

Surface-Induced Anisotropic Orientations of Interfacial Ethanol Molecules

at Air/ Sapphire($1\bar{1}02$) and Ethanol/Sapphire($1\bar{1}02$) Interfaces

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Abstract

Sum frequency vibrational spectroscopy was used to study the interfacial arrangement of ethanol molecules at the vapor/ α -Al₂O₃ ($1\bar{1}02$) and α -Al₂O₃ ($1\bar{1}02$)/ethanol liquid interfaces. The spectra in the C-H range show that ethanol molecules adsorbed from vapor onto α -Al₂O₃ ($1\bar{1}02$) surface have a well-defined anisotropic arrangement following the structure of the α -Al₂O₃ ($1\bar{1}02$) surface. The arrangement can be explained by the formation of two specific hydrogen bonds between the adsorbed ethanol molecule and hydroxyls on the sapphire surface. At the α -Al₂O₃ ($1\bar{1}02$)/ethanol liquid interface, the first ethanol monolayer assumes a similar anisotropic arrangement as in the case of an ethanol monolayer on the dry sapphire surface. The second monolayer has a rather broad orientation distribution that is azimuthally nearly isotropic, but with molecules flipped 180 degrees with respect to those in the first monolayer.

Introduction

In recent years, there has been increasing interest in studying the microscopic structures of solid/liquid interfaces as they are crucial for understanding functionalities of the interfaces that play a key role in many disciplines. However the advance has been slow because of limitations of the currently available molecular probes. Among the various surface analytical tools, sum frequency vibrational spectroscopy (SFVS) is unique in being capable of probing buried interfaces and providing their vibrational spectra. It has been successfully applied to a number of solid/liquid interfaces, most recently, on water/oxide interfaces. [1-3] Oxide surfaces are often protonated, and can establish hydrogen (H) bonds with adsorbed water molecules. The bonding geometry depends on the degree of protonation or deprotonation of an oxide surface. The interfacial water structure is believed to form a dynamically fluctuating H-bonding network partially reflecting the ordered oxide surface structure due to the H-bonded water molecules at the oxide surface. It is interesting to know whether such surface-induced ordering exists, and how far it extends into the bulk water. Unfortunately, such information is difficult to deduce from the interfacial water spectrum (usually in the OH stretch range), partly because the spectrum is often complicated by overlapping contribution from the hydroxyls at the oxide surface. Past studies have considered other liquid/oxide interfaces to probe possible existence of such surface-induced ordering. For example, an earlier SFVS experiment on short-chain alcohol/silica interfaces indicated that significant surface-induced orientation order could be extended to the second monolayer of ethanol molecules at the interface. [4] Recent MD simulations on fused-silica/ethanol and fused-silica/acetonitrile interfaces have yielded similar conclusions. [5, 6]

In this article, we report our study of the ethanol/ α -Al₂O₃ ($\bar{1}\bar{1}02$) interface using SFVS. The system was chosen to see whether the anisotropic crystalline surface of α -Al₂O₃ ($\bar{1}\bar{1}02$) would induce an

orientation order as well as an in-plane anisotropy in orientation in the interfacial layer of ethanol molecules. Ethanol was chosen because its CH stretch modes can be easily distinguished in SFVS from OH stretches of the hydroxyls. Like water, the molecules can be H-bonded to the oxide surface, and with each other, although the bonding geometry is very different from that of water. Studies using surface force microscopy and Fourier-transform infrared spectroscopy have suggested that alcohol molecules may have in-plane arrangement on a fused silica surface, forming well aligned clusters extended up to tens of nm into the bulk liquid.[7,8] These techniques, however, cannot provide resolution of interfacial molecules at the molecular level, and hence the interpretations may not be certain. We have performed SFVS measurements on both an ethanol monolayer on the α -Al₂O₃ ($\bar{1}\bar{1}02$) surface in air and on the α -Al₂O₃ ($\bar{1}\bar{1}02$)/ethanol liquid interface. We found from the spectral analysis, that in the ethanol monolayer case, ethanol molecules appear to have adsorbed on the α -Al₂O₃ ($\bar{1}\bar{1}02$) surface with their OH terminal groups connected to the appropriate surface sites with two H-bonds. Accordingly, the molecules are strongly bonded to the surface with the methyl group protruding out and assuming an azimuthal orientation distribution that reflects the effective C_{1V} symmetry of the α -Al₂O₃ ($\bar{1}\bar{1}02$) surface.[9] In the case of the α -Al₂O₃ ($\bar{1}\bar{1}02$)/ethanol liquid interface, the spectra indicate that while the first molecular monolayer on the sapphire surface is still well-ordered, orientational ordering of molecules in the second monolayer, though very much randomized thermally, is still appreciable, with an average polar orientation opposite to that of the first monolayer. The overall orientation distribution of the interfacial ethanol molecules still exhibits C_{1V} symmetry.

