Transmission IR Micro-Spectroscopy of Interfacial Water between Colloidal Silica Particles*

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Interfacial water among silica particles were measured on silica colloid suspensions (0–31.1 vol.%) by transmission infrared micro-spectroscopy. The difference absorption index k spectra from the pure water of silica colloid suspensions with varying volume fractions have residual components in the O-H stretching region: the 3620 cm$^{-1}$ component increased linearly with the silica volume fraction, while the 3620 cm$^{-1}$ component increased and the 3380 cm$^{-1}$ component decreased with much less linearity. The 3060 and 3620 cm$^{-1}$ components are considered to be characteristic to the surface silanol and interfacial water and affected by overlapping diffuse electrical double layers among silica particles.

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I. INTRODUCTION

Liquid water at solid surfaces has been reported to have some properties different from those of bulk based on experiments and computer simulations. Such water, called interfacial water, is thought to play a key role in geological, biological, environmental, and material sciences [1–3]. The water-mineral interaction between the interfacial water and minerals is thought to be important for understanding the mineral dissolution, fluid flow and weathering processes [4]. Interfacial water spreading in the range of several water molecular layers (≈1–2 nm) has been studied in many experiments such as surface force apparatus (SFA) [5, 6], X-ray scattering [7, 8], atomic force microscopy (AFM) [9], and vibrational spectroscopy.

Concerning the vibrational spectroscopy, infrared (IR) measurements were often used to investigate the water structure, because the O-H stretching band reflects hydrogen bond distances [10]. In particular, sum-frequency generation (SFG) and second harmonic generation (SHG) spectroscopy were often used to measure the interfacial water at solid/water boundaries. SFG and SHG have been used for solid/water or air/water interfaces [11–19], because of their selectivity of the interfacial water due to its molecular orientation.

Silica is one of the representative solid earth’s surface materials and have also been studied by material scientists. Silica/water interfaces were studied by SFG [15–17] and liquid-like (≈3400 cm$^{-1}$) and ice-like (≈3200 cm$^{-1}$) water components were found on silica surfaces.

Interfacial water in solid/water/solid system, which is called as confined water, has been studied mostly by molecular dynamic simulations [20–23]. Modified ion distributions in pore waters of silica [20] and mica [21] have been observed. The diffusion coefficients were found to be smaller for pore sizes less than about 1 nm [21, 22].

Anomalous dielectric constants in nanopores (1.2 nm) of silica were also reported [23]. These modified properties can be related to the electrical double layer (EDL) [24]. Water in porous silica as the hydrophilic substrate was often studied experimentally [25–27]. Although numerical simulations such as molecular dynamics (MD) and ab-initio calculation were carried out for explaining experimental results [28, 29], there is few quantitative spectroscopic evaluation relating the above simulation and experimental results. Different natures of interfacial waters from the bulk liquid water were explained only qualitatively by the breaking of hydrogen bonding network surrounding the silica particles [25].

The SFG method characterizes only the water molecules at the very interface. However, in geological environments, water can be present in thicker films (1–100 nm) on minerals such as quartz [30], and little is known on the changes of water structure with thickness.

Attenuated total reflection (ATR) IR spectroscopy can be used to study mineral/water interfaces by means of evanescent waves with thick solution layers placed on mineral films. The measured depth of penetration of evanescent waves in the OH stretching region is about 500–200 nm [31]. This depth is too thick to observe structural modifications of interfacial water. Moreover, OH band shapes are distorted by effects of variation of penetration depth of evanescent wave with wavenumber and anomalous dispersion due to complex refractive index [31]. Therefore, appropriate corrections are necessary to extract structural information on interfacial water.

In this study, quantitative transmission IR spectra are measured on colloidal silica suspensions with appropriate corrections and the spectroscopic features of interfacial water are extracted. The transmission spectroscopy is the most reliable quantitative method following the Lambert-Beer’s law. The concentrations of colloidal silica suspensions were changed in order to vary thicknesses of interfacial water among silica particles. Increase/decrease of different OH band components of water with decreasing distances among silica particles are determined. The results are discussed based on overlapping electrical double layers spreading on the silica surfaces.

