

Interfacial water structure at polymer gel/quartz interfaces investigated by sum frequency generation spectroscopy†

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Motivation

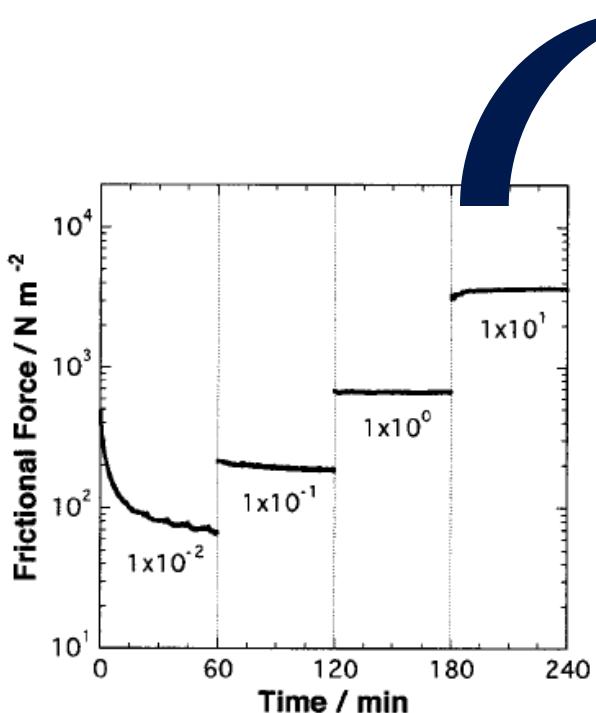


Figure 1. Time profile of the frictional force for a ring-shaped PNaAMPS gel rotated against a piece of PNaAMPS gel under various angular velocities as measured by a rheometer in pure water at 25 °C. The numbers in the figure are the angular velocities in rad/s.

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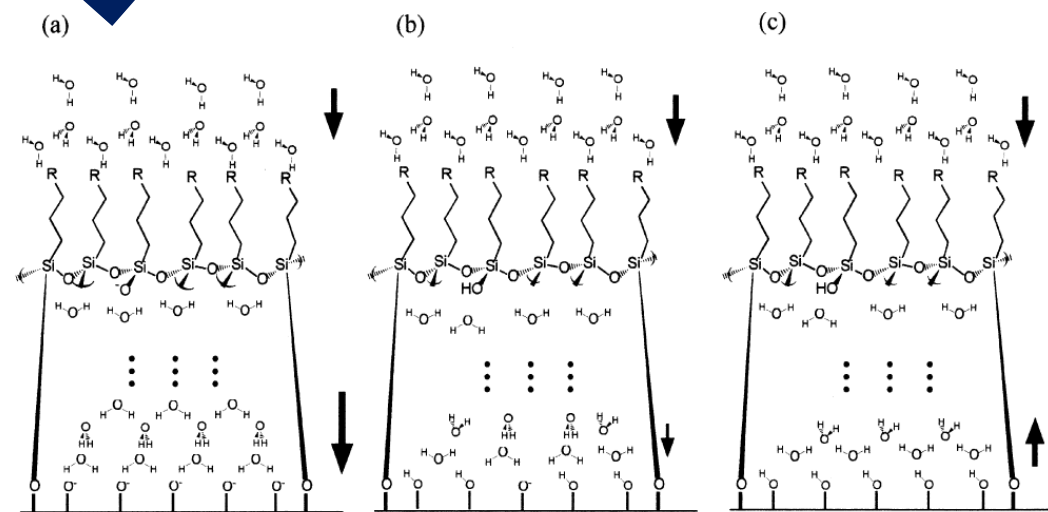


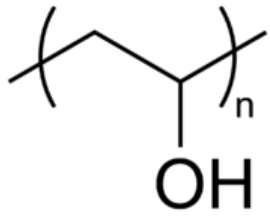
Fig. 10 Schematic structural models of interfacial water molecules on the quartz/OTS/solution interface in (a) alkaline, (b) neutral and (c) acidic phosphate buffered solutions. Arrows show the direction of the dipole moment of the interfacial water molecules.