Experimental Arrangement and Analysis

The sapphire sample we used in the experiment was an epi-polished single crystal of α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ purchased from Princeton Scientific Corporation. It was 5 mm thick, and the root-mean-square roughness of the polished surface was ~ 0.2 nm obtained from AFM measurements. The sample cleaning procedure followed the recipe of Refs.[10,11]. The surface was first cleaned in a sonic bath of acetone, methanol, and pure water for 10, 10, and 60min in sequence. It was then mildly etched in a 10~15mM solution of HNO_3 sonic bath for 30min, then rinsed thoroughly with deionized water, and blow-dried with filtered dry nitrogen gas. To remove the remaining water and organic contaminants on the surface, the sample was heated at $\sim 350^\circ\text{C}$ for 1 hour. [9,12] To prepare an ethanol monolayer on the cleaned α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ surface, we exposed the sample to ethanol vapor using the scheme described in Ref.[13,14], with *in situ* monitoring of ethanol adsorption on the surface by SFVS generation in reflection from the surface. When the adsorption of ethanol reached nearly a monolayer, the SFVS signal appeared saturated. [4] The α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ /ethanol liquid interface was prepared by capping the ethanol solution in a container with a cleaned α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ sample.

Our SFVS setup has been described elsewhere. [15,16] The experimental arrangement of the measurement followed the description in Ref.[9,12]. The spectral range taken was from 2800 to 3000 cm^{-1} covering the CH_x stretch modes, and from 3000 to 3800 cm^{-1} covering the OH stretch modes. We focused more on the former range to deduce information on the average orientation of the ethanol molecules at interfaces. The SF output is given by

$$\begin{aligned}
S &\propto |\hat{e}_{SF} \cdot \vec{\chi}_{S,eff}^{(2)}(\omega_{SF} = \omega_{vis} + \omega_{IR}) : \hat{e}_{vis} \hat{e}_{IR}|^2 \\
\vec{\chi}_{S,eff}^{(2)} &= \vec{L}(\omega_{SF}) \cdot \vec{\chi}_S^{(2)} : \vec{L}(\omega_{vis}) \vec{L}(\omega_{IR}) \\
&= \vec{L}(\omega_{SF}) \cdot \vec{\chi}_{S,NR}^{(2)} : \vec{L}(\omega_{vis}) \vec{L}(\omega_{IR}) + \sum_q \frac{\vec{A}_{q,eff}}{(\omega_{IR} - \omega_q + i\Gamma_q)} \\
\vec{A}_{q,eff} &= \vec{L}(\omega_{SF}) \cdot \vec{A}_q : \vec{L}(\omega_{vis}) \vec{L}(\omega_{IR})
\end{aligned} \tag{1}$$

Here \hat{e}_i is the polarization unit vector for the field at ω_i , $\vec{L}(\omega_i)$ is the Fresnel transmission coefficient, and $\vec{\chi}_S^{(2)}$ is the nonlinear surface susceptibility with $\vec{\chi}_{S,NR}^{(2)}$ referring to the nonresonant background and A_q , ω_q , and Γ_q denoting the amplitude, frequency, and damping coefficient of the q th mode, respectively, assuming discrete resonances. By normalizing against a quartz reference, and using SF measurements with different input and output polarization combinations, we could obtain spectra of $|\chi_{S,eff}^{(2)}|_{\alpha\beta\gamma}^2$ and $\text{Im}(\chi_{S,eff}^{(2)})_{\alpha\beta\gamma}$, the latter from an additional phase measurement of $(\chi_{S,eff}^{(2)})_{\alpha\beta\gamma}$.

