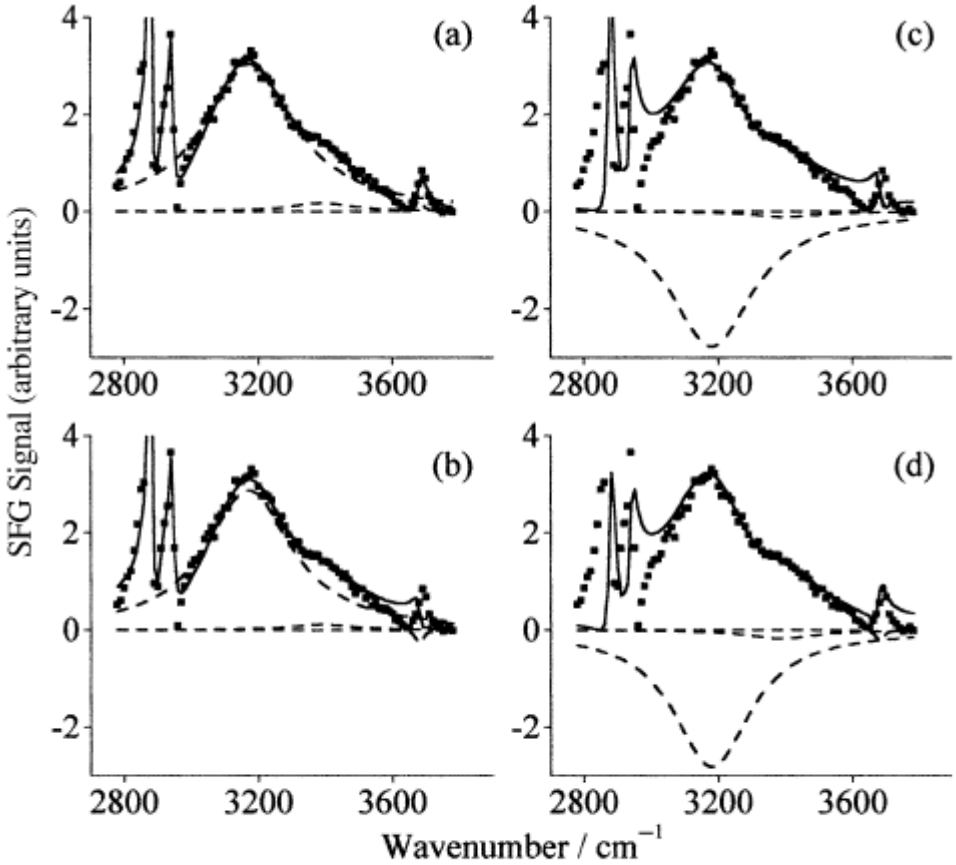


Fig. 7 A set of fitting curves for the SFG spectrum shown in Fig. 6 (solid lines) and deconvoluted OH peaks (dashed lines) under the phase conditions stated in Fig. 5.

(a) $\phi_{\text{bond OH}} = \phi_{\text{free OH}} = 0$; (b) $\phi_{\text{bond OH}} = 0$, $\phi_{\text{free OH}} = \pi$; (c) $\phi_{\text{bond OH}} = \pi$, $\phi_{\text{free OH}} = 0$; and (d) $\phi_{\text{bond OH}} = \pi$, $\phi_{\text{free OH}} = \pi$.

Fit to the Fig.6

Result and discussion – pH dependence of water structure at the qz/OTS/solution inter