Phys. Chem. Chem. Phys. 3, 3463 (2002)

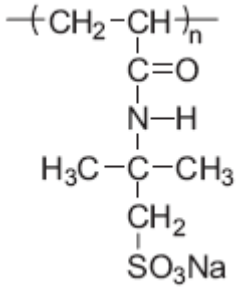
Experimental setup and Sample

Gel sample

Polyvinyl alcohol (PVA)

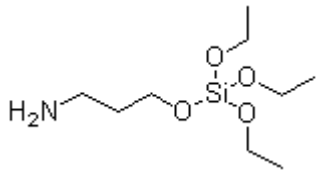


Poly(2-acrylamido-2-methylpropanesulfonic acid sodium salt (PNaAMPS)

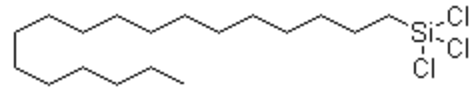


Modified quartz surface

aminopropyltrimethoxysilane (APS)



octadecyltrichlorosilane (OTS)



Setup

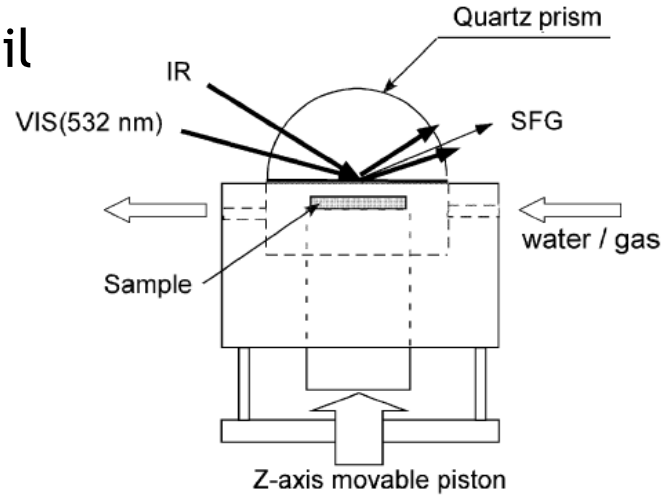


Fig. 1 Schematic illustration of the SFG cell adapted for SFG spectroscopy.