Results & Discussion

The SFVS spectra of the ethanol monolayer on the α -Al₂O₃($\bar{1}\bar{1}02$) surface in the CH stretch vibrational region with three different input/output polarization combinations, SSP(denoting S-, S-, P-polarized SFVS output, visible and infrared inputs, respectively), SPS, and SSS, are shown in Fig. 1. They are very similar to those obtained from sorption of an ethanol monolayer on fused silica, [4] and can be fit using Eqs. (1) and (2). The fitting yields 3 significant resonance modes at ~ 2878 , ~ 2965 , and ~ 2942 cm⁻¹ that can be assigned to the symmetric stretch (r+), antisymmetric stretch (r-), and Fermi resonance (r+FR) between symmetric stretch and bending modes of the terminal methyl group,[17,18] but can be improved by including 2 other weak modes that can be identified as the symmetric stretch (d+) at ~ 2852 cm⁻¹, and the antisymmetric stretch (d-) at ~ 2920 cm⁻¹ of the methylene group.[17-18] The fitting parameters for all cases are given in Table S1 of the Supporting Information. The amplitudes A_q of r+ and r+FR are positive, and that of r- is negative, indicating that the methyl group points away from the substrate.[19] The weak methylene modes suggest that the methylene plane must be inclined close to the surface plane, consistent with the orientation of the terminal methyl group. Negative A_q of d+ corresponds to CH₂ pointing toward the substrate.[19]

Presented in Fig.1 are also spectra of ethanol taken with the sample at azimuthal angles $\gamma=0, 90, 180,$ and 270° , where γ is the angle between the incidence plane and the $(\bar{1}\bar{1}20)$ glide plane of α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ containing the $[1\bar{1}0\bar{1}]$ direction and the surface normal. The spectra at $\gamma=90^\circ$ and 270° are essentially the same, implying that for SFVS, the ethanol monolayer has an effective mirror symmetry with respect to the glide plane. The SSP spectral intensity at $\gamma\sim 180^\circ$ is stronger than that of $\gamma=0^\circ$, indicating that the adsorbed ethanol molecules are tilted in the backward direction with respect to $[1\bar{1}0\bar{1}]$. The results show that the structure of the ethanol monolayer indeed reflects the effective C_{1v} surface symmetry of the α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ substrate.

To know more specifically how the ethanol molecules adsorb on α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$, we used values of A_q at different γ and with SSP, SPS, and SSS polarization combinations for the r+ mode listed in Table S1 to find the orientation of the ethanol molecules quantitatively. They were deduced following the scheme described in Refs.[9, 14]. The details of our calculation are given in the Supporting Information. Assuming that the orientational distribution function of the methyl group of ethanol is a δ -function in θ_0 and ϕ_0 , we obtained $\theta_0=38^\circ \pm 7^\circ$ and $\phi_0=\pm 132^\circ \pm 8^\circ$, where θ_0 and ϕ_0 are the polar and azimuthal angles of the symmetric axis of the methyl group with respect to the surface normal and the $[1\bar{1}0\bar{1}]$ direction, respectively. This orientation suggests how the ethanol molecules are H-bonded to the α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ surface. We know from our earlier work that the α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ surface has a structure composed of three relaxed layers in which oxygen atoms are bonded to 1, 2, and 3Al, respectively, as shown in Fig. 2. [9,20] The surface has effective 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: one from Al_2OH is H-bonded to O of the neighboring Al_3O , one from AlOH_2 is H-bonded to O of the neighboring Al_2OH , and the third one is a dangling OH from AlOH_2 . [9] Their stretch frequencies are at $\sim 3365, 3520,$ and 3670 cm^{-1} , and their orientations are specified by $(\theta \sim 69^\circ, \phi \sim \pm 67^\circ), (\theta \sim 62^\circ, \phi \sim \pm 127^\circ),$ and $(\theta \sim 36^\circ, \phi \sim \pm 78^\circ),$

