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# Structures and Charging of α-Alumina (0001)/Water Interfaces Studied by Sum-Frequency Vibrational Spectroscopy

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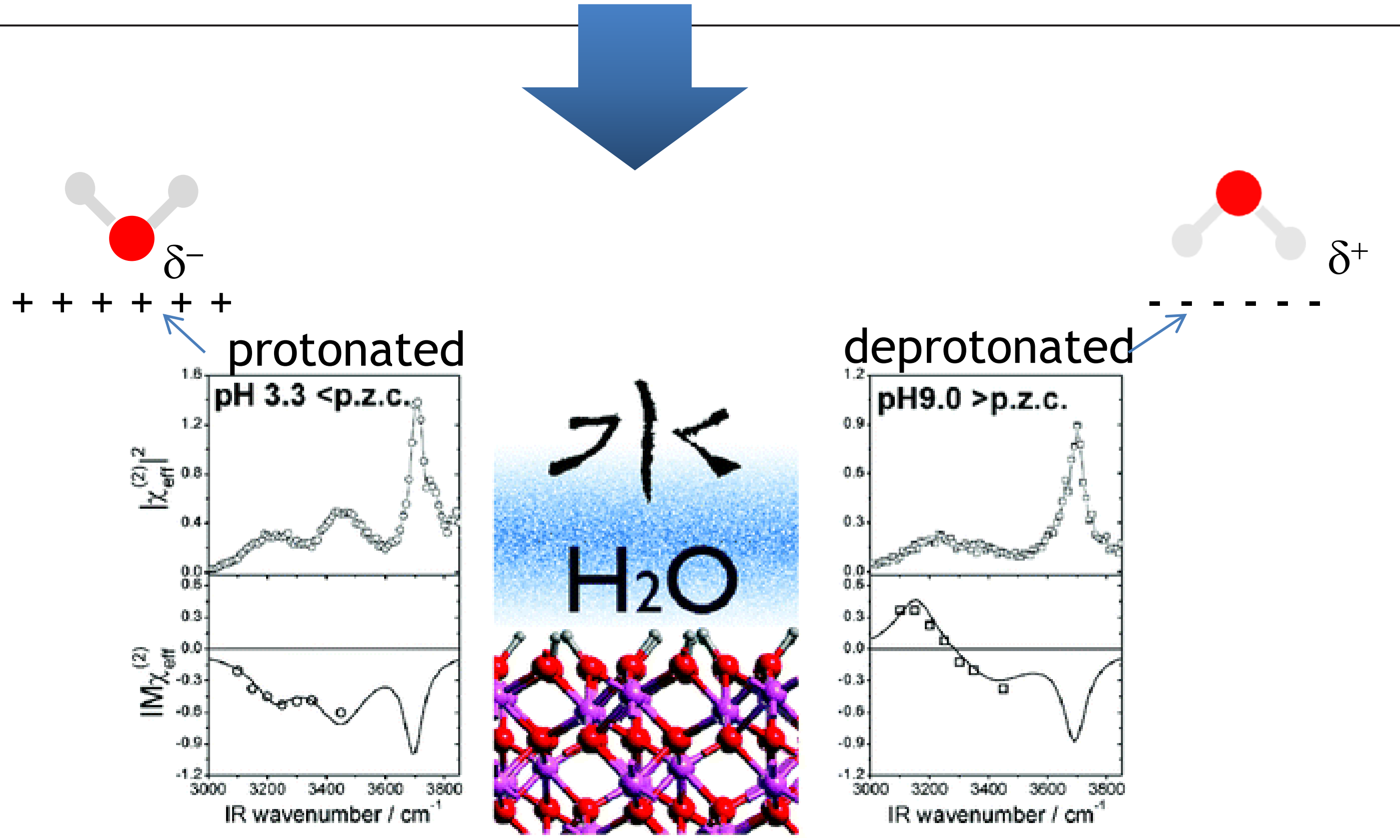
# Abstract

***Abstract:*** Sum-frequency vibrational spectroscopy in the OH stretch region was employed to study structures of water/$\alpha$-$Al_2O_3$ (0001) interfaces at different pH values. Observed spectra indicate that protonation and deprotonation of the alumina surface dominate at low and high pH, respectively, with the interface positively and negatively charged accordingly. The point of zero charge (pzc) appears at pH $\approx$ 6.3, which is close to the values obtained from streaming potential and second-harmonic generation studies. It is significantly lower than the pzc of alumina powder. The result can be understood from the p*K* values of protonation and deprotonation at the water/$\alpha$-$Al_2O_3$ (0001) interface. The pzc of amorphous alumina was found to be similar to that of powder alumina.



