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Molecular Structure of a Mineral/Water Interface: Effects of Surface NanoRoughness of α -Al₂O₃ (0001)

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Surface disorder on a nanometer scale is shown to have fundamental influence on the molecular structure of α -Al₂O₃(0001)/water interfaces which have been studied by sum-frequency vibrational spectroscopy. On rough surfaces, we observe isolated surface hydroxyl groups which do not couple to the network of hydrogen-bonded water molecules of the interface and which we assign to aluminol groups in hydrophobic nanopores of the surface. The pH dependence of O–H stretching vibrations of water molecules at the rough interface is distinctly different from that of an atomically smooth interface and points to different pK values for deprotonation of surface hydroxyl groups at defect sites and regular terrace sites.

1. Introduction

The interaction of water with the surface of a mineral is of fundamental importance for the stability and reactivity of the mineral in aqueous environments. α -Al₂O₃ (corundum) is a particularly interesting material with respect to surface water interaction. Al₂O₃ and its hydroxides are common minerals on earth, and water adsorption on their surfaces is relevant to geochemical processes.¹ Owing to its unique properties such as mechanical hardness and chemical stability in acidic or basic aqueous solutions, α -Al₂O₃ is widely used as a material for optics and ceramics, as catalyst and support for catalysts,^{2,3} as substrate for semiconductor systems and as material for moisture sensors.^{4,5} The structure of hydrated α -Al₂O₃(0001) surfaces has been the subject of experimental⁶ and theoretical^{7–9} research, as it is expected to have significant influence on the reactivity of the hydrated surface. Although conclusions on the atomic termination of the hydrated surface are partly at variance, there is agreement that the interaction of water molecules with the clean surface causes dissociation and formation of a hydroxyl-terminated surface.^{6,8}

Previous research on the molecular structure of hydrated single-crystal α -Al₂O₃ surfaces has mainly concentrated on studies performed under ultrahigh vacuum conditions¹⁰ or under humid environmental conditions where a molecularly thin film of water is adsorbed at the surface.⁶ For α -Al₂O₃ surfaces in contact with aqueous solutions the pH value of the solution is a crucial parameter that has a strong influence on the molecular structure of the aqueous interface. It is generally assumed that terminating hydroxyl groups which are present at surfaces of oxidic minerals with a high density (>10 OH groups per nm²)⁸ can be protonated or deprotonated in aqueous solutions^{11–14} and that the surface becomes positively or negatively charged, depending on the pH value. The pH value for which the surface has no net charge is called the isoelectric point of the surface

(IEPS) or point of zero charge. pH values between 8 and 10^{11,14,15} but also between 4 and 5^{12,13,16} have been reported for the IEPS of single-crystal and powdered α -Al₂O₃ samples.

Optical sum-frequency generation (SFG) has been applied as a spectroscopy of water vibrations at interfaces between oxide minerals and aqueous solutions with high sensitivity to ordering of water molecules at the interface.^{15,17,18,19,20} Previous studies of SiO₂ in contact with aqueous solutions revealed two different, strongly hydrogen-bonded interfacial H₂O species with OH stretching frequencies at about 3200 and 3450 cm^{–1}.^{17,18,19,21} The increase of the intensity of the former band, previously referred to as ‘ice-like’ water, for increasing pH values has been ascribed to the ordering influence of an interfacial electric field originating from the negative surface charge of deprotonated hydroxyl surface groups.^{17–19} The importance of structural properties of the surface, characterized and quantified by scanning probe techniques, on molecular properties of the interface have not been addressed so far, however. In a previous SFG study of Al₂O₃ in aqueous solutions the pH dependence of the water vibrational resonances was related to the IEPS of the surface;¹⁵ however, the crystallographic orientation of the surface was not specified and surface structure was not characterized.

In this letter we demonstrate for the first time the importance of surface disorder for the molecular structure of oxide-water interfaces by applying SFG spectroscopy to structurally characterized α -Al₂O₃(0001) surfaces. We show that disordered surfaces with nanometer roughness form oxide/water interfaces which are distinctly different from atomically smooth surfaces with respect to the organization of the interfacial water layer.

