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Effect of pH on the Water/α-Al_2O_3 ($1\bar{1}02$) interface structure studied by Sum-Frequency Vibrational Spectroscopy

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Abstract

Sum frequency vibrational spectroscopy (SFVS) was used to study the structure of water/α-Al_2O_3 ($1\bar{1}02$) interfaces at different pH values. The OH stretch spectra are dominated by interfacial water contributions at lower frequencies, and by bonded hydroxyls on the Al_2O_3 surface at higher frequencies. Protonation and deprotonation of various oxide functional groups at the α-Al_2O_3 surface as pH varies can be monitored quantitatively by changes of the spectrum, allowing their pK reaction values can be estimated. The point of zero charge of the interface is found to be at pH ~ 6.7.

Introduction

Metal oxide surfaces in contact with water are terminated by functional groups (oxygens connected to one or more metal ions) that can create local positive or negative charges due to protonation or deprotonation, respectively. Since chemical reactions at oxide/water interfaces, especially those in geochemistry, heterogeneous catalysis, semiconductor processing, electrochemistry, corrosion, and atmospheric chemistry, are very sensitive to both net surface charge and the arrangement of surface charged species,[1-5] it is crucial to understand protonation/deprotonation processes and the accompanying hydrogen bonding geometry at the molecular level. Much previous work on metal oxide surfaces has been done using

unspecified powder or polycrystalline materials, which limit systematic evaluation of the results at the molecular level.[6-9] In contrast, single crystal metal oxides serve as ideal model system for the fundamental study of water/oxide interfaces, because they allow use of crystallographic controls to select specific surface structure and types of surface functional groups.

We have been systematically studying water/α-Al_2O_3 interfaces using SFVS methodology. α-Al_2O_3 (corundum with gem varieties known as sapphire and ruby) is anhydrous and has layers of edge-sharing AlO_6 octahedral units, a structural aspect seen in many minerals, so that it can serve as a proxy surface for studying the interfacial reactivity of clays and various aluminosilicates. Also, artificially grown highly-perfect corundum crystals cut to a variety of surface planes are readily obtainable, while many well-ordered natural mineral surfaces and their synthetic analogs are generally difficult to find. Thus, a more complete and less ambiguous interfacial characterization can be done using high quality corundum samples.

A fundamental property of the water/oxide interface is the point of zero surface charge (pzc), i.e., the pH value where the surface is electrically neutral. The pzc is determined by the functional groups at the surface and their specific reactivities with respect to protonation/deprotonation. Previous studies on the charging properties of alumina powder have been performed through measurement of electrophoretic mobility or by potentiometric titration. The pzc values for α-Al_2O_3 crystalline powders have been reported to be in the range between pH 8 and 10.[6-9] In contrast, studies on single-crystal corundum using streaming potential measurements and SHG and SFVS spectroscopy, have produced different results.[10-17] These studies showed pzc values for α-Al_2O_3 (C-, R-, and A-plane) are all around pH~5 to~6. There have been several suggestions proposed to explain this discrepancy, all of which indicate that the difference in Al-O coordination (and hence types of surface functional groups) are responsible for the large disparity in pzc values.[10,11,13] It is thus essential to study the molecular details of a particular surface structure if one is to

achieve a thorough understanding of the charging behavior and overall reactivity.

SFVS is uniquely suitable for investigating structures of solid/liquid interfaces. It is a second-order nonlinear process that is forbidden in centrosymmetric media, but very sensitive to interfacial structure where inversion symmetry is broken. Yeganeh et al. first used SFVS to probe the corundum/water interfacial structure at different pH values, but the crystalline surface they employed was not specified.[14] There have been several recent reports of studies on water/α-Al_2O_3 (0001) interfaces by SFVS.[15-17] However, to our knowledge, water/α-Al_2O_3 interfaces cut in different well-defined orientations/have not yet been explored by SFVS.

In this paper, we report the SFVS study with phase information on interfacial water structure and charging behavior at the $(1\bar{1}02)$ (i.e., R plane) surface of α-Al_2O_3 as a function of pH. We found that each surface vibrational spectrum could be decomposed into two bands, one at ~3230 cm^{-1} and the other at ~3490cm^{-1}. The former varies significantly with pH, and can be assigned to interfacial water molecules, while the latter can be assigned to one type of hydroxyl group on the surface. Protonation and deprotonation of the corundum surface at different pH values creates positive and negative charges on the surface, respectively. The resulting surface fields are expected to induce corresponding net polar orientations of interfacial water molecules, with oxygen and hydrogen terminal atoms facing the interface, respectively. Indeed, we observed a reversal in the sign of the amplitude of the 3230 cm^{-1} band around pH = 6.7, which can thus be identified as the pzc of the water/α-$Al_2O_3(1\bar{1}02)$ interface in agreement with the value deduced in earlier studies.[18-20] The band at 3490 cm^{-1} appears to arise mainly from the hydrogen-bonded (H-bonded) hydroxyl groups of $AlOH_2$ at the surface, as it has a relatively narrow linewidth, a fixed peak position, and a polarization dependence that closely resembles the band observed on the dry α-$Al_2O_3(1\bar{1}02)$surface .[21] The sudden decrease of this feature's amplitude with increase of pH from 9 to 10

indicates that the pK value for deprotonation of $AlOH_2$ is around 9.5. One would anticipate that the α-$Al_2O_3(1\bar{1}02)$ surface in water would have the same hydroxyl groups associated with Al_2OH and $AlOH_2$ as the dry surface.[21] However, in the sum-feqequency vibrational spectrum, the OH stretch mode due to Al_2OH is relatively weak and may be masked by the OH band of the interfacial water. The free OH of $AlOH_2$ at the dry surface also is observed to disappear presumably because it is hydrogen-bonded to an adsorbed water molecule.