respectively.[9]. Here, θ is the polar angle of O→H away from the surface normal and ϕ the azimuthal angle away from the $[1\bar{1}0\bar{1}]$ direction in the surface plane. We realize that an ethanol molecule could adsorb on this protonated surface with its OH forming two H-bonds with hydroxyls on the surface as shown in Fig. 2, one between O of ethanol and H of the dangling OH of AlOH_2 , and the other between H of ethanol and O of Al_2OH . We can roughly determine the orientation of the OH in ethanol corresponding to the most probable H-bond configuration using Skinner's description of H-bonding, which requires the length of H-bond, bending angle of OH---O, and angle between lone pair orbital of O and the H---O bond to be 1.5-2.1Å, $>150^\circ$, and $<38^\circ$, respectively. [9,21] As shown in Fig. S1 in the Supporting Information, if we define \hat{x} and \hat{z} to be along $[1\bar{1}0\bar{1}]$ and the surface normal, respectively, and choose O of AlOH_2 to be at the origin, then we have H of the dangling OH of AlOH_2 and O of a neighboring Al_2OH at (0.23 Å, -0.63 Å, 0.67 Å) and (1.96 Å, -1.57 Å, -1.40 Å), respectively. (The O of another neighboring Al_2OH , labeled as O2 in Fig. S1 of Supporting Information is at (-0.58Å, -2.26 Å, -1.40 Å).) The likely positions of H and O of the adsorbed ethanol molecule are at (1.51 Å, -2.00 Å, 0.37 Å) and (1.08Å, -1.76 Å, 1.19 Å), respectively, leading to a corresponding orientation of $\theta_0 \sim 35^\circ$ and $\phi_0 \sim 160^\circ$ for the methyl group of the adsorbed ethanol molecule, close to the orientation of $\theta_0=38^\circ \pm 7^\circ$ and $\phi_0=-132^\circ \pm 8^\circ$ deduced from experiment. (There is an adsorbed ethanol molecule at an equivalent position on the opposite side of the AlOH_2 row (See Fig.S1 in the Supporting Information) that has an orientation of $\theta_0 \sim 35^\circ$ and $\phi_0 \sim -160^\circ$.)

The spectral change in the OH stretch range resulting from ethanol monolayer deposition on the α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ surface is most significant around 3670cm^{-1} where the major contribution to the spectrum is from the dangling OH from the AlOH_2 functional group. (Fig. S2 in the Supporting Information) With ethanol H-bonded to the dangling OH, the peak at $\sim 3670\text{cm}^{-1}$ is strongly suppressed. However the rest of the OH spectrum is difficult to interpret, not only because the original spectrum of the hydroxyls on the α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ surface is complicated, but also because H-bonding of ethanol to the hydroxyls

could alter the spectrum, and the OH of the adsorbed ethanol should also contribute to the observed spectrum.

The observed orientation anisotropy of the ethanol monolayer on the α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ surface is a manifestation of orientation order induced by the crystalline surface structure in the chemically adsorbed monolayer. It would be interesting to know how far such a surface-induced order could extend into the bulk liquid. Hence we have studied the α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ /ethanol liquid interface using SFVS. Figure 3 depicts the SSP spectra at $\gamma \sim 0, 90, 180$ and 270° . In all spectra, in contrast to the case of an ethanol monolayer on the α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ surface, the antisymmetric methyl stretch (r^-) at $\sim 2965 \text{ cm}^{-1}$ now appears stronger than the symmetric methyl stretch (r^+) at 2878 cm^{-1} . This is similar to what was observed in previous study of alcohols/silica interfaces [4], and can be understood as resulting from the formation of a bilayer with oppositely polar-oriented molecules. Molecules in the first monolayer are tightly anchored on the α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ surface with a well-defined orientation, but those in the second monolayer with oppositely polar-oriented molecules are expected to have a rather broad orientation distribution because the van der Waals interaction between two ethanol molecules with their methyl groups facing each other is weak (comparable to the thermal energy). Thus, contributions from molecules in the two monolayers to the r^+ peak in the SFVS spectra tend to cancel each other, although the cancellation is not perfect because of the broad orientation distribution of molecules in the second monolayer. The contributions of the two monolayers to the r^- peak, on the other hand, do not cancel each other well, leading to an r^- peak comparable in strength to that in the ethanol monolayer/ α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ case.

