The Interfacial Structure of Water/Protonated α-Al_2O_3 (112□0) as a Function of pH

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Abstract

Sum Frequency Vibrational Spectroscopy (SFVS) was used to study the structure of the protonated α-Al_2O_3 (112□0), and water/ α-Al_2O_3 (112□0) interfaces as a function of pH. By combining SFVS spectra with an oxygen-terminated model suggested by X-ray reflectivity, we are able to understand several details of the protonated α-Al_2O_3 (112□0) interface structure. For example, the spectral changes observed for the water/ α-Al_2O_3 (112□0) interface with varying pH could be accounted for by the protonation/deprotonation of particular surface hydroxyls. Our spectra also indicate that the point of zero charge for this interface is at pH~6.7.

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Introduction

The surfaces and interfaces of metal oxides play an important role in many natural and technological processes such as mineral dissolution, adsorption/desorption reactions, soil and aquifer toxin and nutrient transfer, heterogeneous catalysis, corrosion/weathering, and electron transfer-mitigated microbial respiration.[1-9] The most important basic knowledge needed to understand these processes on the molecular level, and hence be able to write accurate stoichiometric reactions and consider reaction intermediates, is the interfacial structure and surface termination in contact with aqueous solution. Although there have been many studies of metal oxides at vacuum interfaces using electron, X-ray and optical probes, such methodology cannot be used to examine solid/water interfaces, especially over a range of conditions such as variable pH and solution ionic strength.

In contrast, surface x-ray scattering from solid/aqueous interfaces in the form of x-ray reflectivity and crystal truncation rod diffraction has been developed over the past decade and revealed rich details of the wet solid interface, including quantitative information on surface atom relaxations and occupations, and indirect evidence (e.g. by bond valence approaches) for assigning surface functional group protonation states.[10,11] However, there has been no complementary method sensitive to the details of surface protonation, the types of functional groups present, their protonation state and bond orientations, and the nature of near surface water organization with which to verify and build on the x-ray structural information. Sum frequency vibrational spectroscopy (SFVS) fulfills this need, and has been used to probe the interfacial structure at several metal oxide/aqueous interfaces.[12-15] SFVS is highly sensitive to the interface region, yet can function with bulk solution present, enabling extraction of detailed molecular structure under varying pH and solute conditions. In this paper, we report the protonated structure of the dry α-Al_2O_3 (112□0) surface, and the resulting interfacial structure changes when exposed to aqueous solution of varying pH using SFVS. α-Al_2O_3 (112□0) is one of the more stable faces on natural corundum crystals, and also is widely used as a substrate for thin film growth. However, there have been few studies of the surface structure compared to α-Al_2O_3 (0001) and α- Al_2O_3 $(1\bar{1}02)$, where detailed interface structure has been revealed by X-ray scattering [16, 17], and numerous other studies have been performed.

The α-Al_2O_3 (112□0) surface was recently studied using X-ray reflectivity.[18] For samples that have been previously annealed below 1373°C, the surface is found to have a stoichiometric bulk termination with some surface atomic relaxation. Compared to the bulk structure, this surface should be terminated by three different kinds of oxygen layers bonded to 3Als, 2Als, and Al with the ratio 1:1:1, respectively. However, once exposed to air, this surface will react with water molecules and the oxygens will be protonated. By probing the nature of this protonation, i.e. the identity and character of the surface hydroxyls, we should be able to confirm the model suggested by X-ray reflectivity. Further, we would like to understand the charging behavior of the interface, and the detailed changes in protonation as pH is varied in contact with bulk solution.

Previously, SFVS has been successfully applied to the investigation of the protonated surfaces of α-Al_2O_3 (0001) and α-Al_2O_3 $(1\bar{1}02)$.[15, 19] By comparison of the surface model suggested from X-ray scattering with the SFVS results, we were able to confirm the presence of protonated surface structures that were consistent with the x-ray models. These surfaces were terminated, respectively, by Al_2OH in the case of (α-Al_2O_3 (0001)), and by $AlOH_2$, Al_2OH, and Al_3O in the case of (α-Al_2O_3 $(1\bar{1}02)$). Based on this interpretation, the interfacial structural changes at the α-Al_2O_3 (0001)/water and α-Al_2O_3 $(1\bar{1}02)$/water interfaces due to varying pH could be explained by SFVS, and the point of zero charge (PZC) deduced.[15,20] In addition, the pK values of protonation/deprotonation reactions for specific surface hydroxyls could be obtained from analysis of specific SFVS band amplitude variations.

In this paper, we first present results for the protonated (dry) surface structure of α-Al_2O_3 (112□0), and then correlate this model with spectral changes observed for the solution interface as a function of pH. We expect, based on the bulk-terminated stoichiometric structure of α-Al_2O_3 (112□0), that only AlO and AlO_2 functional groups at the surface will be protonated in air, giving rise to $AlOH_2$ and Al_2OH functional groups, respectively. Our SFVS spectra show, for the dry α-Al_2O_3 (112□0) surface, only the presence of dangling OH, i.e. hydroxyls where the proton is not involved in a hydrogen bond, from the Al_2OH and $AlOH_2$ functional groups. Based on the bulk-terminated surface structure, the hydroxyl of the Al_2OH functional group cannot form a hydrogen bond (H-bond) with nearby oxygens, resulting in a dangling OH. In the case of the $AlOH_2$ functional group, one of the two hydroxyls can form a H-bond with a nearby singly Al coordinated oxygen, but the other would be a dangling OH. However, the H-bonded OH of the $AlOH_2$ would point in the opposite direction compared to a neighboring analogously H-bonded OH because of the surface symmetry, and hence the SFVS signal from this hydroxyl would vanish. Our SFVS spectra on the dry protonated α-Al_2O_3 (112□0) is therefore in accordance with this suggested protonation model for the stoichiometric surface termination. For the α-Al_2O_3 (112□0)/water interface, we observed the persistence of the dangling OH in the experimental pH range from 2 to 11, indicating that it does not form a H-bond with water molecules in this pH range. This is consistent with what was observed for the dangling OH of Al_2OH on α-Al_2O_3 (0001).[15] We also observed significant spectral amplitude changes for the OH stretch modes of