2.3 Acidic solution – in an alkaline phosphate solution of pH 2

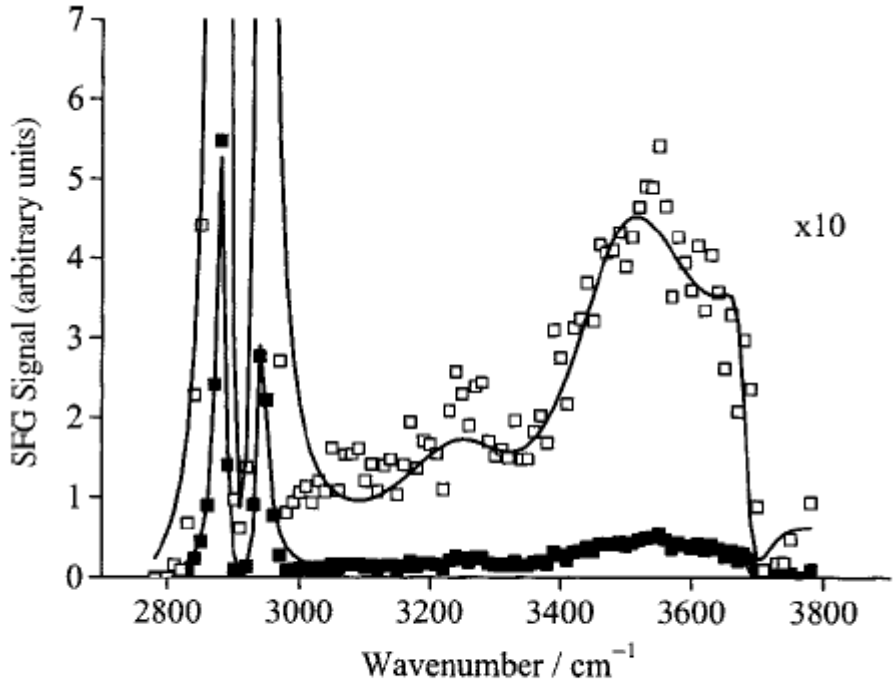


Fig. 8 SFG spectrum of a fused quartz surface modified by an OTS monolayer with full coverage measured in acidic phosphate buffered solution of pH 2. Also shown is the same spectrum at an enlarged scale (10 times) in the OH region.

Result and discussion – pH dependence of water structure at the qz/OTS/solution inter