We can follow the procedure described in Ref. 4 to carry out a more quantitative analysis. We assume a δ -function, $\delta(\theta, \phi)$ for the orientation distribution of molecules in the first layer, with $\theta_0 = 38^\circ$ and

$\phi_0 = \pm 132^\circ$ deduced from our measurement on ethanol monolayer/ α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$, but a flat distribution for ψ (the azimuthal angle of the methyl group around its symmetric axis) between approximately -60° and 60° , considering that the methyl group could rotate freely over this range.[22] For the second ethanol monolayer, we assume a Gaussian distribution function of

$$f(\theta, \phi) = C \exp\left[-\frac{(\theta - \theta_c)^2}{2(\Delta\theta)^2} - \frac{(\phi - \phi_c)^2}{2(\Delta\phi)^2}\right] \quad (2)$$

with $\theta_c = \pi - \theta_0$ and $\phi_c = \pi - \phi_0$ and complete randomization in ψ . As described in the Supporting Information, we find, for the ethanol bilayer,

$$\begin{aligned} \bar{A}_q &= \bar{A}_{q,1} + \bar{A}_{q,2} \\ \bar{A}_{q,1} &= N_s \bar{a}_q(\theta_0, \phi_0) \quad \text{and} \quad \bar{A}_{q,2} = N_s \int \bar{a}_q(\theta, \phi) f(\Omega) d\Omega \end{aligned} \quad (3)$$

Here, $\bar{A}_{q,1}$ denoting the q th mode strength of the first ethanol monolayer is the same as that of the ethanol monolayer at the air/ α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ interface, $\bar{A}_{q,2}$ refers to the mode strength of the second ethanol monolayer, and N_s is the number of ethanol molecules per unit area in a monolayer. The molecular hyperpolarizability of the q th mode, $a_{q,abc}$, with (a,b,c) denoting the molecular coordinates, can be obtained from the bond additivity model. [23, 24] Equation (3) then allows us to calculate the ratio of $A_{q,ijk}$ for the bilayer to $A_{q1,ijk}$ for the first monolayer.(Fig. S3 in Supporting Information) We find that for the calculated ratios to match the measured ratios of $A_{q,yyz}/A_{q1,yyz} = 0.20 \pm 0.02$ and $A_{q,yyx}/A_{q1,yyz} = 0.67 \pm 0.08$ for the $r+$ mode and $A_{q,yyz}/A_{q1,yyz} = 0.38 \pm 0.05$ and $A_{q,yyx}/A_{q1,yyx} = 0.85 \pm 0.07$ for the $r-$ mode, we must have $\Delta\theta = 75^\circ \pm 15^\circ$ and $\Delta\phi = 120^\circ \pm 30^\circ$. Finally, we note that even for an α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ /ethanol liquid interface, the SF vibration spectra still exhibit a dependence on the azimuthal angle of the sample with respect to the incidence plane. This is because the first anisotropically ordered

ethanol monolayer at the interface contributes significantly more signal than the more randomly ordered second monolayer.

The above result indicates that while the ethanol monolayer on the α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ surface is very well oriented, the second monolayer disturbed by thermal agitation has quite a broad orientation distribution. This is similar to the result obtained earlier in the case of alcohols/fused silica interfaces, except that here we have, in addition, surface-induced orientation anisotropy in the first ethanol monolayer. One can expect residual surface-induced ordering, particularly the polar ordering, in the third or even fourth monolayer (with reversal of the net polar orientation in successive layers), but rapid broadening of the orientation distribution should soon make the induced order insignificant. Recent MD simulations [5,6] on alcohols/fused silica and acetonitrile/fused silica interfaces show that the interfacial transition layer can extend to ~ 4 monolayers. It is known that at solid/liquid crystal interfaces, surface-induced orientation order can extend over a molecular correlation of ~ 5 nm.[25] This is however a case where the oriented molecular interaction is larger than the thermal energy. In ordinary liquid, the opposite is true and consequently, the molecular correlation length is short.

In summary we have observed, using SFVS, the surface induced anisotropic orientation of ethanol molecules at the air/ α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ interface as well as at the ethanol/ α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ interface. The first ethanol monolayer appears very well oriented, but the second monolayer has a rather broad orientation distribution. We expect similar results at air/ and liquid/oxide interfaces for molecules that can adsorb with hydrogen bonds onto oxides but have intermolecular interaction among themselves weaker than the thermal energy.

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SUPPORTING INFORMATION

We describe there the detailed analysis of the SFVS spectra and the fitting parameters used. We also include a set of SFVS spectra in the OH stretch range. This information is available free of charge via the internet <http://pubs.acs.org>.