Result - PVA gel/quartz interface

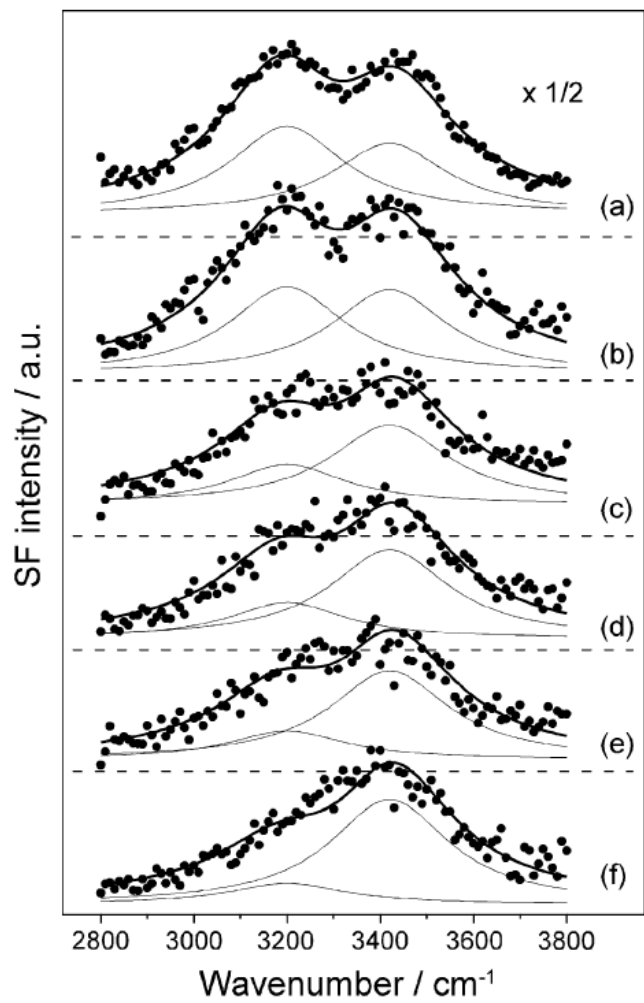


Fig. 2 SFG spectra in the OH stretching (2800–3800 cm⁻¹) region obtained at a quartz surface in water before (a) and after contact of the PVA gel with various applied pressure. (b) 0 MPa (just in contact), (c) 0.2 MPa, (d) 0.4 MPa, (e) 0.6 MPa, and (f) 0.8 MPa.

Layer 1 - quartz ($n_1 = 1.46$)
 Layer 2 - water ($n_2 = 1.33$)

Fresnel factor :

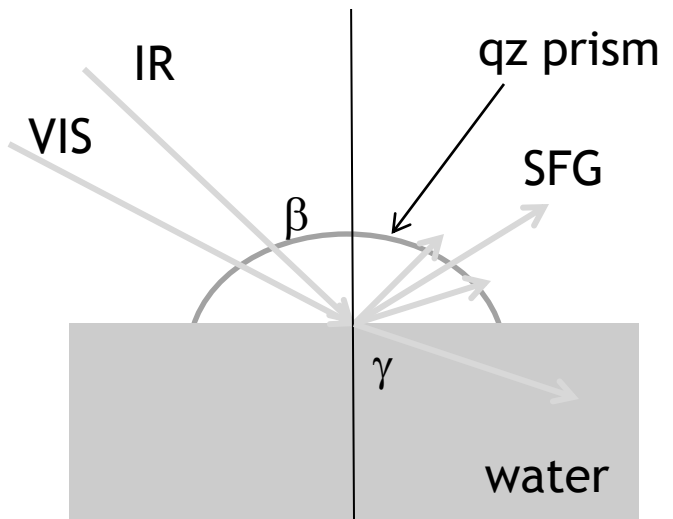
$$X_{SSP} = L_{yy}(VIS)L_{yy}(SFG)L_{zz}(IR)\sin(\theta_{IR}) = 1.38$$

Layer 3 - quartz ($n_3 = 1.49$)

Fresnel factor :

$$X_{SSP} = L_{yy}(VIS)L_{yy}(SFG)L_{zz}(IR)\sin(\theta_{IR}) = 0.065$$

PCCP Result - PVA gel/quartz interface



Incidence angle (IR : 50 deg. and VIS : 65 deg.)
 quartz ($n_1 = 1.46$)
 water ($n_2 = 1.33$)

Fresnel factor :

$$L_{xx} = \frac{2n_1 \cos \gamma}{n_1 \cos \gamma + n_2 \cos \beta}$$

$$L_{yy} = \frac{2n_1 \cos \beta}{n_1 \cos \beta + n_2 \cos \gamma}$$

$$L_{zz} = \frac{2n_2 \cos \beta}{n_1 \cos \gamma + n_2 \cos \beta} \left(\frac{n_1}{n'} \right)^2$$

PCCP Result:
 $X_{SSP} = L_{yy}(VIS)L_{yy}(SFG)L_{zz}(IR)\sin(\theta_{IR}) = 1.38$

0.795 1.105 1.189

Our Calculated Result:
 $X_{SSP} = L_{yy}(VIS)L_{yy}(SFG)L_{zz}(IR)\sin(\theta_{IR}) = 1.99$