interfacial water molecules in the spectral range of 3000 to 3550 cm^{-1} at pH~4.7 and 9.5, signifying an appreciable change in surface charge at the interface that effects water molecule orientations. This can be explained by the deprotonation process of the Al_3OH and $AlOH_2$ functional groups, which induces a rather abrupt change of surface charge at pH~4.7 and 10, respectively.

The surface charge change with increasing pH from positive to negative due to deprotonation is expected to directly induce corresponding net polar orientations of interfacial water molecules, with oxygen and hydrogen terminal atoms facing the interface, respectively. Indeed, this effect was observed in our phase-sensitive SFVS measurement with weakest water amplitude (i.e. lowest surface charge) around pH~6.7, which we interpret as the PZC of the α-Al_2O_3 (112□0) /water interface. This value is in agreement with the value calculated based on the protonation/deprotonation reactions of the surface hydroxyls we detected.

Theoretical background

The basic theory of SFVS for surface studies has been described elsewhere.[21-24] Here, we present only the key points needed for following our data analysis. The sum frequency signal generated by overlapping incoming beams of frequencies ω_{vis} and ω_{ir} at a surface in the reflected direction is given by

$$I(\omega) = \frac{8\pi\omega^2 \sec^2\beta}{c^3} |\chi_{eff}^{(2)}|^2 I_1(\omega_{vis}) I_2(\omega_{IR}) \qquad (1)$$

where I_i is the light intensity at frequency ω_i and β is the reflection angle of the sum frequency output. The effective surface nonlinear susceptibility has the expression,

$$\vec{\chi}_{eff}^{(2)} = [\hat{e}(\omega_{SF}) \cdot \vec{L}(\omega_{SF})] : \vec{\chi} \cdot [\hat{e}(\omega_{vis}) \cdot \vec{L}(\omega_{vis})][\hat{e}(\omega_{IR}) \cdot \vec{L}(\omega_{IR})] \qquad (2)$$

with $\hat{e}(\omega_i)$ being the unit polarization vector and $\vec{L}(\omega_i)$ the transmission Fresnel factor of light of frequency ω_i at the interface. The surface nonlinear susceptibility $\vec{\chi}^{(2)}$ can be approximated by

$$\vec{\chi}^{(2)} = \vec{\chi}_{NR}^{(2)} + \sum \frac{\vec{A}_q}{(\omega_{IR} - \omega_q) + i\Gamma_q} \qquad (3)$$

with the nonresonant contribution denoted by $\vec{\chi}_{NR}^{(2)}$, and the resonant contribution assumed to be capable of

being approximated by discrete vibrational resonances with resonant frequencies ω_q and damping constants Γ_q. The resonance amplitude $\overleftrightarrow{A}_q$ is defined as

$$\overleftrightarrow{A}_q = \int \overleftrightarrow{a}_q(\Omega) f(\Omega) d\Omega \equiv N_q < \overleftrightarrow{a}_q(\Omega) > \qquad (4)$$

where $\overleftrightarrow{a}_q(\Omega)$ is the resonant amplitude of the qth mode from an individual molecule, and N_q and $f(\Omega)$ are the surface density and the orientation distribution function of the molecules contributing to the qth mode. The tensor elements of $\overleftrightarrow{A}_q$ in the lab coordinates (i,j,k) are related to those of $\overleftrightarrow{a}_q$ in the molecular coordinates (ξ,η,ζ) by

$$A_{q,ijk} = N_q \sum_{\xi,\eta,\zeta} < (\hat{i}\cdot\hat{\xi})(\hat{j}\cdot\hat{\eta})(\hat{k}\cdot\hat{\zeta}) > a_{q,\xi\eta\zeta} \qquad (5)$$

Here $a_{q,\xi\eta\zeta}$ is related to the infrared and Raman characteristics of a vibrational mode through the equation [25]

$$a_{q,\xi\eta\zeta} = -\frac{1}{2\varepsilon_0\omega_q}\frac{\partial\mu_\zeta}{\partial Q_q}\frac{\partial\alpha_{\xi\eta}}{\partial Q_q} \qquad (6)$$

where $\partial\mu_\zeta / \partial Q_q$ and $\partial\alpha_{\xi\eta} / \partial Q_q$ are the infrared dipole derivative and the Raman polarizabilty tensor, respectively, of the qth vibrational mode, and Q_q is the classical normal coordinate.

