Selective Observation of Boundary Water near a Solid/Water Interface by Variable-Angle Polarization Specific Attenuated Total Reflection Infrared Spectroscopy and Principal-Component Analysis

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An infrared spectrum of the boundary water near a solid/water interface has been observed, which is distinguished from the bulk water using a novel analytical technique. The technique employs the variable-angle polarization specific (VAPS) attenuated total reflection (ATR) infrared spectrometry and a characteristic of principal component analysis (PCA). To date, near-field optical techniques or artificial polycrystalline water thin-layer formation technique have been used to study the structure of boundary-water molecules below the limitations of spatial resolution. Here, however, we show that the combination technique of VAPS-ATR and PCA analytically overcomes the difficulty of spatial resolution and detection limit, so that we selectively observe the boundary water. The orientation of the boundary-water molecules has been evaluated using the resolved infrared spectra obtained as the PCA loadings. In addition, it was also suggested that there was an intermediate layer between the boundary water layer and bulk water.

Introduction

It is theorized that boundary water molecules at a solid/water or air/water interface have a unique molecular structural network that is apparently different from that of bulk water.[1,2] Infrared spectrometry is a highly sensitive and useful tool for directly analyzing the network structure comprised of a minute amount of molecules. Despite this, the selective observation of the infrared spectrum of boundary water molecules alone has been close to impossible due to the limitation of spatial resolution, since the thickness of the boundary water layer is estimated to be only several angstroms.

Two strategies have been proposed to analyze the structure of the boundary water layer via its infrared spectra. One method involves surface-enhanced infrared reflection−absorption (SEIRA) spectrometry by use of the attenuated total-reflection (ATR) optical geometry with a thin metal overlayer on the ATR-prism surface. ATR-SEIRA has two important advantages: (1) the sensitivity near the interface at the ATR prism is significantly high, and (2) the penetration of the electric field from the prism surface into the adjacent material is limited to approximately 40 Å.[3] In this fashion, the SEIRA spectrometry can, with high sensitivity, observe infrared spectra in a very limited region. Osawa et al.,[3] for example, employed the ATR-SEIRA technique to observe an infrared spectrum of the boundary water. It was possible that the structure of the boundary water was discussed at a certain electric potential of the ATR-electrode (gold) surface.

Unfortunately, however, the absorbance intensity was very minor, since the water molecules at the boundary had a parallel orientation to the surface, which is not a good analytical condition for ATR-SEIRA spectrometry. Another limitation of SEIRA is that it can be applied only to a metal surface.

The second strategy is represented by a study conducted by Bensebaa and Ellis,[4] in which artificial quasi-boundary water layers are prepared on a cold metal surface. Although this approach is an indirect one, molecular orientation in the thin water layer can be controlled by thermal treatment in the temperature range of 100−150 K. Water layers in the polycrystalline state were readily prepared, which presented fine infrared reflection−absorption (RA) spectra that were close to the theoretical expectation. Nonetheless, this technique could not be applied to the real boundary water at room temperature in the presence of the bulk water. These two historical approaches, in this manner, strongly indicate that the selective observation of the infrared spectrum of the boundary water is very difficult.

In the present study, a characteristic of principal component analysis (PCA), which was found recently,[6−8] has been applied to the resolution of the boundary water spectrum, calculated from a collection of variable-angle polarization specific (VAPS) infrared ATR spectra of water. One of the authors (T.H.) had already revealed that minute spectra due to minute chemical constituents could be separated from other dominant components by use of a characteristic of PCA, which has been named FARMS[8] (factor analytical resolution of minute signals). Here we show that the minute signal derived from the very limited region (boundary water) has been readily resolved from the VAPS-ATR spectra of water using FARMS.

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Experimental Section

The planer surface of a hemi-cylindrical silicon (Si) prism in a one-reflection ATR attachment for FT-IR spectrometer was used as the interface for the study of boundary water. This custom-made ATR attachment enables us to measure infrared spectra of boundary layers at the silicon surface at various angles of incidence (45°−80°). For the detail of the ATR attachment, the reader is referred to a previous paper.[5] The Si prism was sonicated in water, ethanol, and chloroform successively for 3 min each. The washed prism was further subjected to ozone cleaning for 10 minutes to remove organic contaminants from the surface. The UV-ozone cleaner was Model UV/253 manufactured by Nippon Laser & Electronics Lab (Nagoya, Japan).