1.53 1.36 1.25

Result - PVA gel/quartz interface

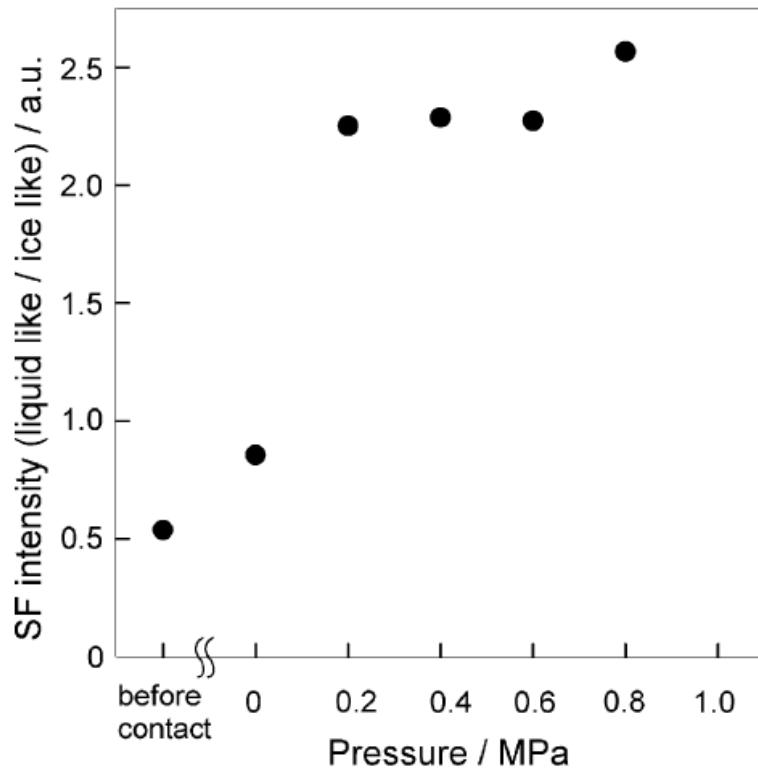


Fig. 3 Effect of applied pressure on the intensity ratio between