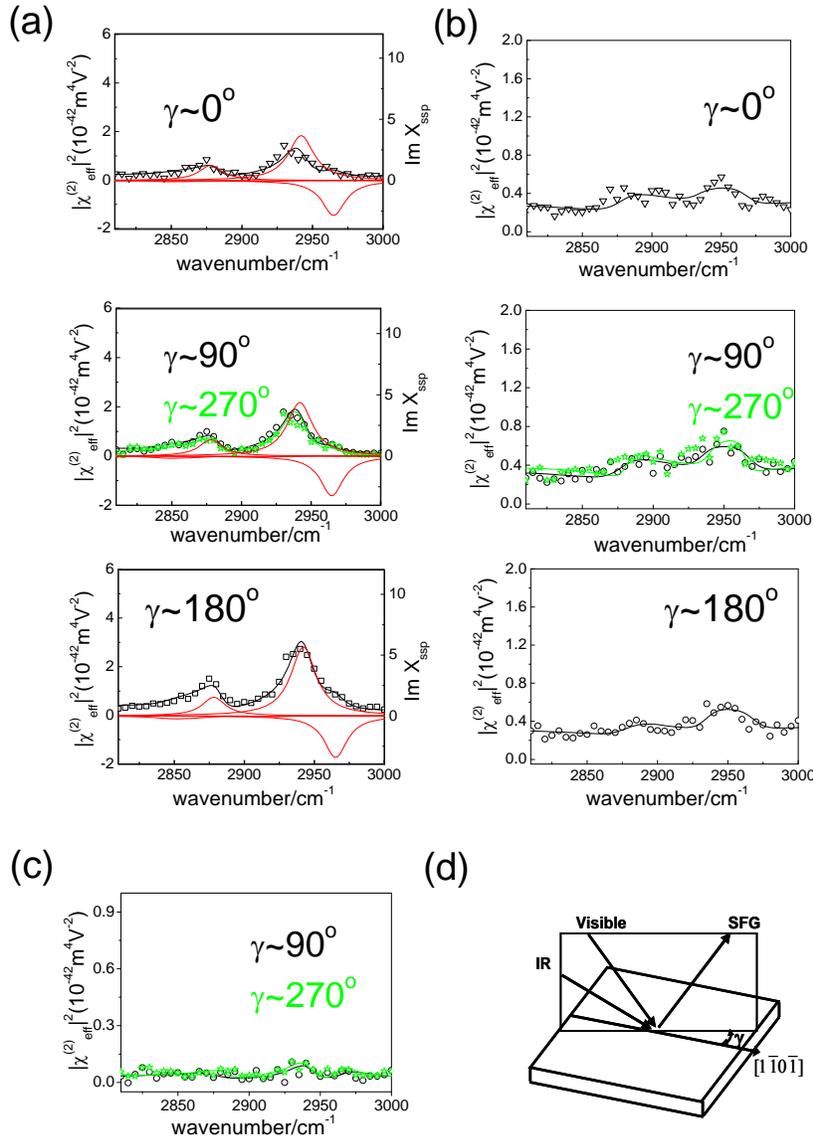


Fig. 1. SFVS spectra of ethanol monolayer on α -Al₂O₃($\bar{1}102$) with polarization combinations (a) SSP, (b) SPS, and (c) SSS. The symbols describe the data points. The black lines are theoretical fits to the $|\chi_{S,eff}^{(2)}|^2$ spectra, and the red lines show the modes that compose the $\text{Im } \chi_{S,eff}^{(2)}$ spectra. (d) Geometry of the beams with respect to the sample surface that defines the angle γ .