For the VAPS-ATR measurements, p- and s-polarized infrared rays were generated by a wide-grid polarizer using a ZnSe substrate, which was installed in the ATR attachment. The polarizer was placed just after the silicon prism. The reflected ray from the silicon surface was introduced to a mercury cadmium telluride (MCT) infrared detector in a Bio-Rad (Cambridge, MA) FTS 575C FT-IR spectrometer. Accumulation of 300 interferogram-scans was performed for each measurement to improve the signal-to-noise ratio of spectra. The resolution was 4 cm^{-1}, and all the measurements were performed in room temperature approximately at 25 °C.

A SEIRA active surface was prepared by evaporation of gold on the silicon-prism surface at a deposition rate of 0.05 Å s^{-1} by heating a tungsten boat with gold particles. The gold particles were 99.9999% pure, and were purchased from Tanaka Kikinzoku (Tokyo, Japan). The evaporation was performed in a Shinku Technology (Nagoya, Japan) vacuumed chamber under the pressure of approximately 3×10^{-4} Pa. The thickness of the evaporated gold was monitored by a quartz-crystal microbalance in the chamber.

Water used for the VAPS-ATR and SEIRA measurements was obtained by a Millipore (Bedford, MA) Milli-Q laboratory water purifier. The final water was passed through a Millipore Millipak-40 filter (pore size is 0.22 μm) to remove residual minute organic contaminants.

The curve fitting by use of Kim et al.'s oscillators model[9] was performed with the spectra-simulation software, SCOUT2, that was provided by Dr. Wolfgang Theiss (*M. Theiss Hard- and Software, Aachen, Germany*). The evaluation of refractive-index dispersion curves was also calculated with the software from two ATR spectra of bulk water. PCA calculation was carried out on the MathWorks (Natick, MA) MATLAB software version 5.3 for Windows with Chemometrics Toolbox purchased from Applied Chemometrics (Sharon, MA). The computer for the calculations was a SONY (Tokyo, Japan) VAIO C1XE with Mobile Pentium II (260 MHz).

Results and Discussion

Recently, PCA that is one of the chemometric techniques has been found to have a unique characteristic to resolve spectra of minute chemical species from those of dominant species,[6−8] which is called FARMS. FARMS is readily achieved, especially when the signal ratio of the dominant to minute species is within the range of 10^2-10^4.[6,7] In principle, this technique can be applied to transmission spectroscopy. To resolve the infrared transmission spectra of water, however, the infrared absorption by the bulk water is too strong for experimental analysis, and the thickness ratio of the bulk water and the boundary water is too large ($\sim 10^7$). On the other hand, infrared ATR spectroscopy provides an evanescent electric field in the water phase, in which the thickness ratio to the boundary water is expected to be
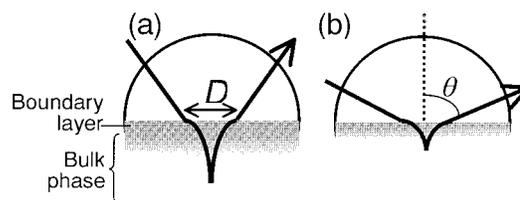

Figure 1. Schematic images of internal reflection in an ATR prism (hemi circle), which depend on angle of incidence [(a) and (b)]. The decay of the electric-field intensity in the thickness direction is shown by the gradation. Goos-Hänchen shift is exaggeratedly shown by *D*. Both electric-field intensity and cross section of the evanescent wave gradually change with the change in the angle of incidence.

appropriate ($\sim 10^2-10^3$); in addition, this ratio can be controlled by changing the angle of incidence. The interaction of the boundary water layer with the evanescent electric field changes independently to that of the bulk water (Figure 1). Therefore, the infrared spectrum of the boundary water layer is expected to be resolved as the second PCA loading[6,7] from the mixed spectra of the boundary and bulk water by use of FARMS.