the SFG signal due to “ice-like” and “liquid-like” water components.

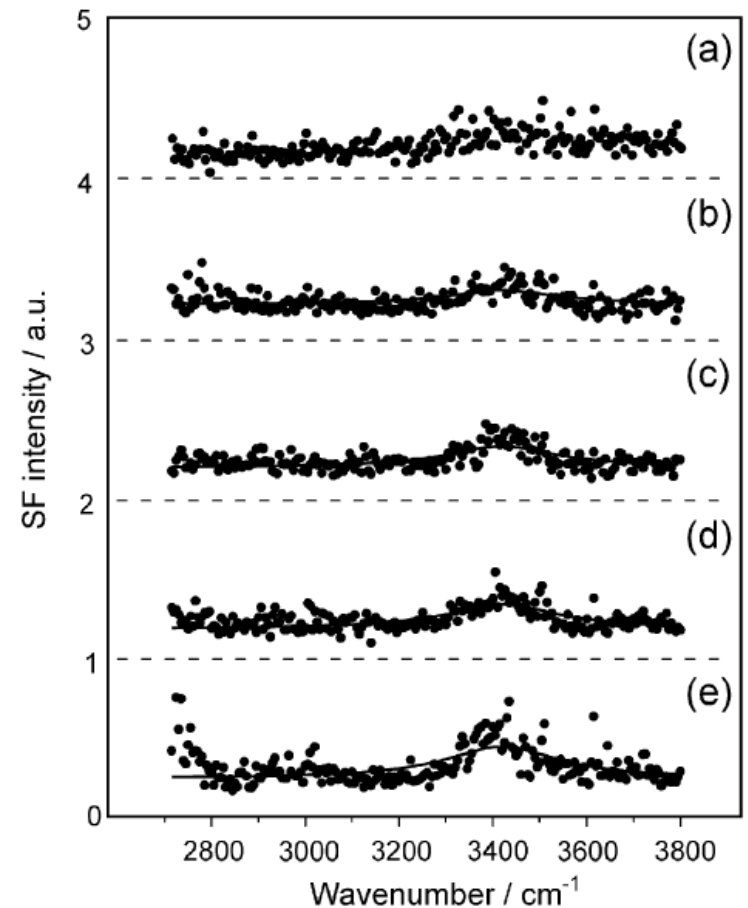
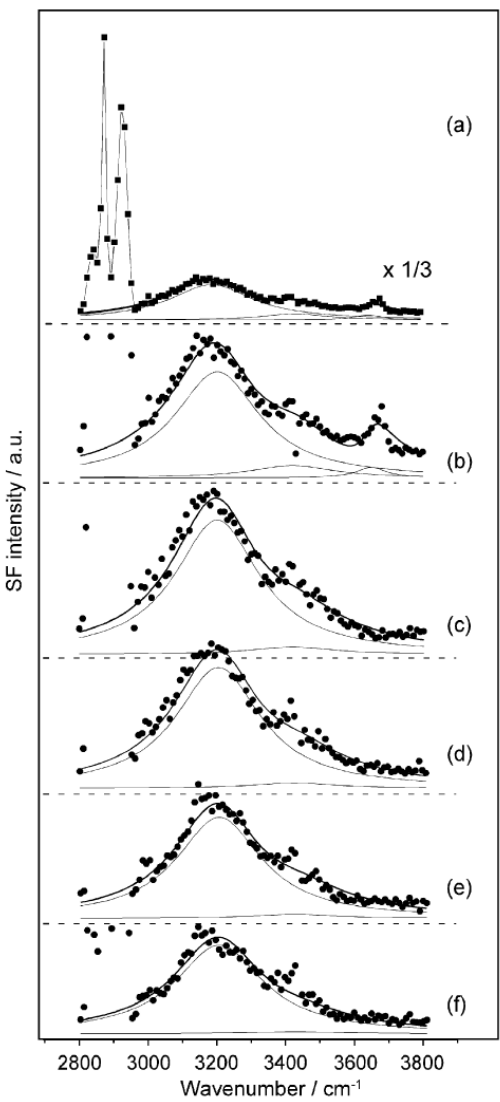