It is possible to determine the parameters characterizing the resonances by fitting the measured $|\chi^{(2)}_{eff}|^2$ spectrum with proper input/output polarization combinations using Eqs. (1-3). However, the fitting may not be unique unless the resonant frequencies and the signs of $\overleftrightarrow{A}_q$ are pre-chosen. The latter often requires a phase measurement of the sum frequency output such that the Im $\chi^{(2)}$ spectrum can be obtained to directly characterize the resonances. For discrete resonances, Im $\chi^{(2)}$ has the expression

$$\mathrm{Im}\,\overleftrightarrow{\chi}^{(2)} = \sum_q \frac{\overleftrightarrow{A}_q \Gamma_q}{(\omega_{IR} - \omega_q)^2 + \Gamma_q^2} \qquad (7)$$

Experimental

We measured the SFVS of the air/α-Al_2O_3 (112□0) interface in the OH stretch region. Our SFVS setup has been described elsewhere.[26-28] Briefly, we used two overlapped input beams, one fixed at visible wavelength 532 nm and the other tunable in the infrared between 2.6 and 3.7μm, with typical energies of ~500 μJ/pulse and ~100 μJ/pulse, respectively, in a spot of 180x300 μm^2 on the sample surface. The pulses had a width of ~20 ps and were incident on the sample at angles of $\beta_{vis}=45^o$ and $\beta_{IR}=57^o$ from the air side. We detected the sum frequency signal in the reflection direction, which was spatially and spectrally filtered and then collected by a gated detector system. Each data point was obtained from averaging over 200 laser shots, and was normalized against that from a z-cut quartz plate. For the α-Al_2O_3 (112□0)/water interface, we followed the experimental arrangement in the description of Ref. [20] in order to avoid the polarization change of light after passing through the crystal. We also carried out phase measurements of the SFVS signal using the interference scheme described in Ref. [27, 28].

The sample used was an epi-polished single crystal of α-Al_2O_3 (112□0) purchased from Princeton Scientific Corporation. The sample was 5 mm thick, and the root-mean-square roughness was less than 0.2 nm on the polished surfaces. Sample preparation followed the recipe of Ref. [17, 19, 20]. The sample surface was first cleaned in a sonication bath using 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 sonication for 30min, rinsed thoroughly with deionized water, and blow-dried by filtered nitrogen gas. To remove the remaining water and any organic contaminates on the surface, the sample was heated at ~350°C for 1 hour. After cooling down to room temperature in a nitrogen atmosphere, the sample was mounted in a sealed Teflon cell for measurement.

Results and Discussion

Protonated α-Al_2O_3 (112□0): The SFVS spectra in the OH region with different polarization

combinations, SSP (denoting S, S, and P polarized SF, visible, IR lights, respectively), SPS, SSS on α-Al_2O_3 (112□0) are shown in Fig 1. We could only observe one well-defined peak at ~3670cm^{-1} with a ~70cm^{-1} broad line-width. Through phase measurements it was revealed that the sign of this feature is positive, implying that the O→H points away from the interface. To find the origin of the SFVS signal, we first need to consider the surface model of α-Al_2O_3 (112□0), namely the bulk-terminated stoichiometric structure suggested by X-ray reflectivity measurements. [18] This surface is terminated by oxygens with three different Al coordination numbers, AlO, Al_2O, and Al_3O in the ratio 1:1:1 as shown in Fig. 2. These oxygens will be protonated by the reaction with water molecules from the air, even in the absence of bulk water. The most important factor determining protonation is the bonding satisfaction of the oxygens, which we can estimate from the bond valence of the oxygens. The bond valence can be determined from the bond length between cation and oxygen, and is a sum considering all cations around a given oxygen. [29, 30] Hence, by using the positions of atoms defined by the X-ray reflectivity measurements, we can estimate the bond valences of oxygens with different Al coordination numbers. The bond valence of the oxygen at the topmost layer, which is bonded to a single Al, is estimated to be 0.46. Since the total bond valence of oxygen is ideally 2, this oxygen is considerably under bonded. If this oxygen were protonated and the proton made a H-bond to a nearby oxygen, the bond valence of this bond would on average contribute 0.8, to the total bond valence, and thus two protons forming two hydrogen bonds could produce a net bond valence of about 2.06. This suggests that we can expect to see $AlOH_2$ on the dry protonated α-Al_2O_3 (112□0) surface. For the next lower oxygen, bonded to two Als, there are two kinds having different Al-O bond lengths. One of these has two Al-O bonds whose projections on the surface plane are aligned parallel with [0001]. The calculated bond valence of this oxygen is 0.99, which indicates that only one proton should bind to it. The other oxygen has two Al-O bonds whose projection into the surface plane lie at 45° with respect to [0001], and has a bond valence of 0.92, also suggesting that only one proton would be allowed. Finally, the lowest oxygen is bound to 3Als, and has a 1.47 bond valence, which is too large for protonation to occur, except possibly under very acidic conditions. However, this oxygen could form a weaker "acceptor" hydrogen bond by weak interactions from other hydroxyl or water protons if these are geometrically available.