One issue that should be considered is that the ATR spectra would be influenced by the real part (*n*) of complex refractive indices ($\tilde{n} = n + ik$) of the prism and the film. In general, FARMS works properly when only the concentration is the dominant factor to have the spectral shape changed. In other words, minute spectra would be readily resolved only when the collection of spectra is influenced by the imaginary part (*k*) of complex refractive indices. In the present case, however, the internal reflection at the ATR prism surface is theoretically influenced by both *n* and *k*. Regardless, we can prevent the issue because of the following reasons.

Of note is that *n* and *k* are not independent parameters. They are perfectly correlated with each other through the Kramers− Kronig relationship, which means that a set of *n* and *k* determines the shape of a spectrum. It should be emphasized, however, that this could be true *only for total reflection spectroscopy*. In particular for the *inner* total reflection, the absorbance (spectral intensity) can be represented by penetration depth only. This strongly suggests that ATR spectra can exceptionally be treated like transmission spectroscopy as a function of concentration. A similar thing happens for RA spectroscopy, in which reflection spectra measured on a metallic surface has an identical shape irrespective of the angle of incidence. In this manner, total reflection spectroscopy is quite convenient for further analyses. In fact, as usual, angle-dependent ATR spectra have identical shape, and only the intensities vary due to the difference of penetration depth. If there were two different structural networks of water, there would be two different sets of *n* and *k*, which yield two different shapes, irrespective of the angle of incidence. Therefore, the ATR spectra have no problem for the PCA analysis.

For reference, we have evaluated dispersion curves of both real and imaginary parts of refractive index of bulk water. The results are presented in Supporting Information. By use of two ATR spectra at different angles (50° and 75°), dielectric functions were optimized to yield the dispersion curves. It is found that the values of the real part are found between 1.08 and 1.57, whose average value is found at 1.33 that is reasonable value for bulk water. It should be noted that all the observed ATR spectra are reproduced by the identical set of *n* and *k* curves.

Figure 2 presents the observed p-polarization infrared ATR spectra of water at various angles of incidence (50°−75°), which are raw spectra. It seems that the spectral shapes are almost
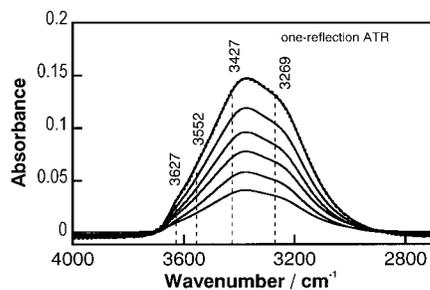
Figure 2. Observed infrared p-polarization ATR spectra of water at angles of incidence of 75, 70, 65, 60, 55, and 50° (from bottom to top). The band locations revealed after curve-fitting are shown by the dashed lines. The fitted curve is represented by a dotted line and is almost identical to the spectrum at 50°.
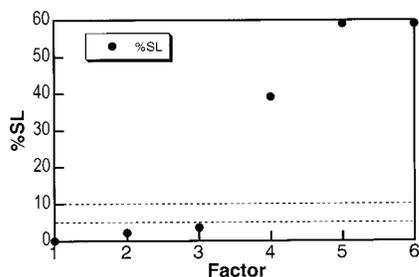

Figure 3. Percent significant level (%SL) calculated for the spectra in Figure 2. Lines of 5% and 10% are shown by the dashed lines.

identical to each other, and only the spectral intensity changes as the angle of incidence. This means that the bulk water mainly dominates the spectral changes due to the depth change of the evanescent field, while the boundary-water contribution is negligible if detected. The peak maximum of the O$-$H stretching vibration band is found at 3375 cm^{-1}, and a shoulder band is found at approximately 3240 cm^{-1}. A curve-fitting technique with the use of Kim et al.'s oscillators[9] was applied to this spectrum to reveal the right positions of fine band components hidden in the overlaid bands. A fitted curve to the spectrum at 50° is plotted by a dashed curve in Figure 2, which is nearly identical to the spectrum. As a result, at least four bands were identified: 3627, 3552, 3427, and 3269 cm^{-1}; these were different from the apparent positions. The latter three band positions are almost consistent with the results by Reimers and Watts.[12]