# Experimental Arrangement

## $\alpha$-$Al_2O_3$ (0001) sample

- Thickness 5-mm, root-mean-square roughness 0.2 nm
- Cleaned in a sonication (acetone, methanol, and pure water for 10, 10, and 60 min. mildly etched by 10-15 mM solution of HNO3 for 30 min.

## As a sample for comparison (amorphous alumina)

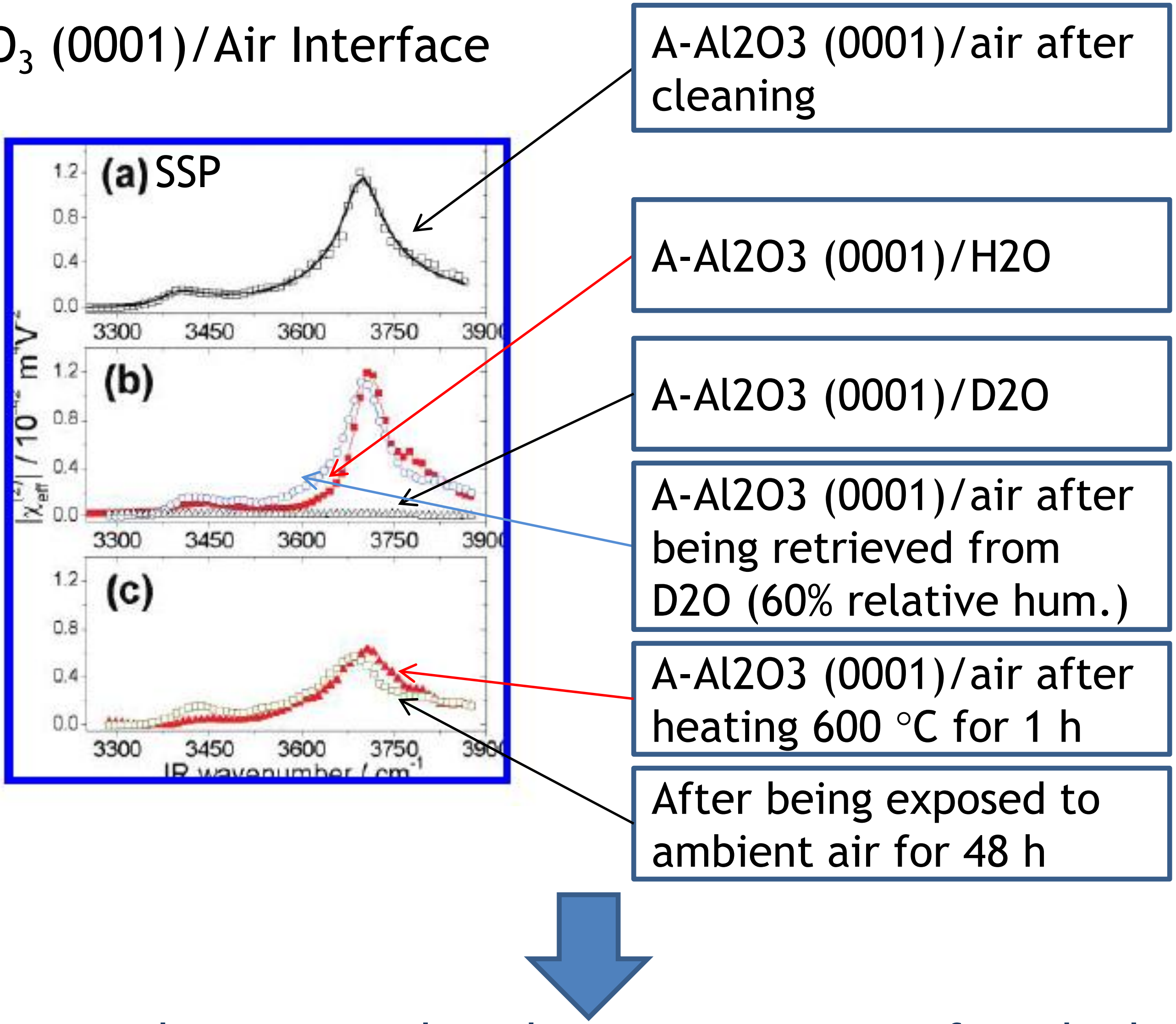
- 10-nm thick was prepared by the atomic layer deposition (ALD) method on a $\alpha$-$Al_2O_3$ (0001) substrate using trimethyllaluminum ($Al_2(CH_3)_6$.
- Cleaned in organic solvents as described above.
- The spectral intensity, comparison with monolayer of octadecanetrichlosilane, indicates that the surface density of residual $-CH_3$ contaminant is less than $1/nm^2$.