The next step in understanding the SFVS spectra is to determine the resonance energy of the stretch vibrations for the hydroxyls in the Al_2OH and $AlOH_2$ functional groups and their orientations. We assume that oxygen forms a tetrahedral bond structure in which the angle between bonds is near 109°. The two hydroxyls of the $AlOH_2$ functional group are considered in different ways. One of them forms a H-bond with a nearby oxygen coordinated to one Al whose vibrational resonance energy must therefore shift to lower energy from that characteristic for a dangling OH, typically ~3670cm^{-1}. These H-bonded OHs lie nearly in the surface plane, and because the transition dipole moments of neighboring H-bonded OH are oriented opposite to each other in the plane, they should cancel each other as shown in Fig. 3, resulting in a negligible SFVS signal. Therefore, only the dangling OH of the $AlOH_2$ functional group should contribute to the SFVS signal. Detailed structural analysis yields polar coordinates of (θ~61°, ϕ~$\pm 90^o$) for this dangling OH based on the tetrahedral bond structure of oxygen, where θ and ϕ are defined as the angles with the surface normal and with the [0001] direction, respectively. Since the OH of the Al_2OH functional group cannot form a H-bond with a nearby oxygen in the surface, it must also act as a dangling OH, and contribute an SFVS signal at ~3670cm^{-1}. However, there are two kinds of Al_2OH with different hydroxyl orientations. The hydroxyl of one Al_2OH group, of which the surface projections of the two bonds between Al and O are parallel to the [0001] direction, aligns with surface projection perpendicular to the [0001] direction, and orients at (θ~54°, ϕ~$+90^o$) or (θ~54°, ϕ~-90°). This hydroxyl thus has a similar orientation to the dangling OH from the $AlOH_2$ functional group, and hence would contribute nearly in the same way to the SFVS spectra, but with a slightly higher frequency. The other Al_2OH hydroxyl surface projection aligns at a ~45° direction with respect to [0001], in which case the hydroxyl orients at (θ~54°, ϕ~37° or ϕ~-143°). However, the fraction of this hydroxyl is 1/3 with respect to the other hydroxyl. Hence the overall SFVS spectrum is expected to be dominated by the other dangling OH groups azimuthally oriented at ϕ~$\pm 90^o$.

To confirm this argument, knowledge of the orientation of the hydroxyls is crucial. The strong signal in the SSP spectra, compared to those at the other polarization combinations in Fig. 1, indicates that the hydroxyl bond orientation tilts toward the surface normal. Using phase measurements it was revealed further that these hydroxyls have their protons pointed away from the Al_2O_3 surface. The SFVS spectra intensity depends on

the angle γ between the incidence plane and the surface plane as shown in Figs.1 and 4. The stronger spectral contribution, with almost the same signal strength at γ~0 and 180° compared to that at γ~90°, indicates that the hydroxyls have an azimuthal orientation distribution peaked near ϕ~±90°. This is because the hydroxyls oriented more toward ϕ~90° interact more strongly with the p-polarized IR input field for γ~0 and 180° than γ~90°, resulting in the strongest signal at γ~0 and 180° and weakest signal at γ~90° as shown in Fig. 4.

Quantitative analysis of the SFVS spectra yields information on the orientation of the surface hydroxyls. As we mentioned earlier, fitting the SF spectra with Eqs. (1)-(3) allows us to determine $(A_q)(\hat{e}_{SF}, \hat{e}_{vis}, \hat{e}_{ir}; \gamma)$, with $\hat{e}_i$ denoting the polarization of the ω_i wave. Equation (5) can then be used to find the orientations of the OH specified by the polar angle θ_0 with respect to the surface normal and the azimuthal angle ϕ_0 with respect to the forward direction along $(1\bar{1}00)$ (See Fig. 4), assuming the orientational distribution function in Eq.(4) is a δ-function in θ and ϕ. By doing this analysis, we find that the hydroxyl contributing to the observed band is oriented at (θ~32°±5°) and (ϕ~±86°±7°). This value is in reasonably agreement with the predicted orientations of the dangling OH hydroxyls, (θ~61°, ϕ~±90°) and (θ~54°, ϕ~±90°) based on the simple tetrahedral oxygen bonding model, indicating that the contribution from the H-bonded hydroxyl in one type of the Al_2OH groups predicted at (θ~54°, ϕ~-45° or ϕ~135°) is indeed small.

α-Al_2O_3 (112□0) /water:

Figure 5 displays spectral change at three different pH values, ~2.8, 5.7, and 11 at γ=0°. (The spectra at γ=180° (not shown) are the same as those at γ=0°.) The spectra can be fitted by using three bands at 3180, 3450, and 3670 cm^{-1}. We observed significant signals from these three bands at pH~2.8 and 11, but the signals at 3180 and 3450cm^{-1} become almost negligible at pH~5.7. The signal at 3670cm^{-1} can be assigned to the dangling hydroxyl of the Al_2OH group. According to previous studies, this type of functional group hydroxyl does not form a H-bond with water molecules. [15] However, the dangling hydroxyl of the $AlOH_2$ functional group can form a H-bond with water molecules, and may contribute to the signal in the H-bonded regions of 3000 to 3550cm^{-1}. The main contribution to the 3180 and 3450 cm^{-1} band is believed to come

from water molecules at the interface as has been observed in previous studies.[20]

The surface population of different hydroxyls can be altered through protonation/deprotonation reactions as a function of pH, which influences the net surface charge. The surface charges create an electric double layer (EDL) with the counter ions in water near the interface. The orientation of water molecules in the EDL is sensitive to the electric field in the EDL, and so any change of the surface charge density can trigger a significant SFVS change in the water spectral bands. Therefore, to understand variations in the SFVS spectra at different pH values, relating the change of surface charge due to protonation/deprotonation reactions with pH is crucial. Since three kinds of oxide groups, AlO, Al_2O, and Al_3O, are predicted on the surface, the following protonation/deprotonation processes are expected at the water/corundum interface over the experimental pH range from pH~2 to ~11. [31-33]