Theoretical background

The basic theory of SFVS can be found elsewhere.[22-25] Here, we present only the essentials needed for the present data analysis. The reflected SF signal is given by

$$S(\omega_{SF} = \omega_{vis} + \omega_{ir}) \propto [\hat{e}(\omega_{SF}) \bullet \vec{L}(\omega_{SF})] \bullet \chi^{(2)} : [\hat{e}(\omega_{vis}) \bullet \vec{L}(\omega_{vis})][\hat{e}(\omega_{ir}) \bullet \vec{L}(\omega_{ir})] \qquad (1)$$

where $\hat{e}(\omega_i)$ and $\vec{L}(\omega_i)$ denote the unit polarization vector, and the transmission Fresnel factor at frequency ω_i, respectively. The surface nonlinear susceptibility $\chi^{(2)}$, assumed to be composed of discrete resonances, is described by

$$\overleftrightarrow{\chi}^{(2)} = \overleftrightarrow{\chi}^{(2)}_{NR} + \sum_q \frac{\vec{A}_q}{(\omega_{IR} - \omega_q) + i\Gamma_q}, \qquad (2)$$

Where $\overleftrightarrow{\chi}^{(2)}_{NR}$ is the nonresonant contribution, $\vec{A}_q$, ω_q, and Γ_q are the amplitude, the resonant frequency and the damping constant of the qth resonance, respectively. The amplitude $\vec{A}_q$ in the lab coordinates (i,j,k) is related to the molecular polarizability $\vec{a}_q$ in the molecular coordinates by

$$A_{q,ijk} = \sum_{\xi,\eta,\zeta} < (\hat{i} \cdot \hat{\xi})(\hat{j} \cdot \hat{\eta})(\hat{k} \cdot \hat{\zeta}) > \qquad (3)$$

Using Eqs.(1) and (2) to fit a measured spectrum allows us to deduce the parameters in Eq. (2), but the fitting may not be unique unless the resonant frequencies and the sign of $A_{q,ijk}$ are predetermined. The latter

often requires a phase measurement of the SF signal. To directly characterize the resonances, the Im $\chi^{(2)}$ spectrum has the expression

$$\mathrm{Im}\,\vec{\vec{\chi}}^{(2)} = \sum_q \frac{\vec{\vec{A}}_q \Gamma_q}{(\omega_{IR} - \omega_q)^2 + \Gamma_q^2} \qquad (4)$$

The sign of A_q describes the absolute orientation of the moiety contributing to the qth resonant mode.

Experimental

Our SFVS setup has been described elsewhere.[26, 27] In the present case, the input beams, one visible at 532nm with ~500 μJ/pulse and the other tunable infrared between 2.6 and 3.7μm with ~100 μJ/pulse, were incident from the corundum side and overlapped in a spot of 180x300 μm^2 at the corundum/water interface. The incidence plane was chosen to include the optical axis of the corundum crystal so that the polarization of the input beams did not change in passing through the crystal. The two beams had incident angles of $\beta_{vis}=45^o$ and $\beta_{IR}=57^o$ at the air/corundum interface and the SF signal in the reflection direction was spatially and spectrally filtered and collected by a gated detector system. Each data point in a spectrum came from averaging the signals over 200 laser shots, and was normalized against that from a z-cut quartz sample. Phase measurement of SFVS was carried out using the interference scheme described previously.[28,29,30]

The sample used was an epi-polished single crystal of α-Al_2O_3($1\bar{1}02$) purchased from Princeton Scientific Corporation. It was 5 mm thick, and the root-mean-square roughness of the polished surfaces was on the order of 0.2 nm. Sample preparation followed the recipe used in earlier work.[11,13,31] The sample surface was first cleaned in a sonic cleaning bath of acetone, methanol, and pure water for 10, 10, and 60 min, respectively, in sequence. It was then mildly etched in a 10~15mM solution of HNO_3 under sonic cleaning for 30min, rinsed thoroughly with deionized water, and blow-dried with filtered dry nitrogen gas. To remove the remaining water and organic contaminates on the surface, the sample was heated at ~350^{o}C for 1 hour in air.[21]

The pH value of deionized water (resistivity 18.3 MΩ· cm) was controlled by dissolution of sodium hydroxide (99.998% pellets, Sigma-Aldrich) or by addition of hydrochloric acid (37 wt % water solution, 99.999%, Sigma-Aldrich), and was measured by a Beckmann pH meter equipped with an AccuTupH double-junction electrode. Solutions with specific electrolyte concentrations were prepared by dissolving sodium chloride (>99.5%, ReagentPlus, Sigma) into a known volume of water.

Results and Discussion

The measured SF intensity spectra of the α-$Al_2O_3(1\bar{1}02)$/water interface in the OH stretch region, with SSP (denoting S-, S-, P-polarized SF output, visible and infrared inputs, respectively) and SPS input/output polarization combinations, are presented in Fig. 1 for three different values of pH in water. Red and black curves in the spectra describe sample positions of $\gamma = 0$ and $\gamma = 180^o$, respectively, where γ is defined as the angle of the $[1\bar{1}0\bar{1}]$ direction with respect to the incident plane, illustrated in the inset of Fig. 1. All spectra can be fitted using Eqs. (1-2) with two resonant modes with frequencies(ω_q) of 3230 and 3490cm^{-1} and linewidths (Γ_q) of 150 and 110 cm^{-1}, respectively. The strength (A_q) of each band changes with pH and γ, and their signs were determined by separate SFVS phase measurements. We plot in Fig. 2 the corresponding Im $\chi^{(2)}$ spectra calculated from Eq.(4) using the parameters, ω_q, Γ_q, and A_q, deduced from the fitting. They show more clearly the two resonant bands with appropriate signs. In Fig. 3 a more complete set of $|\chi^{(2)}|^2$ and Im $\chi^{(2)}$ SSP spectra with different pH is given, and the amplitudes for the two modes deduced from fitting are plotted in Fig. 4. We see in Fig. 4a that the amplitude of the 3230 cm^{-1} band responds to pH in two steps. It changes smoothly from a significant negative value to nearly zero when pH increases from 3.5 to 5.5, and from zero to a significant positive value when pH increases from 8 to 10. The amplitude of the 3490 cm^{-1} band appears to have only a single step of significant change occurring between pH 9 and 10. Such step changes of the amplitudes should be related to the

protonation/deprotonation reactions at the water/α-$Al_2O_3(1\bar{1}02)$ interface.