2. Experimental Methods

Our SFG experiments were performed with tunable infrared pulses from a Nd:YAG laser-pumped optical-parametric amplifier system at a repetition rate of 500 Hz and with a pulse duration of ~25 ps. The pulses were tunable from 1300 to 4000

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cm^{-1} with a pulse energy of $100 \mu\text{J}$ at 3100 cm^{-1} and a bandwidth better than 8 cm^{-1} . The sum-frequency photons were generated in reflection with collinearly impinging 532 nm pulses of $230 \mu\text{J}$ pulse energy and of comparable pulse duration at an angle of incidence of 60° . The polarizations of the sum-frequency photons, of the 532 nm pulses and of the infrared pulses were s, s, and p, respectively. AFM images of $\alpha\text{-Al}_2\text{O}_3$ -(0001) single-crystal surfaces were obtained in ambient air with a Digital Instruments Nanoscope III A system operated in the intermittent contact mode.

We used polished $\alpha\text{-Al}_2\text{O}_3$ -(0001) single-crystal discs (Korth Crystals, Germany) of 0.5 mm thickness and 30 mm diameter. The samples were studied either as received from the manufacturer without any temperature treatment or after annealing for 7 h at 1400 K in air, respectively. The annealed crystals were cleaned for 20 min at 80°C in a 3:1 solution of HCl and HNO_3 . Prior to each experiment both types of samples were cleaned in a 3:1 solution of H_2SO_4 and H_2O_2 for at least 12 h to remove organic contaminations. After cleaning the crystals were rinsed and boiled several times in ultrapure water (specific resistivity $> 18 \text{ M}\Omega \text{ cm}$, total organic contamination $\leq 4 \text{ ppb}$) obtained from a water purification system (Milli Q Gradient A10). The pH values of the aqueous solutions were adjusted with NaOH or HCl (Merck, Suprapur grade) and ultrapure water.

3. Results and Discussion

In Figure 1 we present AFM images of the (0001) surface of unannealed and annealed $\alpha\text{-Al}_2\text{O}_3$. For the unannealed sample the AFM topograph reveals a highly disordered surface with long scratches, indicating a substantial amorphization of a surface layer by the mechanical polishing process (Figure 1a). The surface area imaged in Figure 1 (a) has a roughness of 5.1 \AA (root-mean-square) which is representative for the whole surface as comparable values were measured for other areas of the same sample. Extended annealing of the sample at 1400 K in air causes substantial changes of the surface morphology as shown in Figure 1b. The surface of the annealed single-crystal exhibits well-defined, atomically flat terraces extending typically on hundreds of nanometers. In agreement with a recent study²² the terraces are separated by steps with a height of $2.1 \pm 0.2 \text{ \AA}$ which amounts to $1/6$ of the lattice constant $c_0 = 12.99 \text{ \AA}$ of $\alpha\text{-Al}_2\text{O}_3$ along the [0001] direction. Our AFM results clearly show that polished surfaces of (0001) oriented $\alpha\text{-Al}_2\text{O}_3$ samples which were not subjected to a high-temperature treatment are highly disordered and do not represent a well-defined single-crystal surface.

In Figure 2a we present SFG spectra of an annealed, atomically smooth $\alpha\text{-Al}_2\text{O}_3$ -(0001) sample in contact with solutions of pH values between 2 and 12. The spectra show two vibrational resonances at 3140 and 3450 cm^{-1} which can be assigned to the symmetric O–H stretching vibration of tetrahedrally coordinated water molecules and water molecules with lower coordination, respectively.^{20,23} These bands are similar to those previously observed at SiO_2 /water interfaces,^{17,21} although their dependence on the pH value, discussed below, is very different. Despite of the fact that $\alpha\text{-Al}_2\text{O}_3$ -(0001) is a noncentrosymmetric material the non-resonant SFG signal from the substrate was very low in our scattering geometry, and an elaborate interference technique as applied in the SFG study of the $\alpha\text{-SiO}_2$ -(0001) interface²¹ was not necessary.