The six p-polarization infrared ATR spectra as a function of the angle of incidence were subjected to PCA. Before the PCA analysis, the number of chemically meaningful loadings was evaluated via the calculation of so-called percent significance level (%SL),[13] which is presented in Figure 3. Loadings with %SL less than 5% are generally considered to be meaningful (basis factors). In our case, %SL values of the first three loadings are less than 3.6%, and those of the rest of the loadings are more than 39.1%, which strongly suggests that three distinguishable water molecular species are present near the Si/water interface. Thus far, it has been known that there are bulk- and boundary-water molecular species near the interface, but another species has never suggested experimentally to our knowledge. Since the same results were obtained even when different numbers of spectra were subjected to the %SL analysis, the results were considered not from artifacts.

The first three PCA loadings are presented as spectra in Figure 4. Because the first PCA loading always yields the average spectrum,[14] it is quite similar to the original spectra that correspond to bulk-water species. The second PCA loading is, however, quite different from the first loading. Of note is that
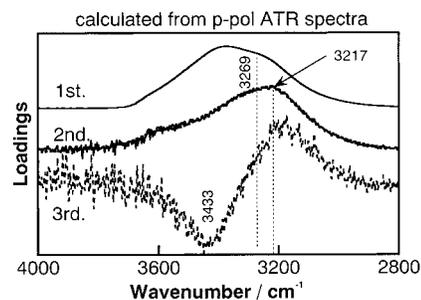

Figure 4. The first, second, and third PCA loadings yielded from the spectra in Figure 2. The fitted curve to the second loading is presented by a dashed curve. The second loading corresponds to the pure infrared ATR spectrum of boundary water only.

both the first and second loadings are obtained as "positive" spectra. When mutually dependent chemical components are present in a sample, the resolved PCA loading should have negative bands due to the dependent (competent) component.[6,7] Therefore, the positive spectra indicate that both spectra represent independent chemical species. In our case, as shown later, the independent species should be the bulk and the boundary water molecules. The peak position of the second loading is found at 3219 cm^{-1}, which is extraordinarily low in wavenumber by comparison to the regular bands,[4] and it is not recognized in the raw ATR spectra. After the curve fitting to the second PCA loading spectrum, the loading was found to comprise at least four bands: 3612, 3580, 3361, and 3217 cm^{-1}.

The eigenvalues[14] that correspond to the first and the second loadings are 8.40×10^0 and 2.61×10^{-3}, respectively. Since an eigenvalue correspond to the squared variance of spectral change in hyperspace,[15] the intensity-change scale of the second PCA loading is roughly evaluated to be 56.8 times less than that of the first PCA loading. Therefore, the thickness-change scale of the first loading (Δd_{p_1}) can be used to evaluate that of the second loading (Δd_{p_2}) where d_p is the penetration depth[16] as

$$d_p = \frac{\lambda/n_1}{2\pi(\sin^2 \Theta - (n_1/n_2)^2)^{1/2}} \qquad (1)$$

The penetration-depth change (Δd_p) at the Si ($n_1 = 3.42$)/water ($n_2 = 1.33$) interface at 3500 cm^{-1}, when the angle of incidence (Θ) changed from 50° to 75°, was calculated to be 53.6 nm. Therefore, the thickness scale of the boundary layer that yields the second PCA loading spectrum is roughly evaluated to be less than 1.0 nm (53.6/56.8). This evaluation supports that the resolved spectrum possibly arises from the boundary water layer whose thickness is estimated to be several angstroms.