The observed spectra must come from OH stretches of the interfacial water molecules and/or OH species residing on the α-$Al_2O_3(1\bar{1}02)$ surface. To understand the spectra, we need to know first what OH species could exist on the α-$Al_2O_3(1\bar{1}02)$ surface. In our earlier work, we found that the dry α-$Al_2O_3(1\bar{1}02)$ surface has a structure composed of three relaxed layers in which oxygen atoms are bonded to 1, 2, and 3 Als, respectively, as shown in Fig. 5.[21, 32] This surface has C_{1v} symmetry with respect to the $(\bar{1}\bar{1}20)$ glide plane. Protonation of the surface leads to the appearance of three OH species, two bonded OH (H bonded to a neighboring acceptor O) associated with Al_2OH and $AlOH_2$, and one free OH associated with the $AlOH_2$ functional group. These hydroxyls have their stretch mode frequencies at ~3365, 3520, and 3670cm^{-1}, respectively, and corresponding orientations of $\theta \sim 69^o$ and $\phi \sim \pm 67^o$, $\theta \sim 62^o$, $\phi \sim \pm 127^o$, and $\theta \sim 36^o$, $\phi \sim \pm 78^o$, respectively. Here, θ is the polar angle of OH away from the surface normal and φ is the azimuthal angle of OH away from the $[1\bar{1}0\bar{1}]$ direction in the surface plane. The strengths of the different bands in the SF vibrational spectrum depend on the orientations of the OH species. As a result, the 3520 and 3670 cm^{-1} bands in the SSP spectrum are relatively strong and the 3365 cm^{-1} band weak. Because of its low bond valence value, oxygen in the Al_3O functional group at the $(1\bar{1}02)$ surface is not easily protonated in air. At the water/α-$Al_2O_3(1\bar{1}02)$ interface, we expect that the three oxide groups, Al_3O, Al_2O, and AlO groups can be protonated or deprotonated, depending on the contacting solution pH. References [18-20] provide estimated pK values for protonation/deprotonation reactions of the different relevant groups:

$$Al_3OH^{+0.5} \leftrightarrow Al_3O^{-0.5} + H^+ \qquad pK\sim 5.9$$

$$Al_2OH_2^{+1} \leftrightarrow Al_2OH + H^+ \qquad pK \sim 0$$

$$Al_2OH \leftrightarrow Al_2O^{-1.0} + H^+ \qquad pK\sim 12.9$$

$$AlOH_2^{+0.5} \leftrightarrow AlOH^{-0.5} + H^+ \qquad 9.9<pK<11$$

$$AlOH^{-0.5} \leftrightarrow AlO^{-1.5} + H^{+} \qquad pK\sim 11.9 \qquad (5)$$

where the superscript on a molecular group denotes the formal charge on the group assuming typical Pauling bond valence criteria.[20] Using Eq. (5) as guidance, we expect the following surface structures: For pH decreasing from 6, the surface gets increasingly positively charged through protonation of the Al_3O groups until saturation occurs; so the surface is mainly composed of Al_2OH, and $AlOH_2$ groups and Al_3O and Al_3OH groups balanced by the protonation/depronation reaction. For pH increasing from 6, the surface becomes increasingly negatively charged through deprotonation of the $AlOH_2$ groups, and is mainly composed of Al_3O and Al_2OH groups and $AlOH_2$ and AlOH groups balanced by their protonation/depronation reaction. Around pH 6, the surface is essentially neutral and composed of Al_3O, Al_2OH and $AlOH_2$ groups. In all cases, interfacial water molecules can be H bonded to the surface: they have their hydrogen H-bonded to the oxygen of the deprotonated sites and their oxygen bonded to the hydrogen of the otherwise free OH on the $AlOH_2$ groups.

We now discuss how we can understand the OH stretch bands in the spectrum of the water/α-$Al_2O_3(1\bar{1}02)$ interface and their variation with pH. Considering first the 3230 cm^{-1} band, which resembles the so-called "ice-like" band often seen in the SSP SF spectrum of other water interfaces, we believe it comes mainly from interfacial water molecules. As seen in Fig. 4, the amplitude of this band changes from negative to positive sign when the pH of interfacial water changes from a low to a high value, while in the middle pH range, it is very weak. This is characteristic of a SFVS spectrum for interfacial water near a surface that can be protonated and deprotonated.[14,15] The negative and positive band amplitudes correspond to net polar orientations of interfacial water molecules with their oxygen and hydrogen ends, respectively, facing the crystalline surface. They are induced by the corresponding positive and negative surface fields created by the positive and negative surface charges on the α-$Al_2O_3(1\bar{1}02)$ surface through protonation of the Al_3O groups and deprotonation of the $AlOH_2$ groups. In the middle pH range, the band