Very different SFG spectra presented in Figure 2b were obtained from a rough $\alpha\text{-Al}_2\text{O}_3$ -(0001) sample with a surface morphology as shown in Figure 1a. These spectra are dominated by a third band with a frequency between 3630 and 3680 cm^{-1}

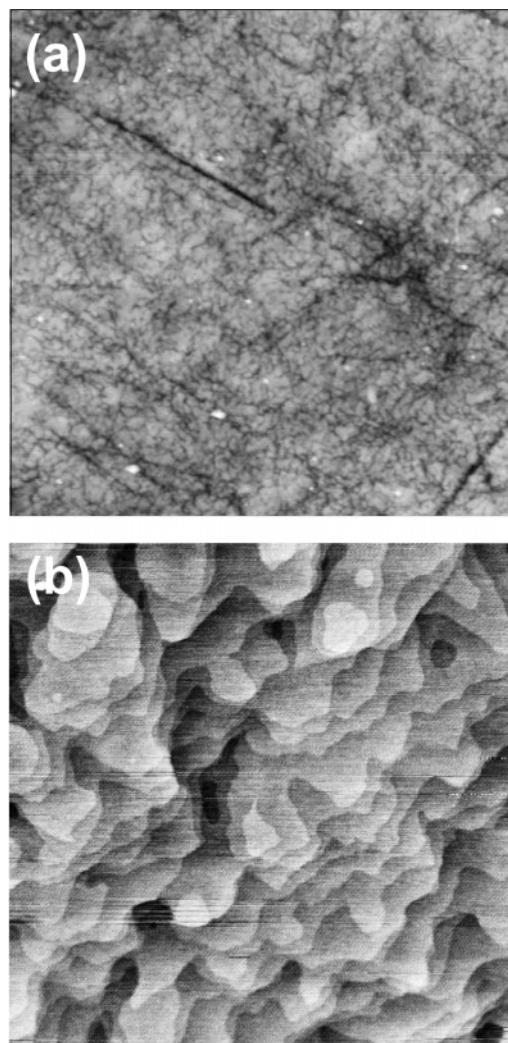


Figure 1. Atomic force microscopy images of $\alpha\text{-Al}_2\text{O}_3$ -(0001) showing ($2 \mu\text{m} \times 2 \mu\text{m}$) surface areas of (a) a sample which has not been annealed (height scale: 9 nm black-to-white) and (b) after annealing for 7 h at 1400 K in air (height scale: 3 nm black-to-white).

which we assign to the O–H stretching vibration of surface hydroxyl groups ('aluminol' groups) that neither do form hydrogen bonds with neighboring aluminol groups ($\sim 3560 \text{ cm}^{-1}$ ²⁴) nor with the interfacial water molecules of the solution. The frequency of this band is indicative of an isolated surface hydroxyl group coordinated to three Al atoms.^{25,7} A hydroxyl band with a frequency of 3677 cm^{-1} has recently been observed in IR spectra of anodic aluminum membranes and attributed to $\text{Al}_3\text{-OH}$ surface groups in 40 nm nanopores.²⁴ We conclude that isolated $\text{Al}_3\text{-OH}$ groups are present on our disordered $\alpha\text{-Al}_2\text{O}_3$ -(0001) surfaces in very small pores with hydrophobic character. The detection of isolated aluminol groups in much smaller pores than previously accomplished²⁴ is presumably related to the superior interface sensitivity of SFG. The comparatively large line widths of the aluminol bands ($60\text{--}160 \text{ cm}^{-1}$) in our spectra can be related to inhomogeneities of the local adsorption sites due to different pore sizes. The complete absence of this band in spectra of $\alpha\text{-Al}_2\text{O}_3$ -(0001) interfaces with atomically smooth terraces and defined atomic steps strongly supports our assignment to isolated aluminol groups in nanopores of the disordered surface.

A second important difference between the SFG spectra of atomically smooth and disordered $\alpha\text{-Al}_2\text{O}_3$ -(0001) interfaces is the distinctly different pH dependence of the bands of tetrahe-