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

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

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

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

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

At low pH, Al_3OH, Al_2OH, and $AlOH_2$ can all exist on the surface, which implies that the surface would have a strong positive charge. Oxygens in water molecules should tend to point toward the Al_2O_3 surface due to the electric field, and hydrogen into the bulk overlying solution. Also, hydrogens (except for those associated with the Al_2OH functional group that retains a dangling OH in past observations) in surface hydroxyls would be expected to make H-bonds with oxygens in nearby water molecules, further promoting oxygen in water molecules of the first water layer in the interfacial region to point toward the interface. On the other hand, if the surface is negatively charged by the presence of only AlOH, Al_3O, and Al_2OH functional groups at high

pH due to deprotonation, the hydrogen in the interfacial water molecules should be reoriented by the surface field to point toward the interface. Also, with deprotonation, the surface oxygens prefer to form a H-bond with the proton of a nearby water molecule, further promoting hydrogen of the first-layer water molecules to point toward the interface. Therefore, a significant surface charge is expected to exist on the Al_2O_3 surface at sufficiently low and high pH, and water molecules at the interface would orient oppositely following with direction of surface electric field, generating a strong SFVS signal due to the water reorientation. This can explain the strong signal from the H-bonded OH of water corresponding to the ~3180 and 3450cm^{-1} bands and the difference in their signs at pH~2.5 and 11 in Fig. 5.[34] The surface charge would be near zero at some intermediate pH, and at that point the dipole moments of water molecules at the interface will be randomly oriented. This leads to a weak signal in the H-bonded region of the spectra at pH~5.7 of Fig. 5, assuming that as in the case of the dry surface, the signal from hydroxyls on the neutral surface is also very weak. Finally, the reaction ($Al_2OH \leftrightarrow Al_2O^{-1.0} + H^+$ with pK~12.9), suggests that the dangling OH of Al_2OH exists throughout the experimental pH range, indicating that the signal at ~3670cm^{-1} should be detected regardless of pH in our measurements, as shown in Fig. 6.

Information on the absolute polar orientations of water molecules at the interface as pH is varied is crucial to confirm our arguments. Figure 6 displays the peak strengths of ~3180 and ~3450cm^{-1} bands at different pH, where the positive sign means that O→H points toward the liquid. The signs of both ~3180 and ~3450cm^{-1} bands change from positive to negative as pH is increased, as is our expectation. In theory, only the two protonation/deprotonation processes, ($Al_3OH^{+0.5} \leftrightarrow Al_3O^{-0.5} + H^+$) and ($AlOH_2^{+0.5} \leftrightarrow AlOH^{-0.5} + H^+$), are related to the change of surface charge over the range from pH~2 to ~11, and the pK values for these reactions should be related to the strength of the water bands in the SFVS spectra. Since the sign of the surface charge associated with a selected surface functional group is changed when the pH varies across a corresponding pK, this is expected to give rise to a rapid change in the observed water peak strengths. Hence, we conclude that the rapid variation of peak strengths of the ~3180 and ~3450cm^{-1} bands near pH~4.7 and 9.5 can be accounted for by the protonation/deprotonation reactions ($Al_3OH^{+0.5} \leftrightarrow Al_3O^{-0.5} + H^+$) and ($AlOH_2^{+0.5} \leftrightarrow AlOH^{-0.5} + H^+$), respectively. In this consideration, we can also predict the point of zero charge

(PZC), which will be the pH where the surface charge is zero. If it happens that the surface water molecule dipoles are nearly randomised at the PZC, then the strength of the water bands also would be close to zero. More generally, with the surface governed by the above two protonation and deprotonation processes, the curve of surface charge density versus pH will have a two-step shape (Fig. 6) and the PZC is expected to be in the mid pH range on the flat portion of the curve. In our case, the observed water band strengths versus pH are plotted in Fig. 6, and the PZC is estimated to be pH~7. If we use the protonation/deprotonation reactions listed above to calculate the surface charge density and assume the observed strengths of the water bands are directly proportional to the surface charge density, we obtain the solid curves in Fig. 6, and fitting yields a PZC of pH~6.7. However, in the above discussion, we neglected the contribution from the H-bonded OH of $AlOH_2$ in the same spectral region. It is seen in Fig. 6 that the strength variation of the ~3450cm^{-1} band as a function of pH does not follow the surface charge variation on α-Al_2O_3 (112□0) well at higher pH. This could be due to contribution from the OH of $AlOH_2$ that is not proportional to the surface charge density. It is also possible that contributions from the reorientation of water molecules that tend to H-bond to the functional groups are not simply proportional to the surface charge density. The 3180cm^{-1} band comes mainly from the second layer of water molecules at the interface, and therefore is less influenced by the H-bonding of water molecules at the surface.

Ions having sign opposite to the surface charge can screen the electric field due to the surface charge, and so the orientation of water molecules can be affected by the amount of counter ions at the interface. This indicates that we can strengthen our argument on surface charge variation with pH by observing the change in the SFVS spectra when salt is added at different pH values. Fig. 7 shows the spectral change after and before adding 50mM NaCl at three different pH values ~2.5, 5.7, and 11. We observed a notable signal decrease of the two water bands at pH ~2.5 and 11 after adding salt, which indicates that the degree of water reorientation by surface field is reduced. The spectra change at pH~5.7 is minimal, which suggests that this pH is close to the PZC, in agreement with the result of Fig. 6.