amplitude is very low, which is characteristic of a neutral water interface with little net dipolar orientation of the water molecules. These are thus clear evidence that this band is mostly from interfacial water molecules. If it were from OH species associated with the α-$Al_2O_3(1\bar{1}02)$ surface, then its resonance amplitude could never change sign despite changes in its absolute strength due to protonation or deprotonation. We can calculate the surface charge density versus pH from the protonation reaction, $Al_3OH \leftrightarrow Al_3O + H$, and deprotonation reaction, $AlOH_2 \leftrightarrow AlOH + H$, if we know their respective pK values. By assuming that the band amplitude is proportional to the surface field, and hence the surface charge density, we can actually fit the data in Fig. 4a using the two pKs as adjustable parameters, and we find pK = 4.9±0.4 and 9.2±0.5 for the protonation and deprotonation reactions mentioned above. They are reasonable when compared with the corresponding estimated pK values given in Eq. (5). We note also from the previous SF result on the dry α-$Al_2O_3(1\bar{1}02)$ surface, that the Al_2OH groups on the surface may contribute to a resonance band around 3365 cm^{-1}. However, this band is rather weak and is negligible compared to the 3230 cm^{-1} water band. The other OH species from Al_3OH, $AlOH_2$ and AlOH groups also do not seem to contribute significantly to this water band.

We next consider the 3490 cm^{-1} band in the SF spectrum of the water/α-$Al_2O_3(1\bar{1}02)$ interface. As seen in Fig. 4b, the amplitude of this band is negative at all pH except for γ = 0 and pH > 9, suggesting that it largely originates from O→H pointing away from the interface. Its frequency is close to the 3520 cm^{-1} band observed on the dry surface, and therefore we can similarly identify it as mainly coming from the OH species associated with $AlOH_2$ with its H bonded to neighboring O in the surface lattice. This assignment is supported by several observations. Compared to the band observed from the dry surface, it has the same strong forward ($\gamma = 0^o$)-backward ($\gamma = 180^o$) asymmetry in strength, and is red-shifted by 30 cm^{-1}. Its somewhat broader linewidth is likely due to interaction with surrounding water. We can extract the orientation of OH from the 3490 cm^{-1} band in the SSP and SPS spectra of Fig. 1 using the same procedure outlined in references [21, 33, 34]. We find, independent of pH, an orientation specified by $\theta = 58^o \pm 15^o$

and $\phi=\pm118^{o}\pm13^{o}$, which is very close to the orientation, $\theta=62^{o}\pm8^{o}$, $\varphi=\pm127^{o}\pm9^{o}$, of the same OH species on the dry surface.[21] Finally, we notice in Fig. 4b that the band amplitude A_q changes abruptly at pH ~ 9, which is close to the pK value of the protonation/deprotonation reaction $\mathrm{AlOH_2} \leftrightarrow \mathrm{AlOH} + \mathrm{H}$. Thus we believe we can confidently assign the 3490 cm^{-1} band to the H bonded OH stretch on $AlOH_2$. However, interfacial water molecules generally also contribute a "liquid-like" band to this spectral range that may not be negligible. In our case, this is evidenced by the observed positive amplitude observed at pH > 9 with $\gamma = 0$ in Fig. 4b since OH on $AlOH_2$ pointing away from the surface can only contribute negatively to A_q. We can separate the contributions from water and $AlOH_2$ to the OH band (still approximating it as a single mode), knowing that OH of $AlOH_2$ has strong forward-backward anisotropy (Fig. 1) which the interfacial water molecules cannot exhibit. The observed SF amplitudes, $A_q(\gamma=0^{o})$ and $A_q(\gamma=180^{o})$, in the forward and backward directions consist of components A_W from water and $A_{OH}(\gamma=0^{o})$ and $A_{OH}(\gamma=180^{o})$ from OH on $AlOH_2$:

$$A_q(\gamma=0^{o}) = A_{OH}(\gamma=0^{o}) + A_W \text{, and} \quad A_q(\gamma=180^{o}) = A_{OH}(\gamma=180^{o}) + A_W \qquad (6)$$

$A_{OH}(\gamma=0^{o})$ and $A_{OH}(\gamma=180^{o})$ are proportionally related because they come from the same OH species: $A_{OH}(\gamma=0^{o}) = \kappa A_{OH}(\gamma=180^{o})$. The proportional constant κ can be obtained from the measured $A_q(\gamma=0^{o})$ and $A_q(\gamma=180^{o})$ at pH ~ 6 where the water contribution A_W is known to be negligible. We can thus separately deduce A_W, $A_{OH}(\gamma=0^{o})$, and $A_{OH}(\gamma=180^{o})$. The results plotted as functions of pH are presented in Fig. 6. It is seen in Fig. 6a that $A_{OH}(\gamma=0^{o})$ and $A_{OH}(\gamma=180^{o})$ are always negative and remain nearly constant until pH ~8.5, and then drop off to a small value at pH ~ 10. Knowing that A_{OH} is proportional to the surface density of $AlOH_2$, we can calculate A_{OH} from the deprotonation reaction $\mathrm{AlOH_2} \leftrightarrow \mathrm{AlOH} + \mathrm{H}$. The solid curves in Fig. 6a calculated with pK = 9.2 for the reaction fit the data quite well. The water contribution A_{OH} at different pH is plotted in Fig. 6b. The data, although of poorer

quality, shows a similar two-step change with pH as that of the 3230 cm^{-1} band of water in Fig. 4a. They can also be roughly fitted by the protonation reaction $Al_3OH \leftrightarrow Al_3O + H$ with pH = 4.9 and the deprotonation reaction $AlOH_2 \leftrightarrow AlOH + H$, with pK = 9.2, assuming that A_W is proportional to the surface charge density. Negative and positive A_W at low and high pH values reflect the presence of positive and negative charges at the surface.