Fig. 4 SFG spectra in the OH stretching (2800–3800 cm^{-1}) region obtained at a quartz surface under an Ar gas flow before (a), and after contact of the PVA gel with various applied pressure: (b) 0 MPa (just in contact), (c) 0.2 MPa, (d) 0.4 MPa, and (e) 0.6 MPa.



Result - OTS modified quartz



Polyvinyl alcohol (PVA)

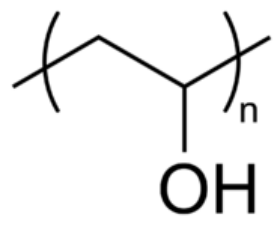
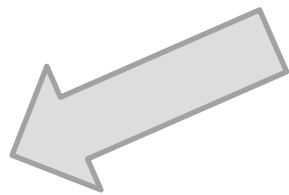


Fig. 5 SFG spectra in an OH stretching (2800–3800 cm⁻¹) region obtained at the OTS modified quartz surface in water before (a), (b) and after contact of the PVA gel with various applied pressure: (c) 0 MPa (just in contact), (d) 0.2 MPa, (e) 0.6 MPa, and (f) 0.8 MPa.

Result - PNaAMPS gel/quartz interface (APS modified) - pH2

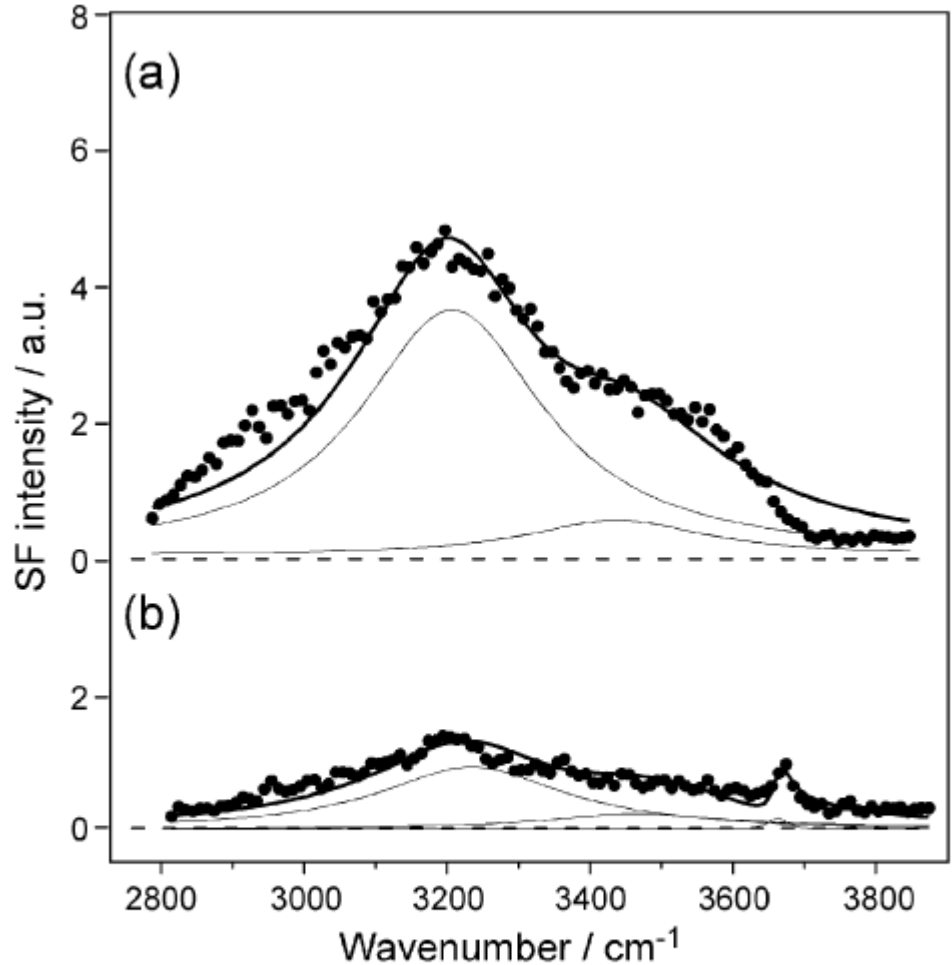
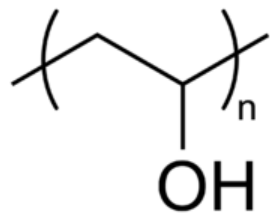
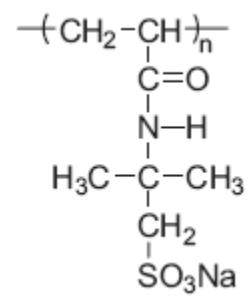


Fig. 6 SFG spectra in the OH stretching (2800–3800 cm⁻¹) region obtained at the APS modified quartz surface in water before (a) and after (b) contact of the PNaAMPS gel in a phosphate buffer solution of pH 2.

Polyvinyl alcohol (PVA)



Poly(2-acrylamido-2-methylpropanesulfonic acid sodium salt) (PNaAMPS)