Conclusions

SFVS has been successfully applied to the determination of hydroxyl speciation and water structure at the protonated (dry) α-Al_2O_3 (112□0) surface and at the corresponding wet surface. The SFVS spectra at the protonated α-Al_2O_3 (112□0) surface could be explained by the presence of $AlOH_2$ and Al_2OH surface functional groups consistent with the X-ray reflectivity bulk termination model, in which the surface is terminated by three different oxygen layers bonded to 3Als, 2Als, and Al with ratio 1:1:1, respectively. The existence of Al_3O on the surface was confirmed by the rapid spectral amplitude changes for the α-Al_2O_3 (112□0)/water interface at pH~4.7, which could be accounted for by the protonation/deprotonation process, $Al_3OH^{+0.5} \leftrightarrow Al_3O^{-0.5} + H^+$. We also observed a rapid spectral change of the α−Al_2O_3 (112□0)/water interface at pH~9.5, resulting from the process $AlOH_2^{+0.5} \leftrightarrow AlOH^{-0.5} + H^+$ Further, the sign change of Im $\chi^{(2)}_{SSP}$ spectra of the ~3180 and ~3450cm^{-1} bands extracted by phase measurements indicated that the PZC for the interface is about 6.7, which is in reasonable agreement with the value calculated directly from known literature pK values for the above-mentioned protonation/deprotonation reactions.

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(34) The surface and bulk pHs are generally different in the presence of the electric double layer. In our case, however, the difference is small because the surface charge density is not very high.

Figure captions

Figure 1. SFVS spectra for the dry corundum (112□0) surface with (a) SSP, (b) SPS, and (c) SSS polarization states at different γ=0, 90, and 180°, where the red line represents the fit using Eq. (3) in the text.

Figure 2. Surface structure of Al_2O_3 (112□0), where red and blue spheres represent oxygen and aluminum atoms, respectively.

Figure 3. Proposed protonated surface of Al_2O_3 (112□0), where white circles represent hydrogen atoms.

Figure. 4 Resonant amplitude versus azimuthal orientation of the sample for the hydroxyl band at 3670 cm^{-1} in SSP spectra, where the red line represents the fit using Eq. (4) on each of the spectra.

Figure 5. SFVS spectra of (a) $|\chi^{(2)}_{SSP}|^2$ and (b) Im $\chi^{(2)}_{SSP}$ of Al_2O_3(112□0) /water interfaces with the SSP polarization combination at three different pH values: 2.8 (top), 5.7 (middle), and 11 (bottom), where the line represents the fit using Eqs. (3) and (6).

Figure 6. SFVS resonant amplitudes of OH stretch bands at (a) 3670cm^{-1}, (b) 3450cm^{-1}, and (c) 3180cm^{-1} versus pH, where the red lines in (b) and (c) represent surface charge density as a function of pH calculated from the known pKa values of the protonation and deprotonation processes and the net protonation of the surface.

Figure 7. SSP spectra of Al_2O_3 (112□0) /water interfaces at γ=0° for three different pH values, 2.5, 5.7, and 11, (a), (b) and (c), respectively. Red circles indicate addition of 50 mM NaCl solution, and the lines represent fits to the bands using Eq. (4).

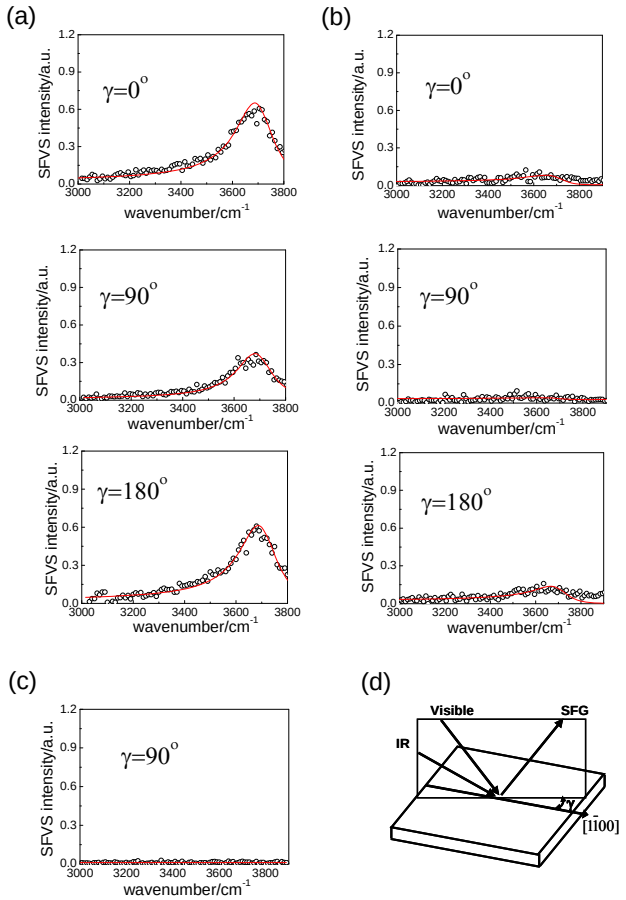
(a)
(b)
(c)
(d)
γ=0°
γ=90°
γ=180°
SFVS intensity/a.u.
wavenumber/cm-1
Visible
SFG
IR
γ
[1̄100]

Figure 1.