According to Osawa et al.,[17] when a SEIRA spectrum of water is observed at a Au/water interface with an electric potential of 0.77 V [vs reversible hydrogen electrode (RHE)], a very weak spectrum is observed in which a broad band approximately at 3200 cm^{-1} and a sharp band at 3612 cm^{-1} are found. The broad band at the low wavenumber suggested that the boundary water molecules formed a monolayer with an ice-like network structure. On the other hand, the sharp band suggested that the boundary molecules had a non-hydrogen-bonded OH moiety. The result obtained as the second loading in the present study is also comprised of a broad band centered at 3217 cm^{-1} and a sharp component at 3612 cm^{-1}. This good consistency strongly suggests that the boundary water spectrum is readily resolved by PCA from the collected ATR spectra. The important point in the present study is that such minute chemical information
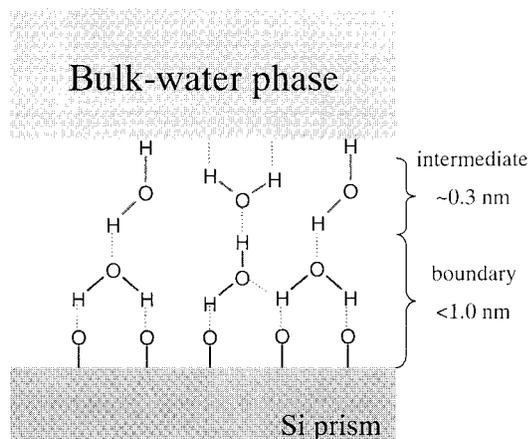
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Figure 5. Schematic image of boundary- and intermediate-water molecules between the Si surface and bulk water as determined by the present analysis. Hydrogen-bonding among the water molecules is schematically drawn by the thin dotted line.

Figure 6. SEIRA spectrum of water near the Si surface measured at an angle of incidence of 70° (solid curve). An ATR spectrum at 50° is presented for comparison.

has been readily obtained on a nonmetallic surface without using surface enhancement effect.

Nuzzo et al.[18] performed infrared RA measurements of an ultrathin water layer (approximately 1.0 nm) on a cold metal surface that was chemically treated to be hydrophobic. They clearly demonstrated that a low-wavenumber peak appeared approximately at 3250 cm^{-1} when the water molecules formed a polycrystalline film. Bensebaa and Ellis[4] also performed similar experiments for thin water layers on metal surfaces. They readily made a crystalline-state water film via annealing (145 K), and found that the crystalline film yielded a band at 3230 cm^{-1}. Therefore, we consider that the boundary water molecules in this study have a polycrystalline structure near the Si surface. Nevertheless, the band position (3217 cm^{-1}) is still lower than the positions reported for the artificial polycrystalline water films. This suggests that the *real* boundary water molecules form a network structure with stronger intermolecular hydrogen-bonding, which will be more finely discussed later.

The third loading spectrum has a complicated feature, in which positive and negative bands appear simultaneously, which are approximately 3200 and 3430 cm^{-1}, respectively. This strongly suggests that this spectrum is arisen from dependent chemical components as the discussion earlier. The wavenumbers are almost the same as those of the band from the boundary water (second loading) and that from the bulk water (1st loading), respectively. Since a loading presents a spectrum as if it derived from an identical chemical species, the third loading suggests that there is an intermediate layer, in which bulk and boundary water molecules are mixed to form inseparable species (dependent components). The eigenvalue of the third loading is 3.58×10^{-4}, which is a little less than that of the second loading. With the eigenvalue, the thickness of the intermediate layer was evaluated to be approximately 0.3 nm, which corresponds to the thickness of one monolayer. Since the %SL markedly increases for the fourth and higher loadings, it is most possible that there exist bulk-, intermediate-, and boundary-water species near the interface.

The evaluation of thickness above suggests that the intermediate layer consists of nearly single layer, which is formed by the boundary- and bulk-water molecules via hydrogen-bonding. These images are schematically presented in Figure 5. Previous theoretical[19−26] and experimental[27] studies have already suggested that the thickness of boundary water layers with specific molecular arrangements is about several layers from the solid surface. The results in the present study are consistent with the
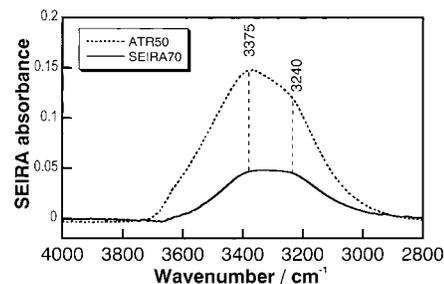
previous discussion, and we can further propose a schematic that the specific-arrangement layers consist of *the* boundary layer and the intermediate layer.