2.3 Acidic solution – in an alkaline phosphate solution of pH 2

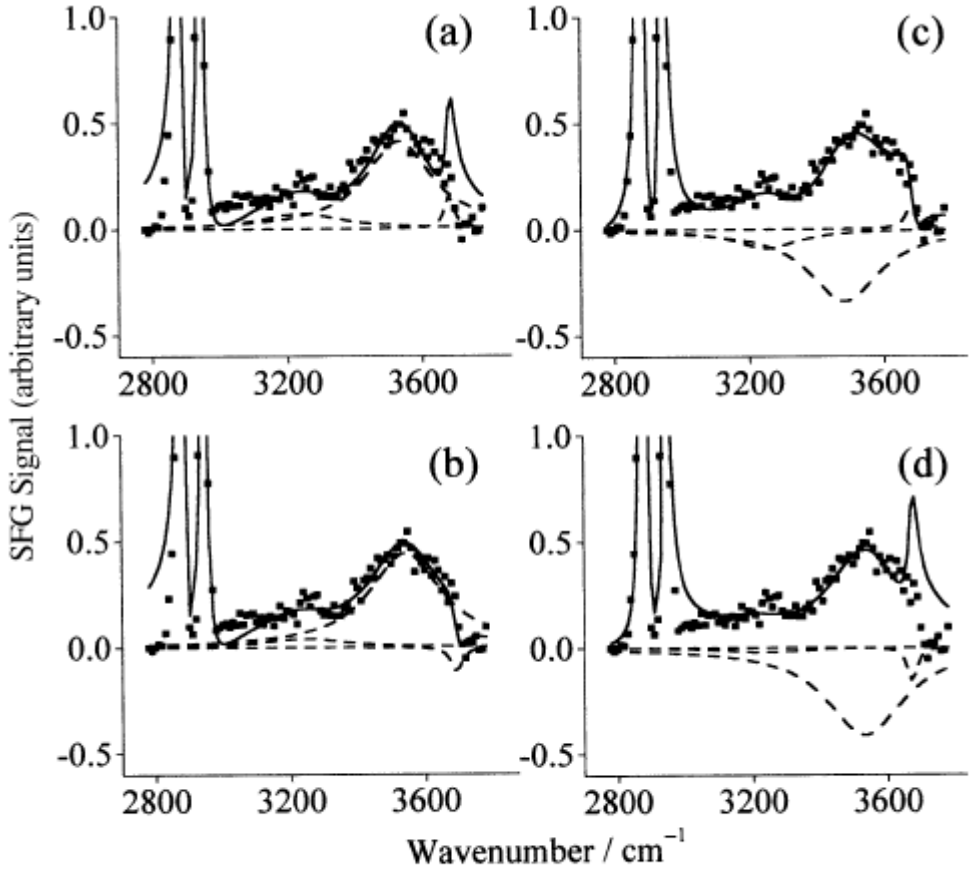


Fig. 9 A set of fitting curves for the SFG spectrum shown in Fig. 8 (solid lines) and deconvoluted OH peaks (dashed lines) under the phase conditions stated in Fig. 5.

(a) $\phi_{\text{bond OH}} = \phi_{\text{free OH}} = 0$; (b) $\phi_{\text{bond OH}} = 0$, $\phi_{\text{free OH}} = \pi$; (c) $\phi_{\text{bond OH}} = \pi$, $\phi_{\text{free OH}} = 0$; and (d) $\phi_{\text{bond OH}} = \pi$, $\phi_{\text{free OH}} = \pi$.

Fit to the Fig.8

Result and discussion – pH dependence of water structure at the qz/OTS/solution inter