There are other hydroxyl groups attached to the α-$Al_2O_3(1\bar{1}02)$ surface that could contribute to the OH stretch spectrum in the pH ranges we have studied, but cannot be identified in our spectra. These are OH species associated with Al_2OH that exist at all pH, with AlOH at pH > ~9, with $AlOH_2$ at pH < ~9 (referring to the originally dangling OH on the dry surface), and with Al_3OH at pH < ~5. As we mentioned earlier, the band associated with Al_2OH is relatively weak and likely negligible. The originally dangling OH on AlOH and $AlOH_2$ is suppressed by H-bonding to a water molecule if the surface is submerged in water. Because its H-bonding strength with water can vary over a wide range, this OH band may have a low peak strength and very broad bandwidth, causing it to be indistinguishable from other bonded OH bands. Finally, the OH species on Al_3OH is expected to be weak because O is already strongly bonded to 3 Als, and its stretch frequency may appear below the spectral range we have studied. Thus the OH species of $AlOH_2$ that is H-bonded in the surface lattice appears to be the only one contributing significantly and distinctively in the SFVS spectrum.

We can determine the point of zero charge (pzc) of the water/R-sapphire interface from the change of the water band at 3230 cm^{-1} with pH in Fig. 4a. The nearly zero amplitude at ~5.8 < pH < ~7.8 indicates that the interface is neutral in that range. This sets the pzc at pH ~ 6.7, which is close to the theoretically predicted pzc of pH ~ 7.8,[18-20] and the experimentally measured pzc of 5.2 by second harmonic generation.[13] To be sure that the nearly zero strength of the water band represents a neutral interface, we have measured the spectral changes upon addition of salt to the water solutions at different pH values. The interfacial water spectrum is expected to change if salt ions are attracted to the charged surface, but not if

the surface is neutral. We present in Fig. 7 the SF spectra of water/α-$Al_2O_3(1\bar{1}02)$ interfaces with and without 50mM NaCl in water at pH = 2.4, 5.8, and 10.5. It is seen that with NaCl, the water band is clearly reduced for pH at 2.4 and 10.5 (because of screening of the surface field by ions), but is weak and hardly changed at pH 5.8 as expected from a neutral interface. We also notice that in all cases, the ~3490cm^{-1} band is not much affected by the addition of salt, providing additional evidence that this band is dominated by hydroxyls on the α-$Al_2O_3(1\bar{1}02)$ surface, with little contribution from interfacial water molecules.

Conclusion

We have used SFVS to study the structure of water/α-Al_2O_3 $(1\bar{1}02)$ interfaces as a function of pH. The spectra in the OH stretch region exhibit two bands at ~3230 and ~3490cm^{-1} that can be identified as coming mainly from interfacial water molecules and the H-bonded hydroxyl associated with the $AlOH_2$ groups on the surface of α-Al_2O_3, respectively. Protonation and deprotonation of the oxide sites at the surface can be monitored by the spectral change of the SFVS water band because the field created by the surface charges can reorient the interfacial water molecules. Using these assumptions we deduce pK values of 4.9 and 9.2 for the protonation/deprotonation reactions of Al_3OH and $AlOH_2$ groups at the surface, respectively. The same pK value of 9.2 is also obtained from the spectral change of the 3490cm^{-1} band for OH on $AlOH_2$. Variation of the water band with pH also allows us to find the range of pH in which the interface is neutral, and thus determine that the point of zero charge of the interface is at pH ~6.7. This work provides another example that surface-sensitive SFVS is an effective tool for probing structures of relevant oxide/water interfaces at the molecular level, and shows that different crystalline surfaces of the same crystal may behave differently in relation to their different surface structures. To further explore the last point, we are in the process of studying the A-plane $(11\bar{2}0)$ surface of corundum using SFVS.

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Figure Captions

Figure 1. SFVS of α-Al_2O_3 ($1\bar{1}02$)/water interfaces with SSP and SPS polarization combinations at three different pH values: 2.7 (top) , 5.8 (middle), and 9.7 (bottom), where red and black circles describe the spectra at γ=0° and 180°, respectively. (X2 indicates amplifying the spectra by 2 times in order to clearly show the spectral features.)

Figure 2. Im $\chi^{(2)}$ spectra deduced from the corresponding SSP-$|\chi^{(2)}|^2$ spectra in Fig. 2: (a) γ=0° and (b) γ=180° with pH=2.7 (top), 5.8 (middle), and 9.7 (bottom). The circles are data points obtained directly from SFVS phase measurements.

Figure 3. SSP spectra of (a) $|\chi^{(2)}_{SSP}|^2$ and (b) Im $\chi^{(2)}_{SSP}$ for α-Al_2O_3 ($1\bar{1}02$)/water interfaces at several different pH values at γ=180°.

Figure 4. Amplitudes of the OH stretch modes at (a) 3230 cm^{-1} and (b) 3490 cm^{-1} versus pH. The blue curve in (a) is a theoretical fit. (described in the text) Red and Black circles in (b) describe data points for γ=0 and 180°, respectively.

Fig. 5. Protonated surface structure of α-Al_2O_3 ($1\bar{1}02$) deduced from SFVS spectra and CTR measurements. (a) Side view and (b) top view.

Figure 6. Contributions to the 3230 cm^{-1} band from (a) OH on $AlOH_2$ and (b) water versus pH. Red and black circles in (a) refer to data points of $A_{OH}(\gamma=0°)$ and $A_{OH}(\gamma=180°)$, respectively, for OH on $AlOH_2$ and the lines are a theoretical fit (described in the text).

Figure 7. SSP spectra of α-Al_2O_3 ($1\bar{1}02$)/water interfaces at γ=180° for three different pH values, 2.4 (top) , 5.8 (middle), and 10.5 (bottom) with (red circles) and without (black circles) addition of 50 mM of NaCl in the water solution.