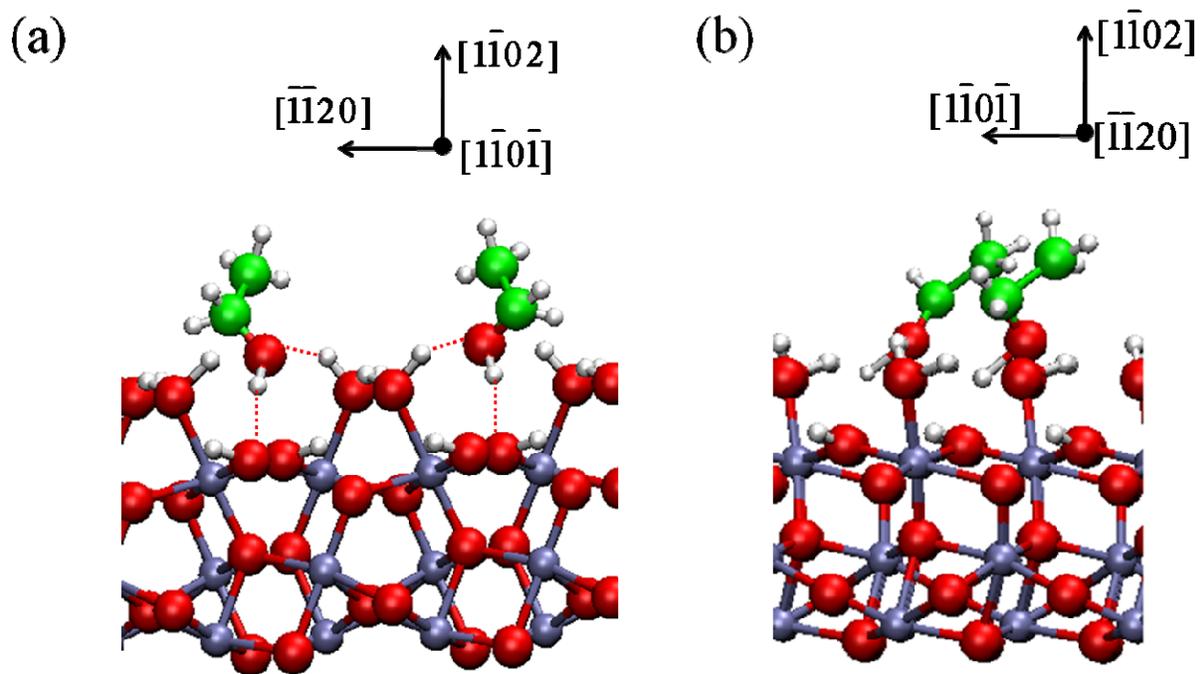


Fig 2. Two side views of the proposed structure of α - $\text{Al}_2\text{O}_3(\bar{1}\bar{1}02)$ with ethanol molecules H-bonded to the surface. Red, blue, green, and white spheres represent oxygen, aluminum, carbon, and hydrogen atoms, respectively. Dotted lines denote H-bonds.

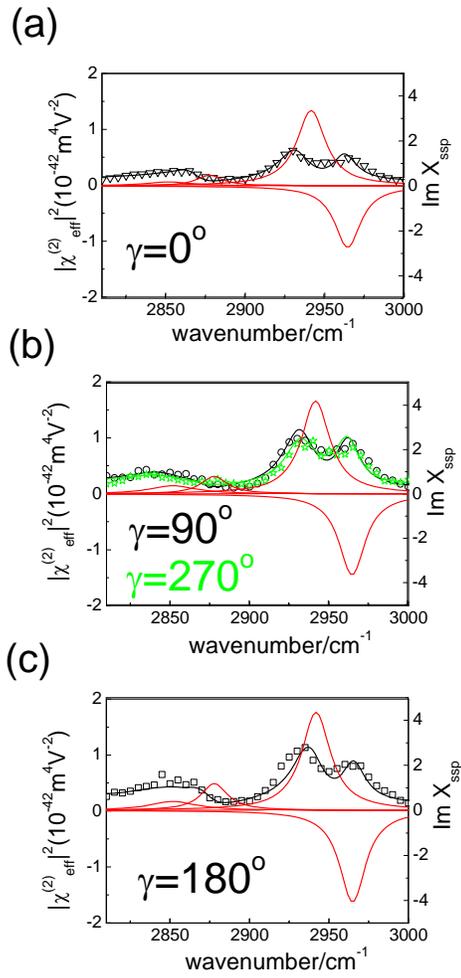


Fig.3. SSP-SFVS spectra of the ethanol liquid/ α -Al₂O₃($\bar{1}\bar{1}02$) interface. The symbols describe the data points. The black lines are theoretical fits to the $|\chi_{S,eff}^{(2)}|^2$ spectra, and the red lines show the modes that compose $\text{Im } \chi_{S,eff}^{(2)}$ spectra.

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