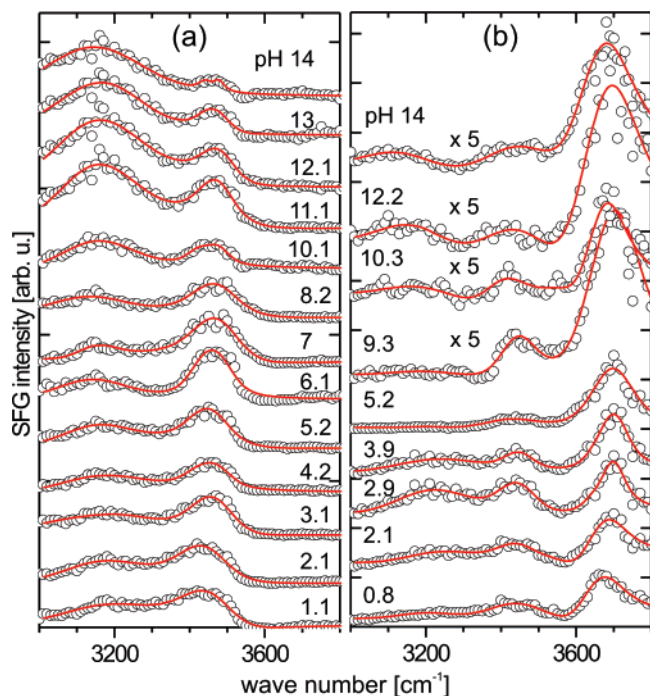


Figure 2. pH dependence of SFG spectra from α - $\text{Al}_2\text{O}_3(0001)$ in aqueous solutions: (a) surface with atomically smooth terraces as in Figure 1b. (b) surface with a roughness as in Figure 1a. Lines are fits to the data.

drally coordinated interfacial water molecules. For a closer analysis we have simulated our experimental spectra with a model function for the sum-frequency susceptibility, $\chi^{(2)}$, which consists of a non-resonant contribution $\chi_{\text{NR}}^{(2)}$ and inhomogeneously broadened vibrational line profiles.²¹ These profiles were obtained by convolution of a homogeneous profile for each vibrational mode q

$$\chi_q^{(2)} = \frac{A_q e^{i\varphi_q}}{\omega_q - \omega_{\text{ir}} - i\Gamma_q} \quad (1)$$

with Gaussians. Due to the large inhomogeneous broadening of the O–H stretching modes a variation of Γ_q over a considerable range had no discernible effect on the spectral parameters of the resonances, and Γ_q was set to 1 cm^{-1} . The adjustable parameters in our simulations were $\chi_{\text{NR}}^{(2)}$, A_q , ω_q , φ_q , and the inhomogeneous line width, Δ_q .

The pH dependence of the amplitude A_q of the 3140 cm^{-1} band of the atomically flat surface (Figure 3a) exhibits a minimum between $\text{pH}=8$ and $\text{pH}=9$ and a steep increase above $\text{pH} 9$. Polar order in molecular layers is a prerequisite for dipole-allowed SFG.^{17,20} Consequently, we relate this minimum to a loss of structural order in the hydrogen-bonded network of water molecules at the interface which is expected for pH values close to the IEPS as both protonated and deprotonated aluminol groups are present on the surface. Our SFG results for the smooth α - $\text{Al}_2\text{O}_3(0001)$ surface are consistent with an IEPS between 8 and 9 which is in line with the pH values of zeta potential reversal recently determined for suspensions of α - Al_2O_3 powder.¹⁴ The increase of the amplitude of the 3140 cm^{-1} band above $\text{pH} 9$ signals the formation of a more homogeneous network of hydrogen-bonded water molecules, assisted or caused by the interfacial electric field originating from negative surface charges of deprotonated aluminol groups.^{17,18} In contrast, the amplitude of the 3450 cm^{-1} band is virtually independent of the pH between 1 and 11 proving that this molecular species is