## The pH solution

- Sodium hydroxide or hydrochloric acid (37 wt % water solution)

# Results – SSP SFVS of following interfaces :

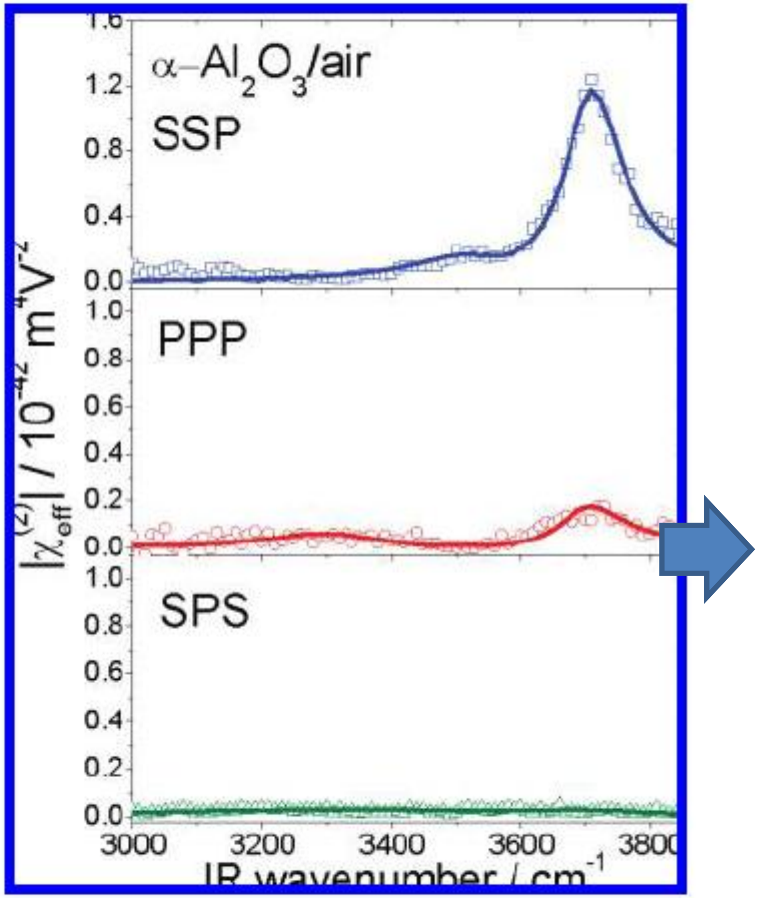
α-$Al_2O_3$ (0001)/Air Interface




These results suggest that the spectrum came from hydroxyls at the alumina/air interface.