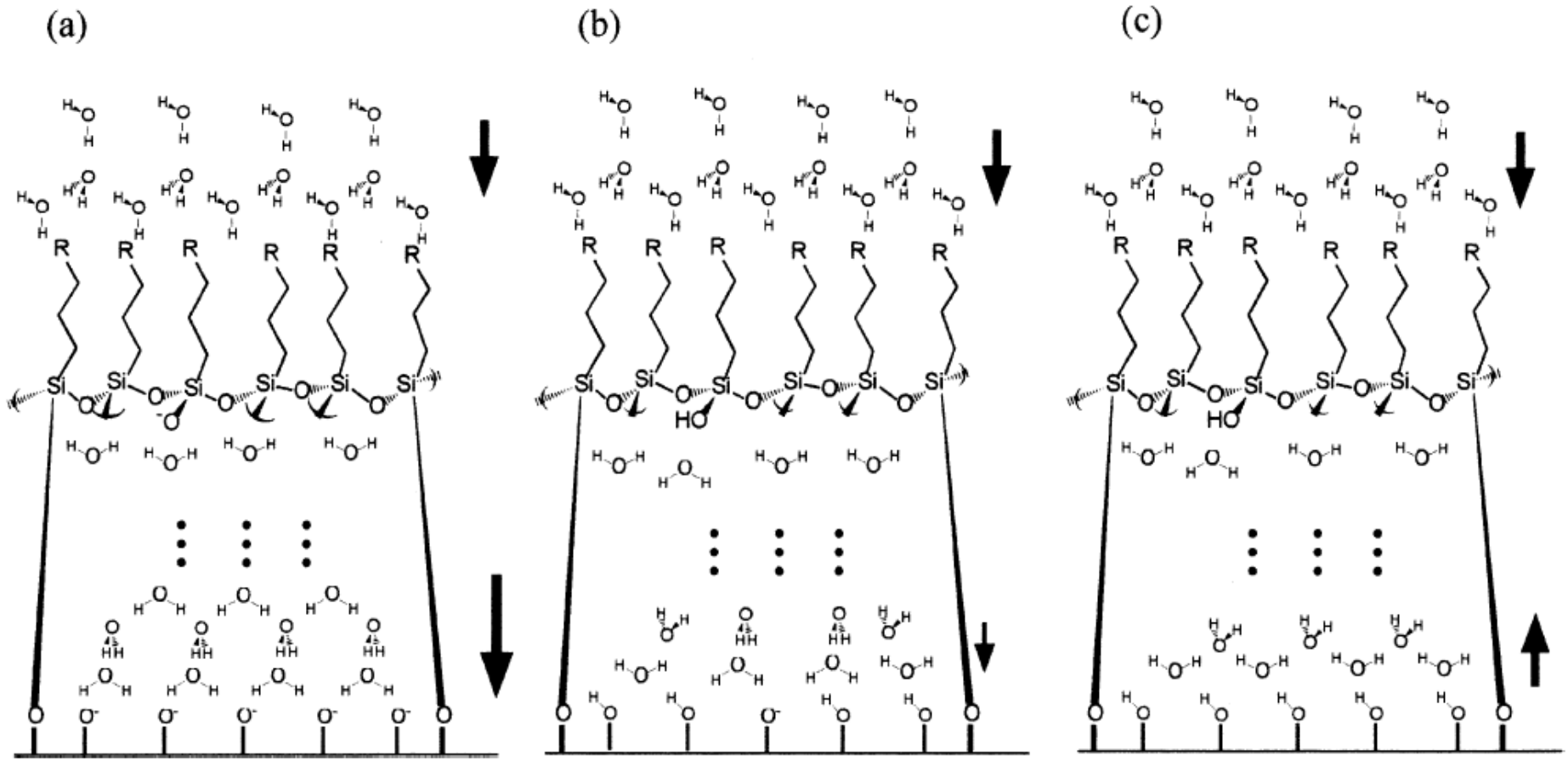


Fig. 10 Schematic structural models of interfacial water molecules on the quartz/OTS/solution interface in (a) alkaline, (b) neutral and (c) acidic phosphate buffered solutions. Arrows show the direction of the dipole moment of the interfacial water molecules.

Result and discussion – Effect of OTS coverage on the structure of water and OTS mole