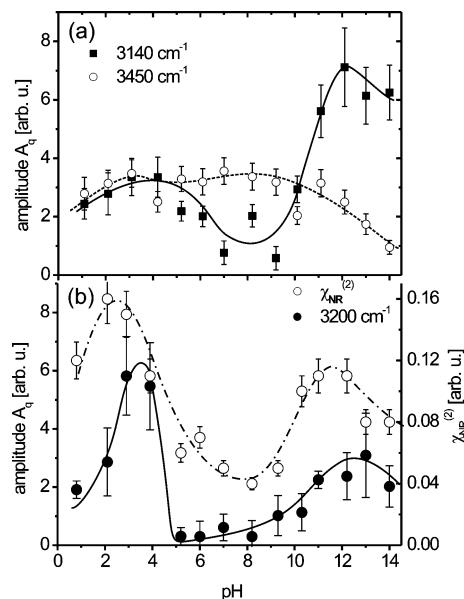


Figure 3. (a) SFG amplitudes (A_q) of tetrahedrally (3140 cm^{-1}) and non-tetrahedrally (3450 cm^{-1}) bonded water molecules, respectively, for a α - $\text{Al}_2\text{O}_3(0001)$ surface with atomically smooth terraces. (b) SFG amplitude (A_q) of tetrahedrally bonded water molecules (3200 cm^{-1}) and nonresonant SFG contribution ($\chi_{\text{NR}}^{(2)}$) for a α - $\text{Al}_2\text{O}_3(0001)$ surface with a surface roughness as in Figure 1a. Lines are guides to the eye.

much less affected by changes of chemical or electrical properties of the surface. Moreover, its higher frequency indicates less hydrogen-bonding per molecule, similar to a high-frequency component observed in spectra of liquid bulk water.²⁶ We therefore assign this band to water molecules localized farther away from the oxide surface, in a transition layer between the network of highly coordinated interfacial water molecules and the disordered liquid bulk phase. The very different pH dependencies of the two water bands in Figure 3a show that, unlike suggested in a previous SFG study,¹⁵ only the 3140 cm^{-1} band but not the 3450 cm^{-1} band should be used for a characterization of surface-induced order in interfacial water layers.

A much different pH dependence is observed for the band of tetrahedrally coordinated water molecules at the disordered surface (Figure 3b). The corresponding band, here with a frequency of about 3200 cm^{-1} , exhibits a dramatic decrease of amplitude to almost zero between $\text{pH} 4$ and 5 , accompanied with a phase change of about π , and a more gradual increase for higher pH values. Moreover, for pH values in the basic region its strength is reduced compared to the atomically smooth surface indicating a less ordered interfacial water layer on the nanorough surface. The strong decrease at $\text{pH}=4$ indicates a dramatic decrease of protonated surface hydroxyl groups. This observation can be explained if the pK value for deprotonation of aluminol groups at defect sites is lower than that of aluminol groups on atomically smooth terraces. The strong shift of the minimum to smaller pH values does not necessarily imply a likewise large shift of the IEPS of the disordered surface, however. Protonation and deprotonation of surface hydroxyl groups at defect sites may dominate the SFG spectra of water molecules at the nanorough surface due to defect-related enhancement of the microscopic electric fields. Hydroxyl groups of regular sites of the (0001) surface, with a deprotonation at higher pH values according to Figure 3a, may nevertheless contribute substantially to the total surface charge on a nanorough surface. Some support for this presumption comes from the pH dependence of the nonresonant SFG amplitude $\chi_{\text{NR}}^{(2)}$ of

the rough surface shown in Figure 3b which is surprisingly similar to that of the 3140 cm^{-1} band in Figure 3a for $\text{pH} > 5$. $\chi_{\text{NR}}^{(2)}$ originates from electronic transitions and depends to some extent on the electric charge at the surface through electric-field-induced SFG.²⁷ The decrease of the resonant amplitudes in Figure 3 for very low and very high pH values observed for both types of surfaces could be related to the formation of compact Helmholtz layers with the ions opposite to the charged surface not only screening the interfacial field but also disrupting the network of interfacial water molecules.

4. Conclusion

In conclusion, combining scanning probe microscopy and surface vibrational spectroscopy we have demonstrated that surface disorder at the nanometer scale strongly affects the molecular structure of the interface between $\alpha\text{-Al}_2\text{O}_3(0001)$ and aqueous solutions. Both the presence of uncoupled hydroxyl groups, presumably located in hydrophobic nanopores of the surface, and the apparent decrease of the pK for deprotonation of coupled surface hydroxyl groups have been observed on nanorough surfaces. We expect the different deprotonation of surface hydroxyl groups at smooth and rough surfaces to have influence on the reactivity of the surface under aqueous conditions. Future SFG studies of hydrated Al_2O_3 surfaces which are structurally modified on a nanometer scale in a controlled way will help to understand the role of preferred deprotonation at surface defects for the reactivity of mineral interfaces on a molecular level.

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