# Results – SFG with SSP, PPP, and SPS

## $\alpha$-$Al_2O_3$ (0001)/Air Interface




The much weaker 3700 $cm^{-1}$ peaks in SPS and PPP

The amplitude ratio : Aq,eff(SSP)Aq,eff(PPP)/Aq,eff(SPS)=1:0.42±0.03:0.06±0.03

The tilt angle of dangling OH bond is around 26±2°

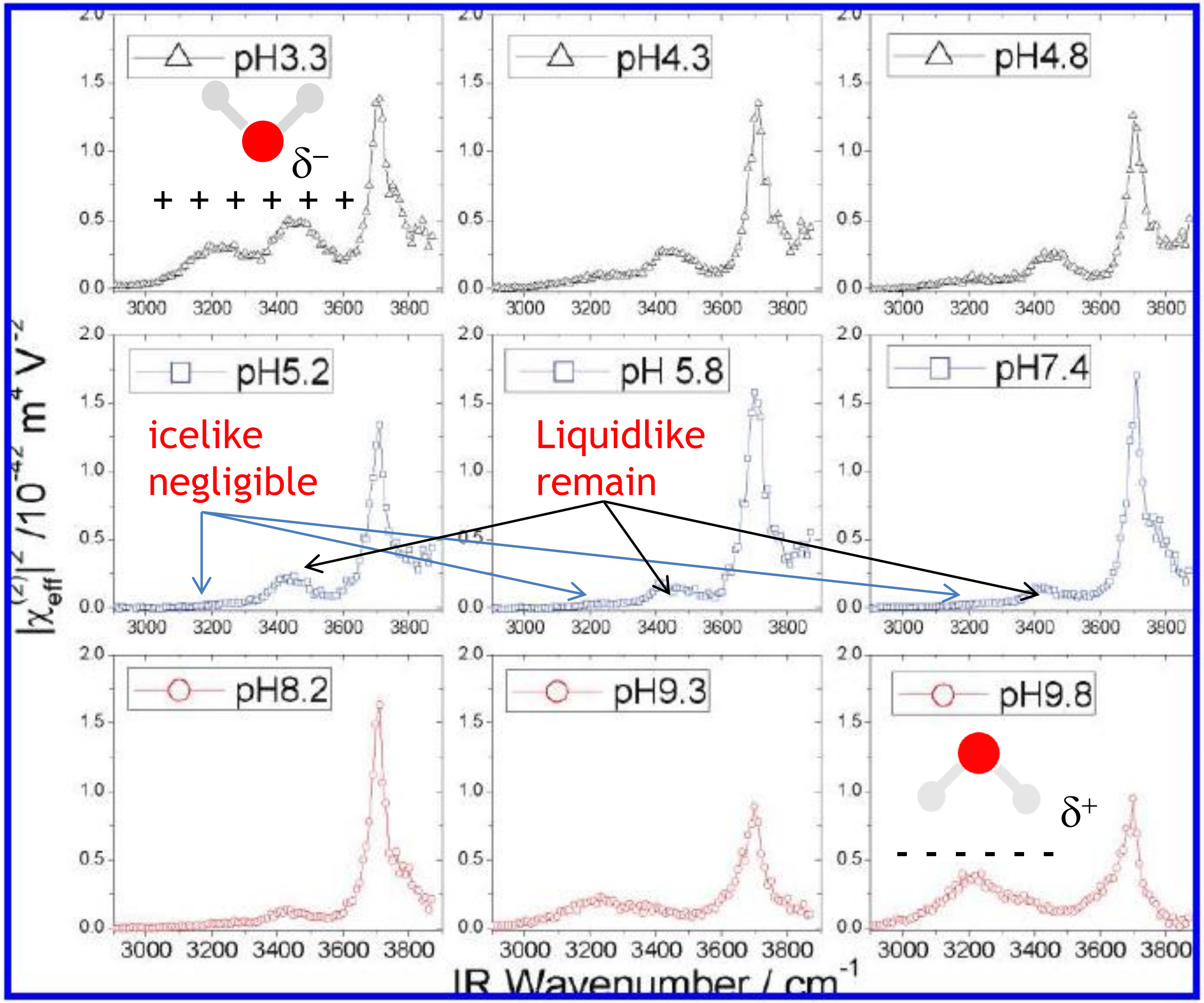
# Results – SSP SFVS

water/ $\alpha$-$Al_2O_3$ (0001)Interface at different bulk pH values

Positively surface

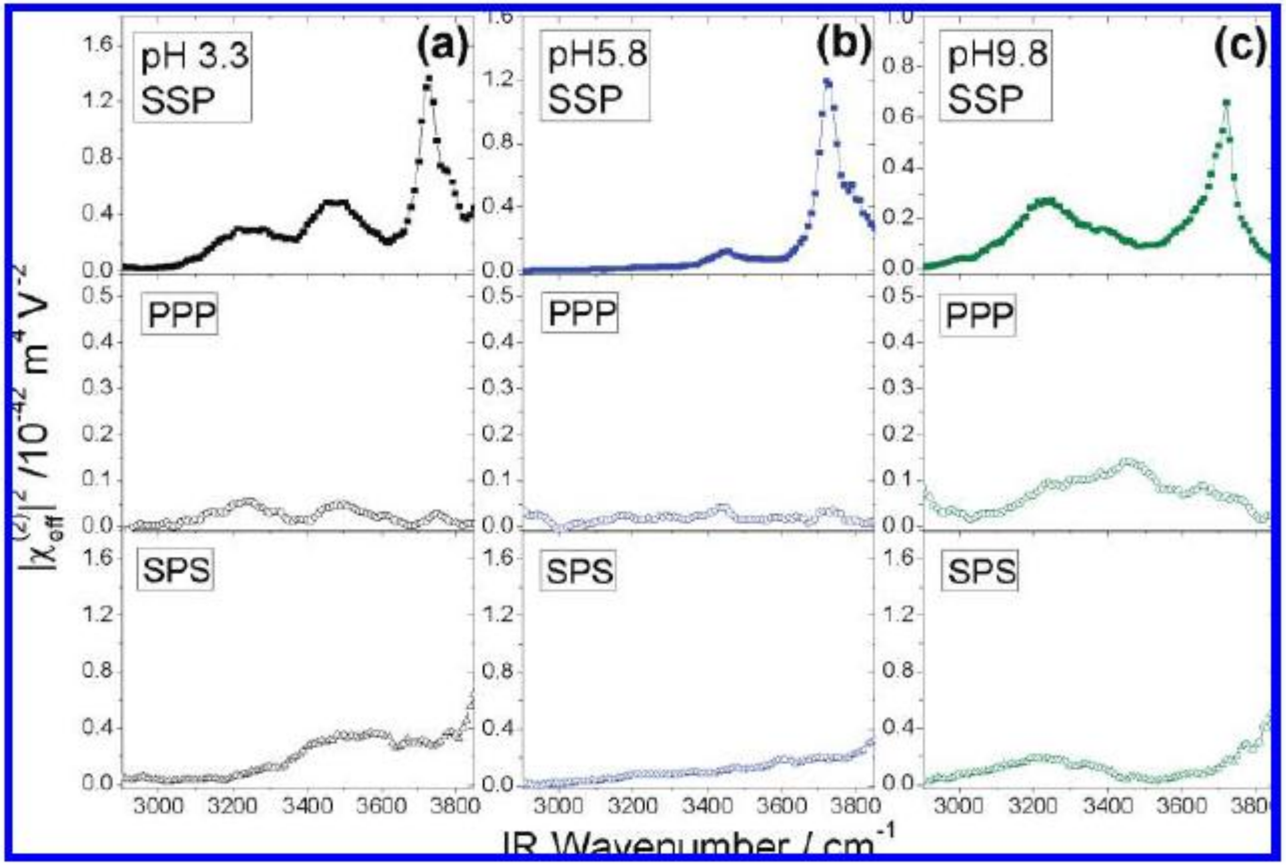
Neutrally surface

negatively surface



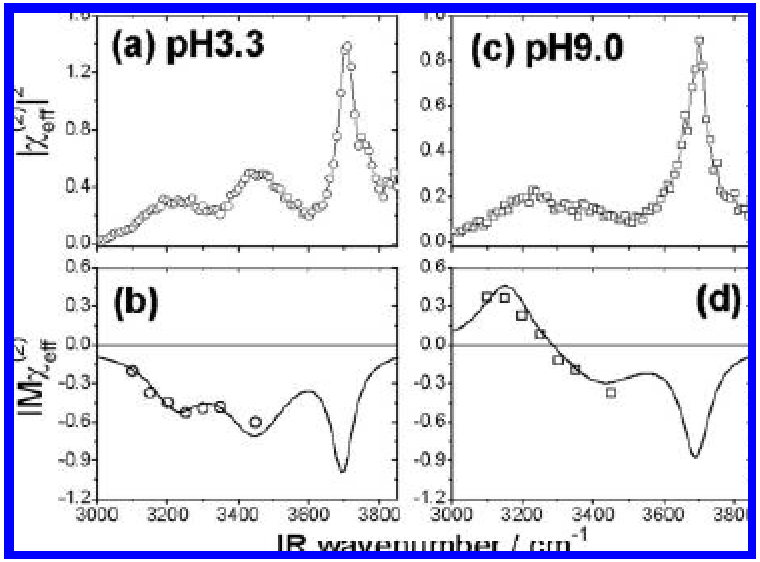