Result - PNaAMPS gel/quartz interface (APS modified) - pH12

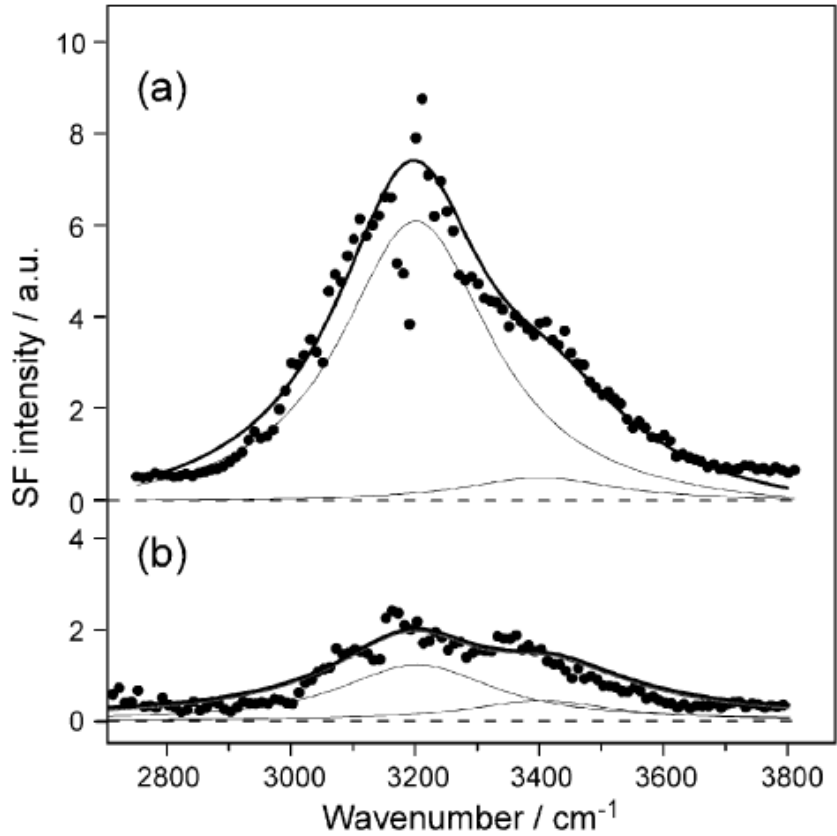


Fig. 7 SFG spectra in the OH stretching (2800–3800 cm⁻¹) region obtained at the APS modified quartz surface in water before (a) and after (b) contact of the PNaAMPS gel in a phosphate buffer solution of pH 12.

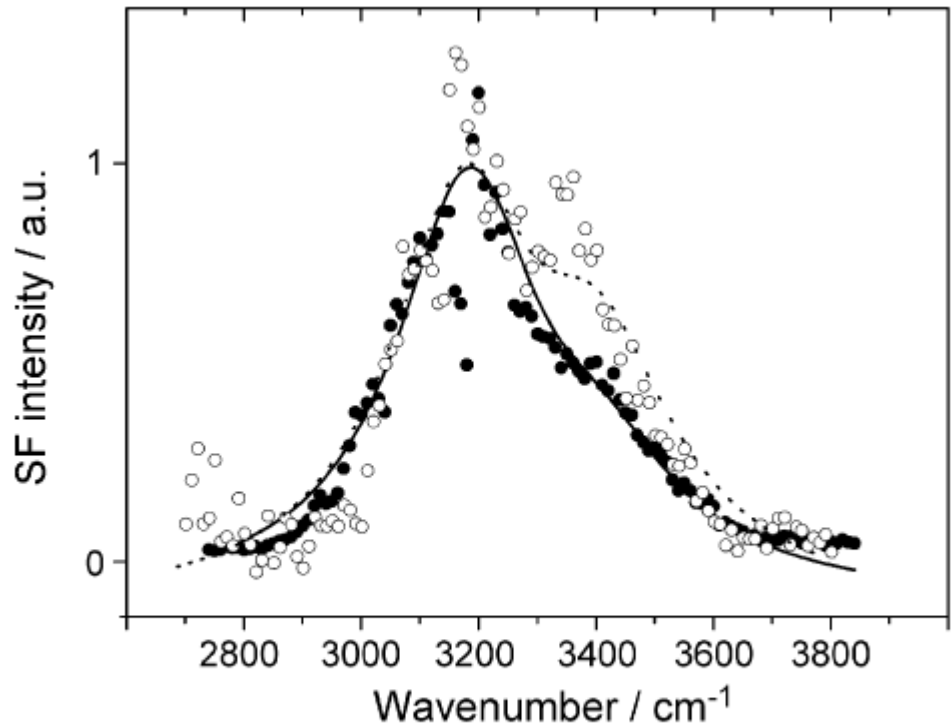


Fig. 8 SFG spectra of Fig. 6 normalized at 3200 cm⁻¹ before (●) and after (○) contact of the PNaAMPS gel.