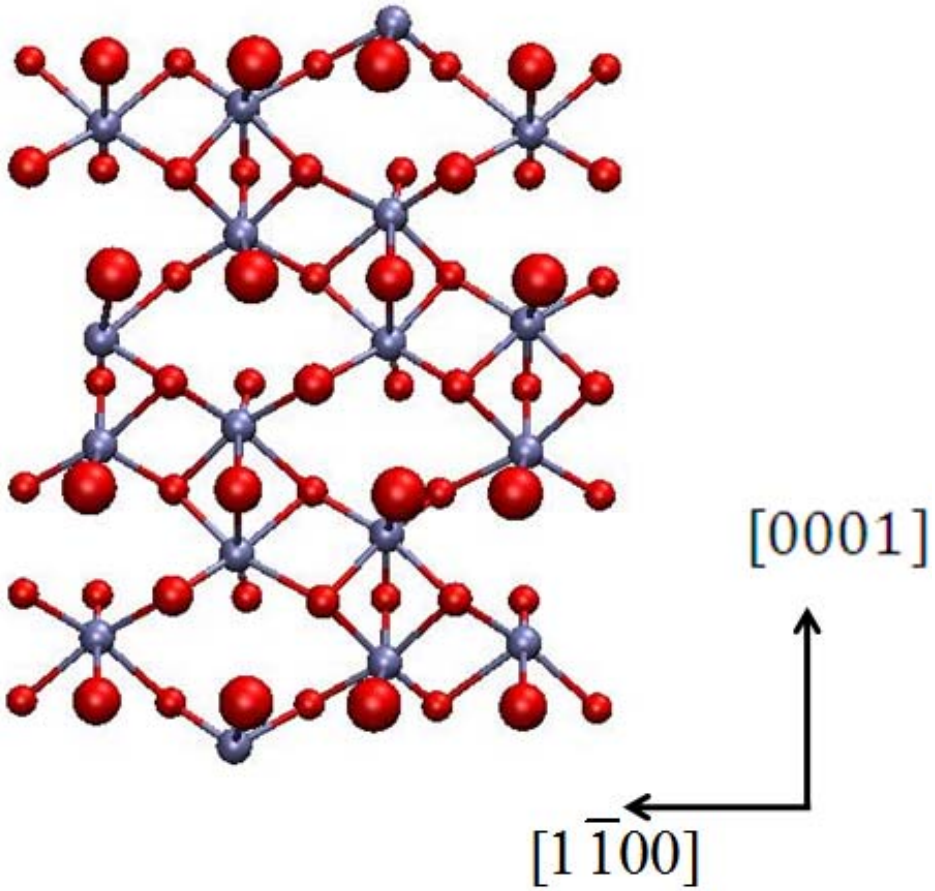

Figure 2.

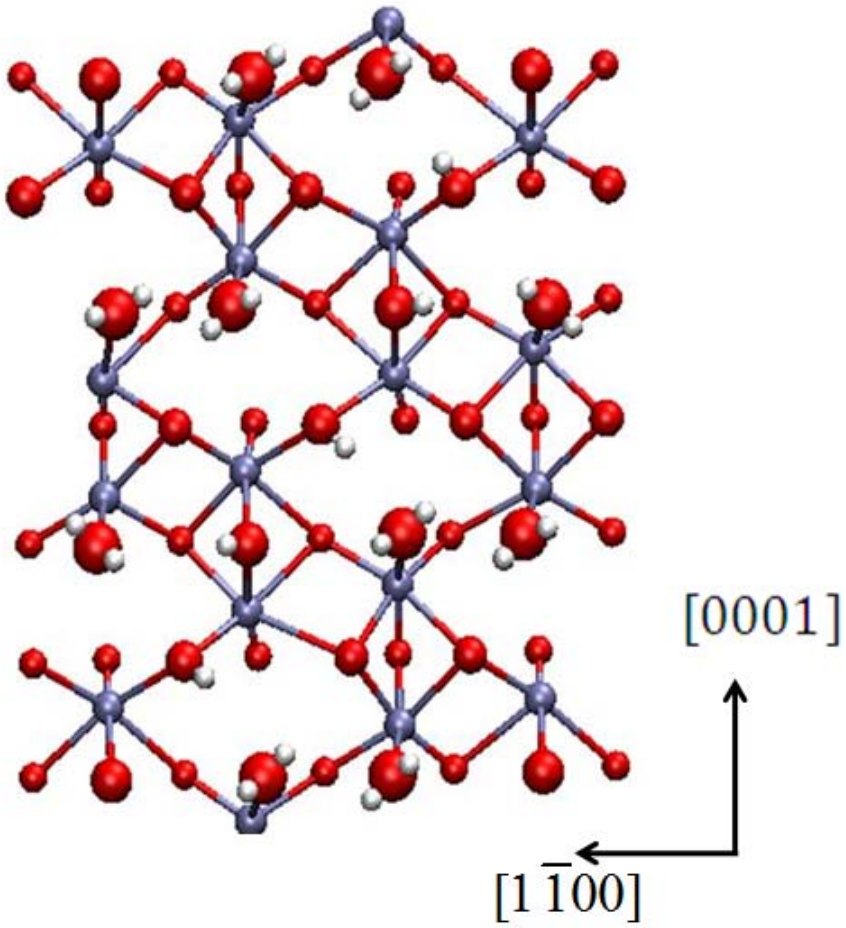

Figure 3.

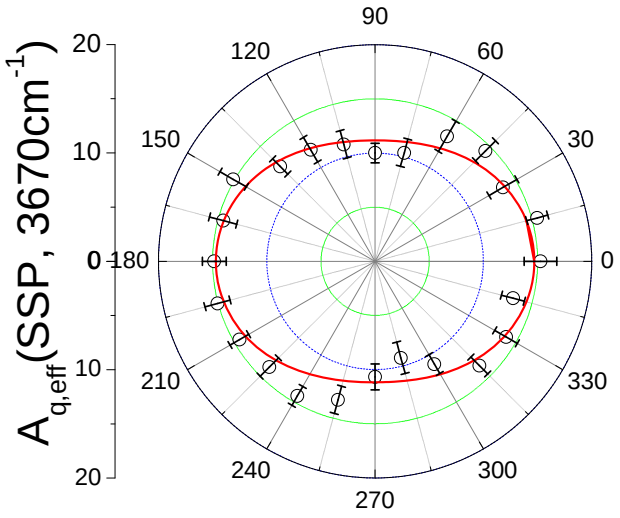
$A_{q,eff}$(SSP, 3670cm^{-1})
20
10
0
10
20
90
120
60
150
30
180
0
210
330
240
300
270