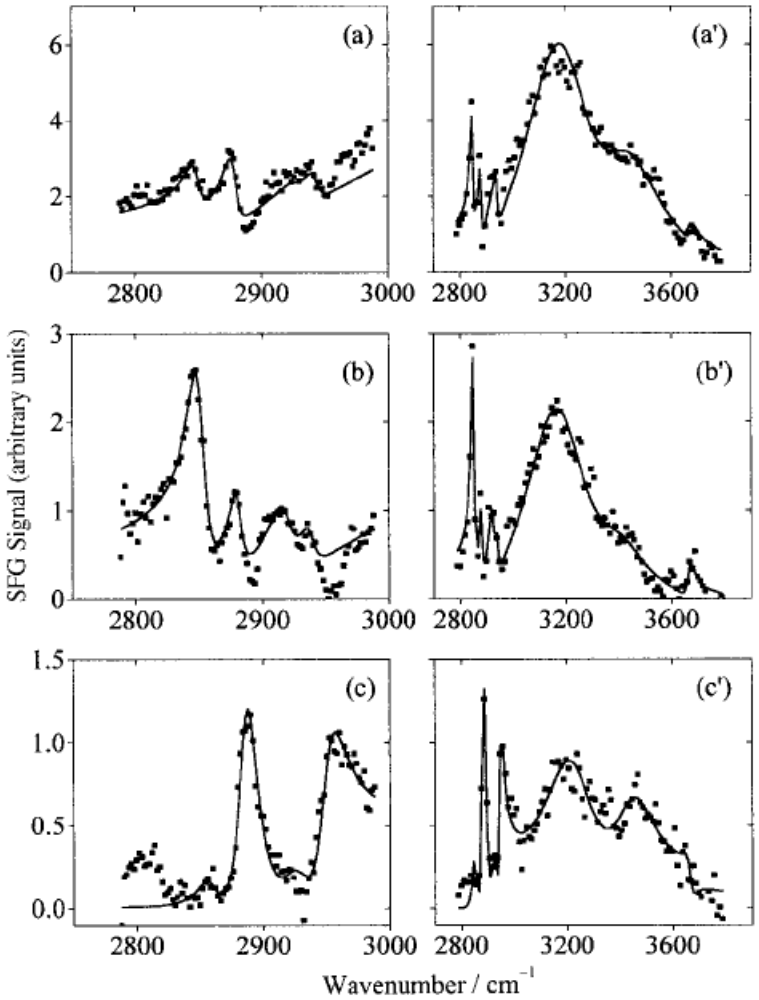
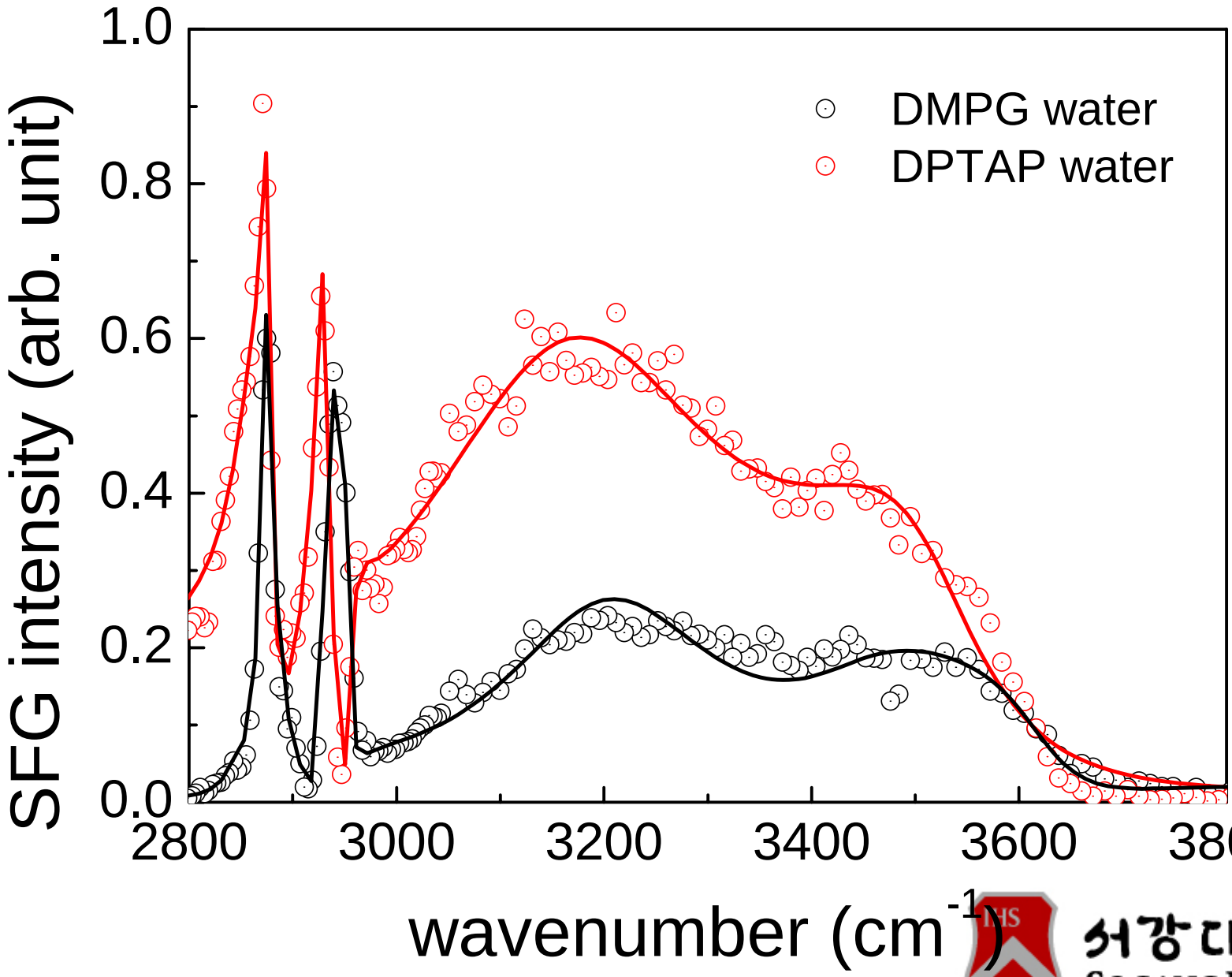


Fig. 11 SFG spectra of a fused quartz surface modified by OTS with low coverage in the C–H stretching region (2770–2990 cm^{-1}) and the CH + OH stretching region (2800–3800 cm^{-1}) in phosphate buffered solutions of (a,a') pH 11, (b,b') pH 7 and (c,c') pH 2.



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