It is of interest that the s-polarization infrared ATR spectra provide only two chemically meaningful loadings: %SL values of only the first two loadings are below 5%, and those for others are above 16%. The first two s-polarization loading spectra (data not shown) are similar to the first and third p-polarization loading spectra in Figure 4. In other words, the second loading by p-polarization spectra is missing in the s-polarization loadings. This indicates that the second loading calculated from the p-polarization spectra corresponds to minor water species that has surface-perpendicular vibrational components for the O−H stretching vibration, which is presented in Figure 5. This species would no absorption to the s-polarization measurements. The molecular orientation of the boundary layer is inconsistent with the schematic in ref 3.

Nevertheless, the newly proposed molecular schematic is understandable when the surface treatment of the Si prism is taken into account. As described in the Experimental Section, the Si-prism surface was cleaned by use of ozone cleaner. The generated ozone not only reacts with surface contaminants to eliminate, but also reacts with Si surface to yield Si−OH bonds. The Si−OH strongly interacts with the boundary water via hydrogen-bonding, which has most boundary molecules to have perpendicular orientation of the bisector of the H−O−H angle to the prism surface (Si−O...H−O−H...O−Si).[28] This strong hydrogen-bonding is considered to be a reason to cause the very low wavenumber for the O−H stretching vibration band (3217 cm^{-1}). Although this wavenumber is sensitive to surface charge of the prism surface especially when the surface has no OH groups, it would be concluded that the oxidized surface would be a controlling factor to make the boundary water molecules oriented perpendicularly to the surface irrespective of surface charge.

Since the strongly hydrogen-bonded O−H bonds have larger absorption index (k) than the free O−H bond, it is possible to consider that the second loading spectrum is derived from a thinner layer than the evaluated value above (<1.0 nm). If the absorption index of the hydrogen-bonded form has, as found in general, double of the free form, the thickness must be corrected to be less than 0.5 nm, which suggests that the thickness of the layer almost corresponds to a monolayer. In this manner, it has been suggested that the infrared spectra of the bulk, intermediate, and boundary water are divisible by the first three PCA loadings.

To verify the discussion above, a SEIRA spectrum was measured at the angle of incidence, 70°. The gold particles were thinly evaporated on the Si surface with 12.0-nm thickness. This spectrum is represented by a solid curve in Figure 6. For comparison, an ATR spectrum at 50° is also presented in the

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figure. Since the penetration depth of SEIRA is shallow, the entire intensity of the SEIRA spectrum becomes smaller than that of the ATR spectrum. It should be noted that the relative intensity of the band at 3375 cm^{-1} to that at 3240 cm^{-1} is significantly different between the SEIRA and ATR spectra. The lower band markedly increases in the SEIRA spectrum, which suggests an increase in the contribution of the boundary water layer. By using the present SEIRA system, a pure spectrum of only boundary- or intermediate-water molecules could not be measured, and instead, mixed spectra of the three kinds of water molecules were obtained. In this manner, it is quite difficult to have pure chemical component spectra experimentally, and if possible, they are observed under very limited conditions. These results and discussion indicate, therefore, that FARMS makes a new way to analyze minute chemical species in a limited space.

Given the results of the present study, we have shown that the matter of spatial resolution can be overcome by use of FARMS that is a characteristic of PCA. Since the spectral information of a minute species is resolved statistically, mixed spectra of boundary and bulk water can be directly used for the analysis, which yields resolved spectra with high signal-to-noise ratio. The PCA analysis of VAPS-ATR spectra enabled us to discuss the molecular orientation, which could not be performed with the raw data even by SEIRA or infrared RA spectrometry. In addition, our PCA results have suggested that the O−H stretching vibration band at ca. 3200 cm^{-1} is arisen from hydrogen-bonded O−H groups, although this band was assigned to the overtone of the O−H bending vibration mode via Fermi resonance enhancement.[29] For the structural analysis of a boundary phase in an aqueous system by infrared spectrometry, in this manner, the combination technique of infrared VAPS-ATR and PCA has proven to be very powerful.

Supporting Information Available: For reference, we have evaluated dispersion curves of both real and imaginary parts of the refractive index of bulk water. This material is available free of charge via the Internet at http://pubs.acs.org.

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