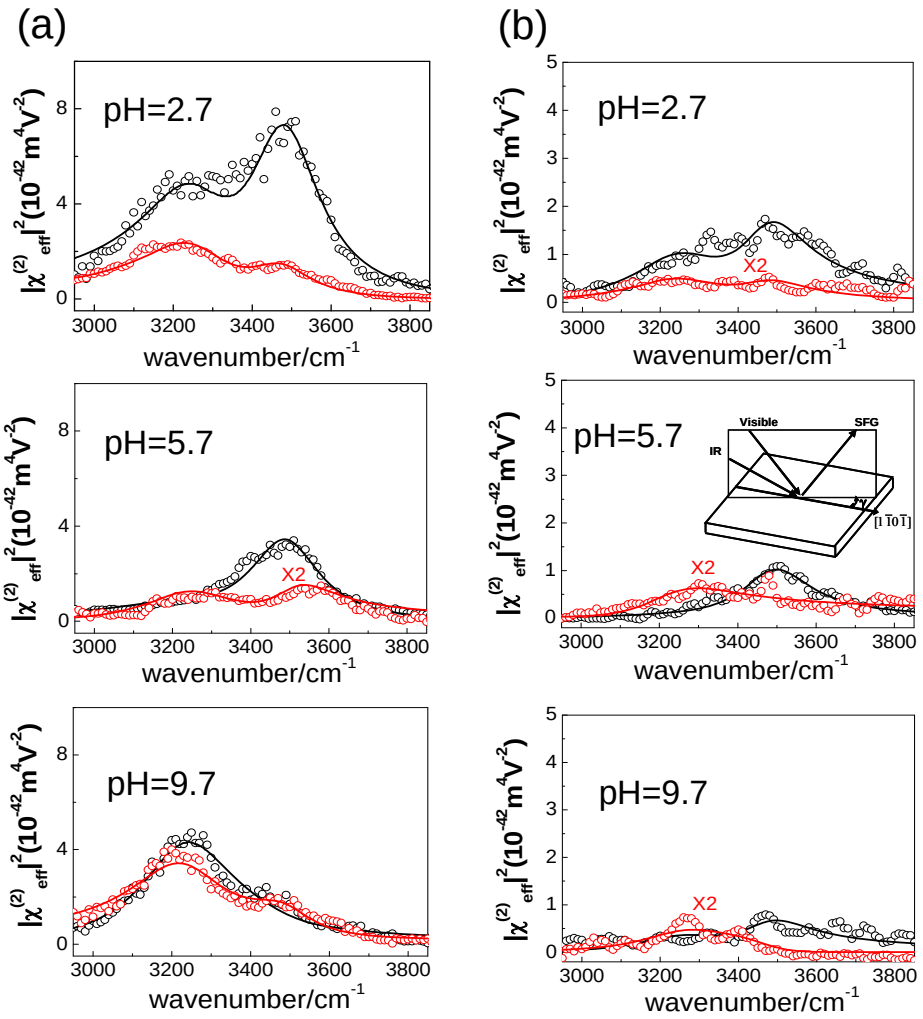

(a)
(b)
pH=2.7
pH=5.7
pH=9.7
X2
Visible
SFG
IR
wavenumber/cm-1
|χ(2)eff|2(10-42m4V-2)