# Results – SFG with SSP, PPP, and SPS

water/ $\alpha$-$Al_2O_3$ (0001)Interface at different bulk pH values

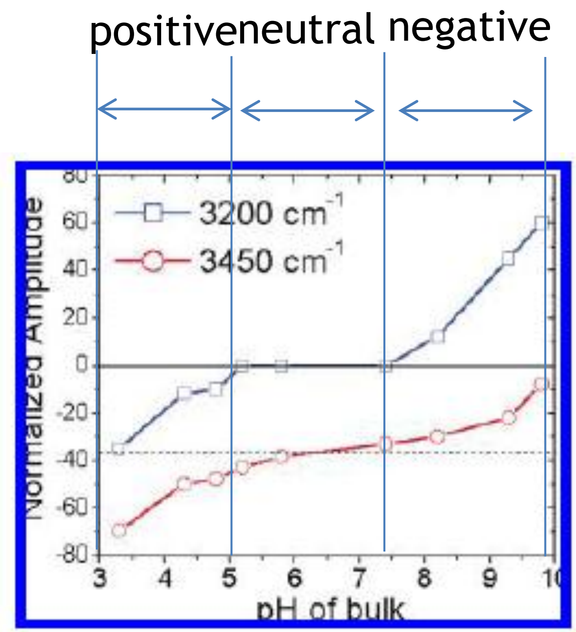


# Results – SSP SFVS

water/ $\alpha$-$Al_2O_3$ (0001)Interface at different bulk pH values



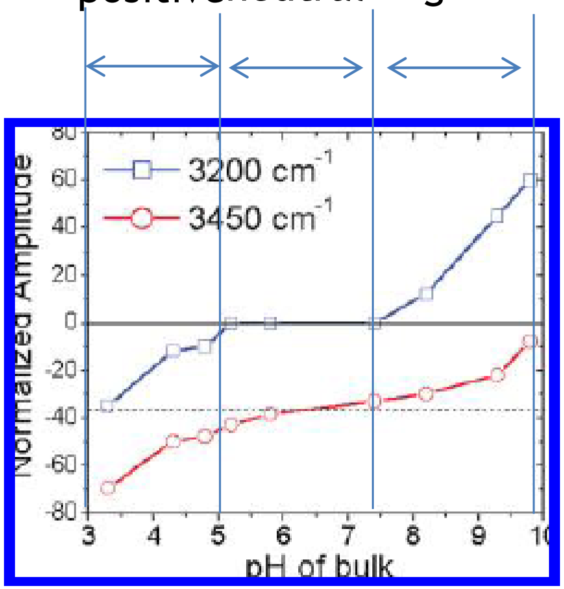




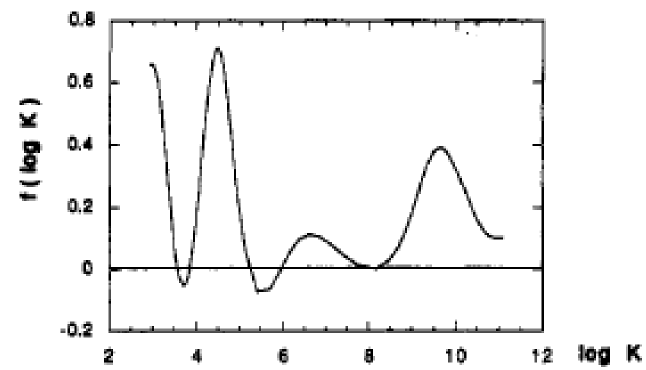
# Results – point of zero charge (PZC) at neutral surface

## water/ $\alpha$-$Al_2O_3$ (0001)Interface at different bulk pH values

positive neutral negative




Heterogeneity of proton binding sites at the oxide/solution interface