Figure. 4

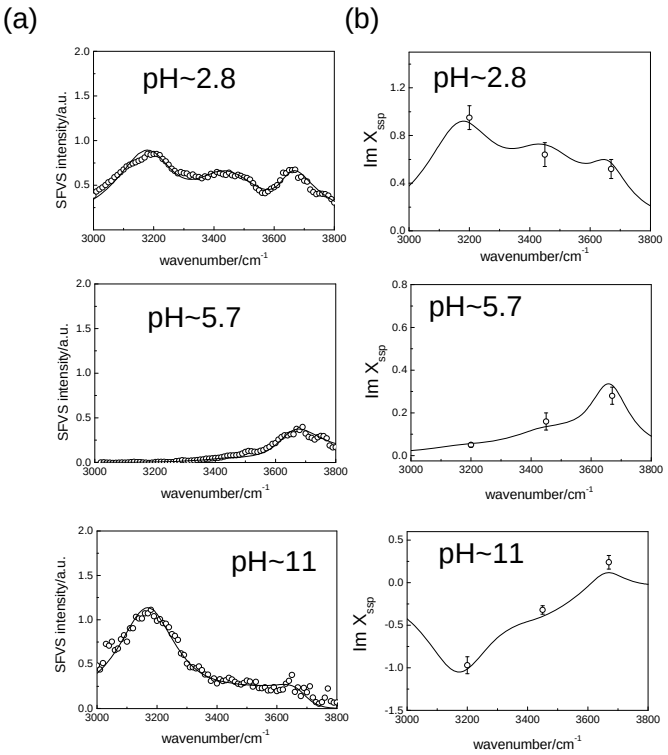

Figure 5.

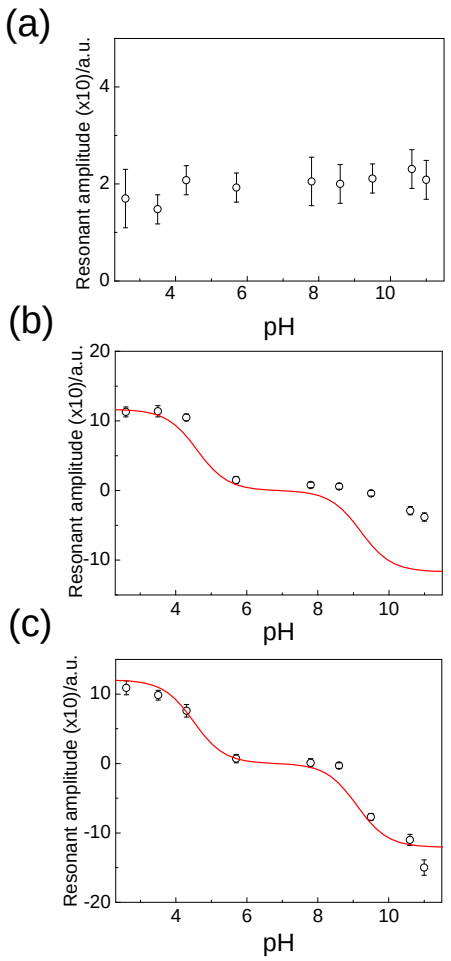
(a)
Resonant amplitude (x10)/a.u.
0
2
4
4
6
8
10
pH
(b)
Resonant amplitude (x10)/a.u.
20
10
0
-10
4
6
8
10
pH
(c)
Resonant amplitude (x10)/a.u.
10
0
-10
-20
4
6
8
10
pH

Figure 6.

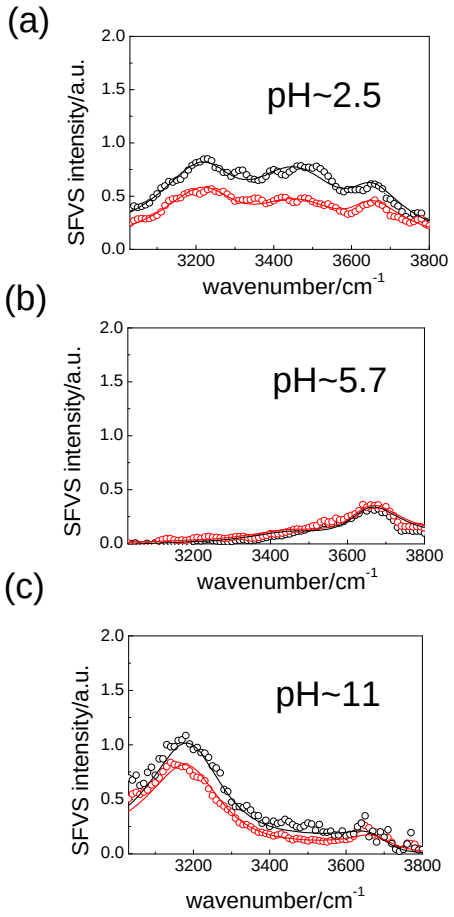
(a)
pH~2.5
SFVS intensity/a.u.
wavenumber/cm-1
(b)
pH~5.7
SFVS intensity/a.u.
wavenumber/cm-1
(c)
pH~11
SFVS intensity/a.u.
wavenumber/cm-1

Figure 7.

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