Fig. 1

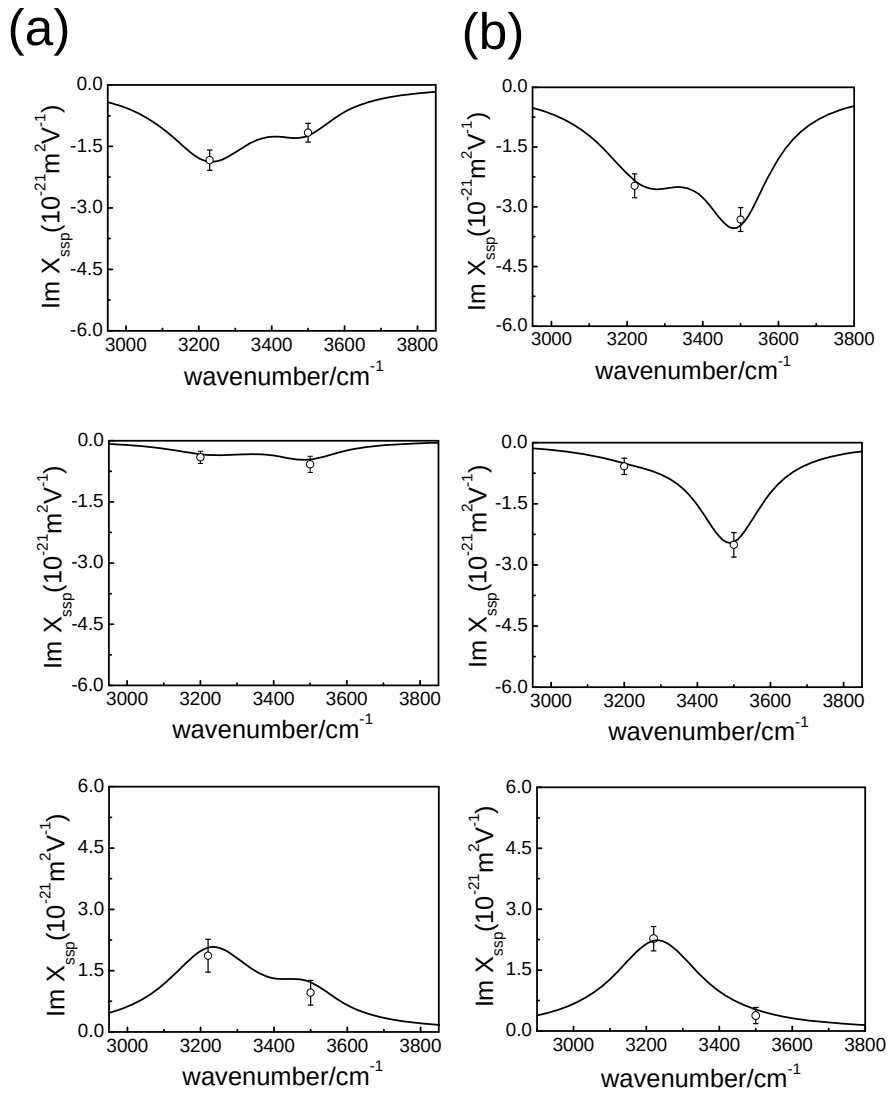

(a)
(b)
Im X_{ssp} (10^{-21} m^2V^{-1})
wavenumber/cm^{-1}
0.0
-1.5
-3.0
-4.5
-6.0
6.0
4.5
3.0
1.5
3000
3200
3400
3600
3800

Fig. 2

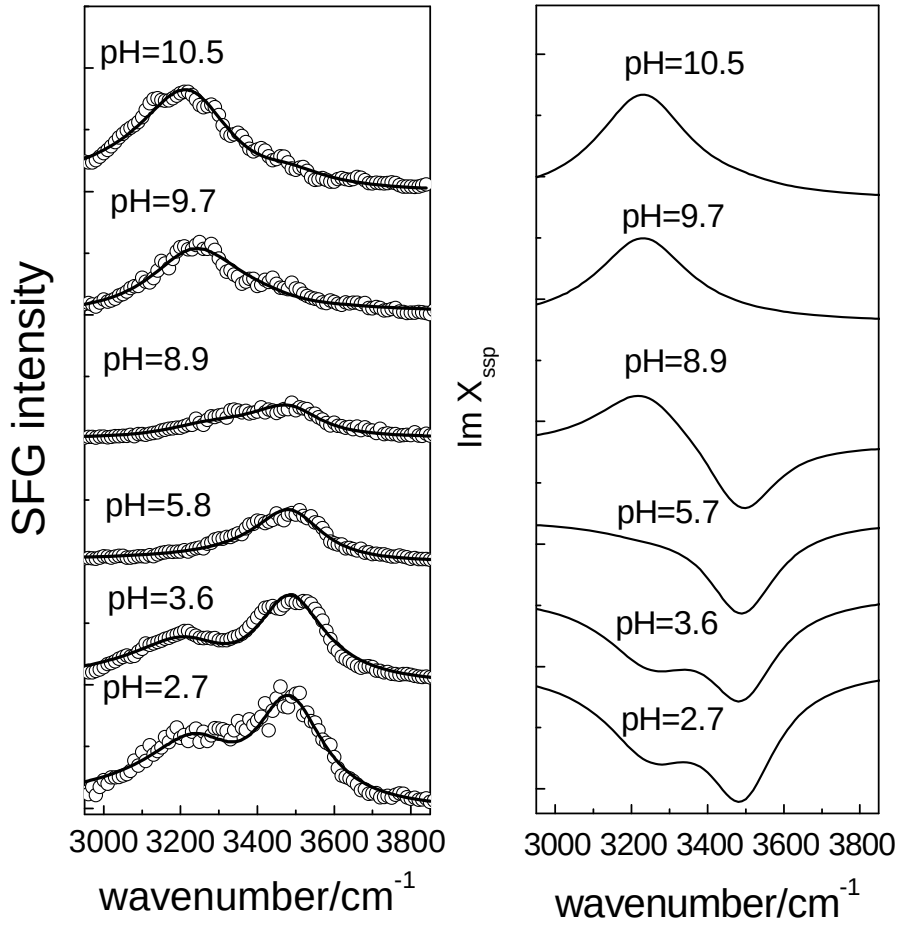
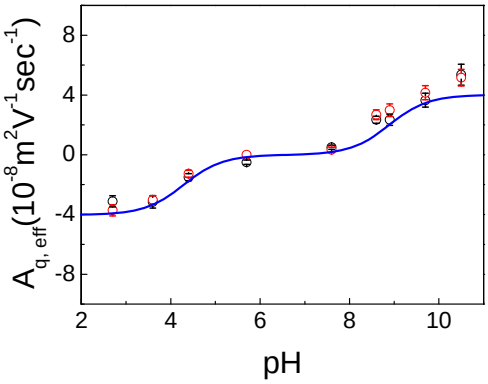

pH=10.5
pH=9.7
pH=8.9
pH=5.8
pH=3.6
pH=2.7
SFG intensity
3000 3200 3400 3600 3800
wavenumber/cm-1
Im Xssp
pH=10.5
pH=9.7
pH=8.9
pH=5.7
pH=3.6
pH=2.7
3000 3200 3400 3600 3800
wavenumber/cm-1

Fig. 3

(a)


8
4
0
-4
-8
2
4
6
8
10
pH
$A_{q,\,eff}(10^{-8}m^2V^{-1}sec^{-1})$

(b)