$$f(\log K) = \sum_{n=0}^{\infty} b_{2n} \left( \frac{\partial^{2n+1}\Theta(\log[\mathrm{H}])}{\partial(\log[\mathrm{H}])^{2n+1}} \right)_{\log[\mathrm{H}]=-\log K}$$

← Proton affinity distribution from isotherm

$$b_{2n} = \frac{(-1)^n \pi^{2n}}{\ln(10)^{2n}(2n+1)!}$$

$$\Theta = \int_{K_{\min}}^{K_{\max}} \theta(K,[\mathrm{H}])\, f(\log K)\, \mathrm{d}(\log K)$$

← The degrees of protonation of the different categories of sites (proton binding)

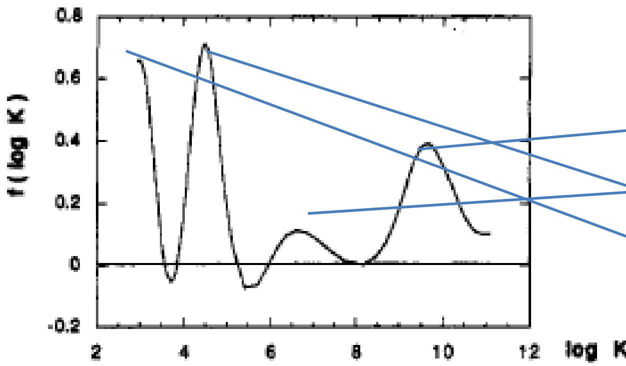
↑ Local adsorption isotherm

Langmuir, **9**, 7 (1993)

# Results – point of zero charge (PZC) at neutral surface

## water/ $\alpha$-$Al_2O_3$ (0001)Interface at different bulk pH values

Heterogeneity of proton binding sites at the oxide/solution interface




$(Al)_2OH^0 \leftrightarrow (Al)_2O^- + H^+ \quad pK = 9.7$

$(Al)_3OH^{+0.5} \leftrightarrow (Al)_3O^{-0.5} + H^+ \quad pK = 6.7$

$(Al)OH^{-0.5} \leftrightarrow (Al)O^{-1.5} + H^+ \quad pK = 4.5$

$(Al)_2OH_2^+ \leftrightarrow (Al)_2OH^0 + H^+ \quad pK \leq 3$

**PZC**

pH= [(pK=6.7)+(pK=3)]/2
= 6.35

$$f(\log K) = \sum_{n=0}^{\infty} b_{2n} \left( \frac{\partial^{2n+1}\Theta(\log[H])}{\partial(\log[H])^{2n+1}} \right)_{\log[H]=-\log K}$$

$$b_{2n} = \frac{(-1)^n \pi^{2n}}{\ln(10)^{2n}(2n+1)!}$$

$$\Theta = \int_{K_{min}}^{K_{max}} \theta(K,[H])\, f(\log K)\, d(\log K)$$

Proton affinity distribution from isotherm

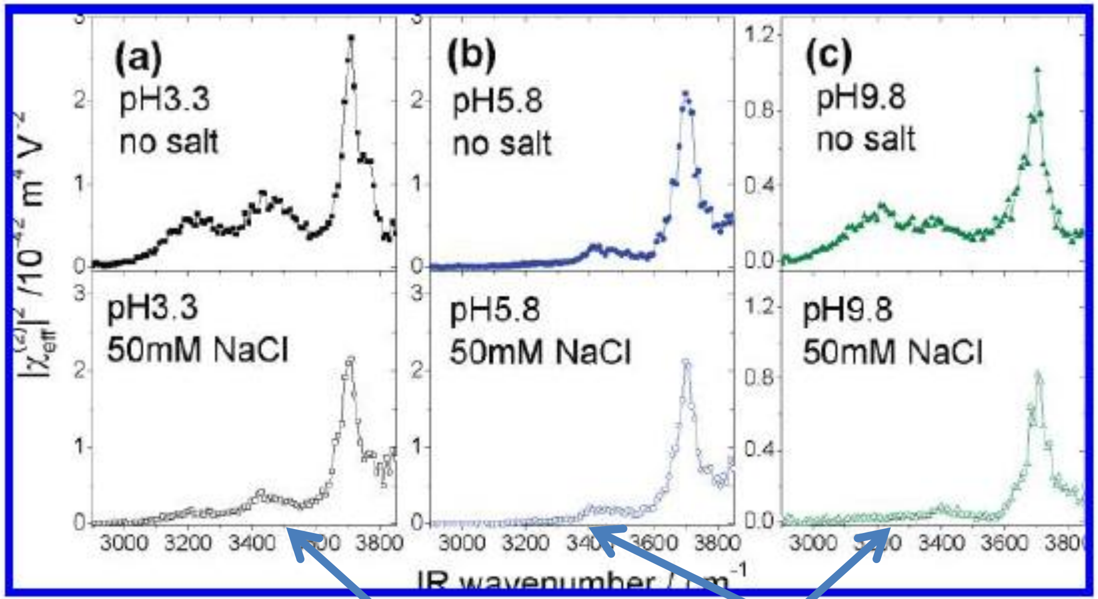
The degrees of protonation of the different categories of sites (proton binding)

Local adsorption isotherm

Langmuir, **9**, 7 (1993)

# Results – SSP SFVS

water/ $\alpha$-$Al_2O_3$ (0001)Interface at different bulk pH values **with Salt solution**




Screening of the surface field by the electrolyte

Salt ions are not attracted to the interface

# Results – SSP SFVS

water/ amorphous alumina Interface at different bulk pH values