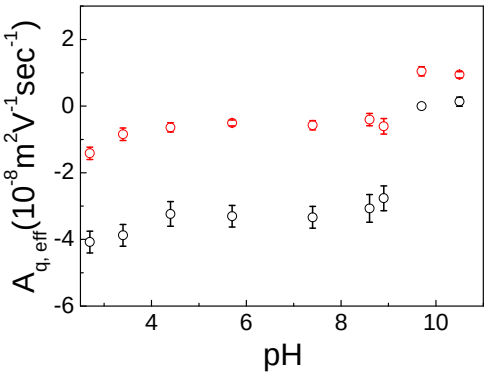

2
0
-2
-4
-6
4
6
8
10
pH
$A_{q,\,eff}(10^{-8}m^2V^{-1}sec^{-1})$

Fig. 4

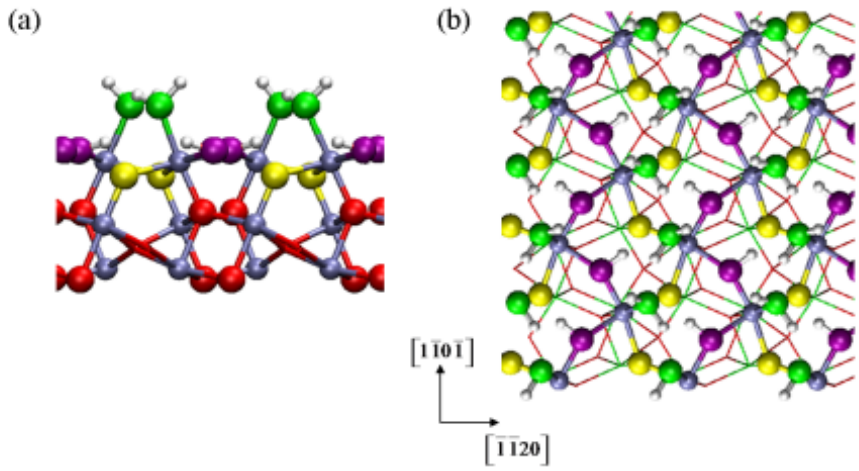
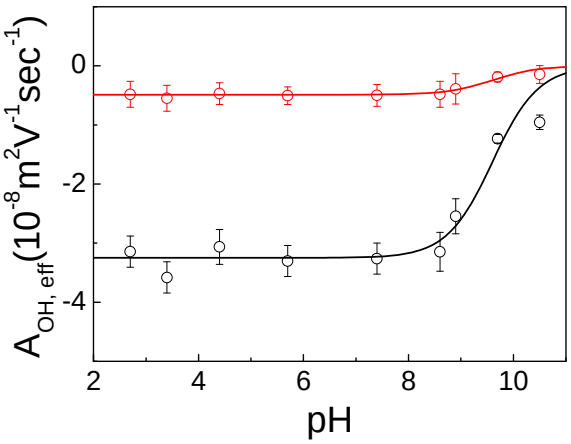


Fig. 5

(a)


0
-2
-4
2
4
6
8
10
pH
$A_{OH, eff}(10^{-8}m^2V^{-1}sec^{-1})$

(b)

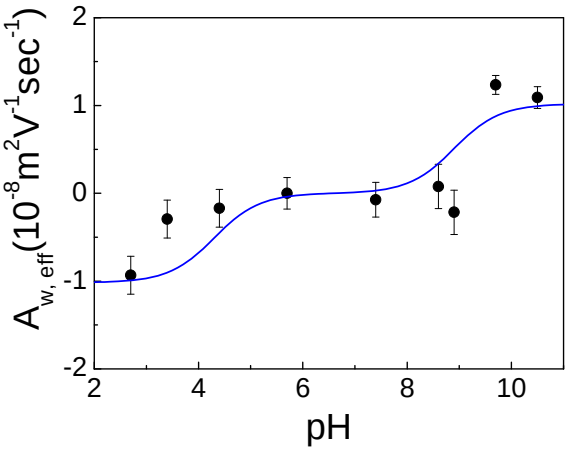

2
1
0
-1
-2
2
4
6
8
10
pH
$A_{w, eff}(10^{-8}m^2V^{-1}sec^{-1})$

Fig. 6

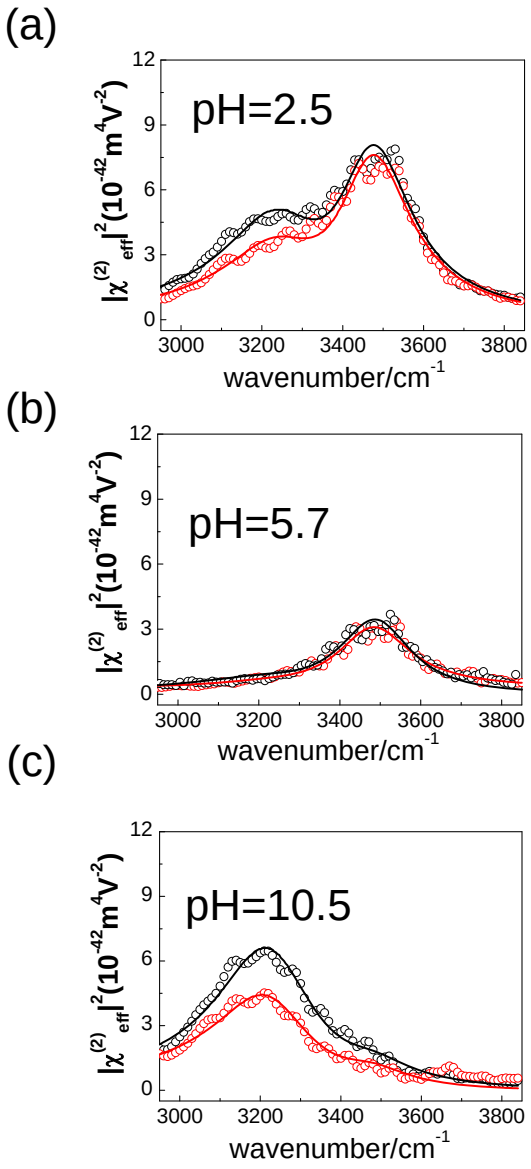

(a)
pH=2.5
(b)
pH=5.7
(c)
pH=10.5
$|\chi^{(2)}_{eff}|^2(10^{-42}m^4V^{-2})$
wavenumber/cm^{-1}
0
3
6
9
12
3000
3200
3400
3600
3800

Fig. 7

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