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FIG. 1. (a) Schematic figure for the sample setup. Colloidal silica suspension was injected between the top CaF$_2$ plate (6.0 mm $\phi$, 1.0 mm thick) and the bottom CaF$_2$ plate (13.0 mm $\phi$, 1.0 mm thick) bound by a silicon resin. (b) Incident and refracted lights through a sample sandwiched between two CaF$_2$ plates. Angles ($\theta$), refractive indices ($n$) and transmission ($T$) and reflection ($R$) at interfaces are indicated.

II. EXPERIMENTAL

A. Colloidal silica suspensions

The colloidal silica suspensions of different concentrations from 0–31.1 vol.% sandwiched between two CaF$_2$ plates were measured by transmission IR micro-spectroscopy (Fig. 1a). A commercial colloidal silica suspension was purchased (Ludox LS, Sigma-Aldrich). The original silica suspension as Na$_2$SiO$_4$ was made by evaporation of the original one by dry air bubbling or heating. According to the manufacturer report, SO$_4^{2-}$ (≤0.02 wt.%) is included in the original colloidal silica suspension as Na$_2$SO$_4$, which gives a range of $\sim$10$^{-4}$–10$^{-3}$ mol/L for different concentrations (0–31.1 vol.%).

B. Transmission IR spectroscopy

Two CaF$_2$ plates of 1mm thick were attached together by using silicon glue to fix the gap between the two plates (Fig. 1a). The thickness of this gap was determined to be about 1–2 $\mu$m by measuring an absorption spectrum of pure water and fixing the spectrum by the absorption by the complex refractive index of pure water [32]. The above suspensions were put between these two CaF$_2$ plates and IR transmission spectra were measured. The small changes of the gap distance (≤2%) after changing the sample was monitored by the IR absorbance of the silicon grew at 2960 cm$^{-1}$.

The IR transmission measurements were conducted by using an FTIR micro-spectrometer (FTIR620+IRT30: Jasco Corp.) equipped with a ceramic IR source, a Ge coated KBr beam splitter and an MCT (HgCdTe) detector. Cassegrainian focusing and objective mirrors were used in the IR microscope. All the transmission spectra were obtained by collecting 64 scans with a spectral range of 700–7000 cm$^{-1}$, 4 cm$^{-1}$ wavenumber resolution and 100 $\times$ 100 $\mu$m$^2$ aperture. The background spectrum was first measured through a 2 mm thick CaF$_2$ plate having the same total thickness of two CaF$_2$ plates. The measured transmission spectra of sample solutions were then recorded as absorbance: $Abs_{\text{meas.}} = -\log_{10}(I/I_0)$ (where $I_0$ is the background spectrum). The maximum error range in the O–H stretching band region (2600–3800 cm$^{-1}$) of the obtained spectra was estimated as ±0.001 in the absorbance unit (dimensionless).

C. Extraction of absorption index $k$ spectra

The obtained spectra include effects of reflections at plate/sample and plate/air interfaces (Fig. 1b). These effects cause the distortion of O–H stretching band in apparent absorption spectra. In order to obtain intrinsic absorption features of water molecules, the absorption index $k(\tilde{\nu})$ is extracted from the measured spectra composed of complex refractive index (n = n + ik) with the real (n(\tilde{\nu})) and imaginary (k(\tilde{\nu})) parts. The procedure is mainly after Keefe et al. [33], using Fresnel equations for reflection and is presented below.

Complex refractive index $n(\tilde{\nu})$ of the sample solutions should be first determined. The imaginary part, or absorption index $k(\tilde{\nu})$ is calculated by the following equation using the measured absorption spectrum $Abs_{\text{meas.}}$.

$$k(\tilde{\nu}) = \frac{\ln 10 \cdot Abs_{\text{meas.}}(\tilde{\nu})}{4\pi d}$$

where $\tilde{\nu}$ is the wavenumber [cm$^{-1}$] and $d$ is the sample thickness [cm]. ln 10 is the conversion factor from the measured absorbance in common logarithmic scale to the natural logarithmic scale.

The real part $n(\tilde{\nu})$ of the refractive index at a given wavenumber $\tilde{\nu}_a$ is calculated from $k(\tilde{\nu})$ by the following Kramers-Kronig transformation [34, 35].

$$n(\tilde{\nu}_a) = n_{\infty} + \frac{2\pi P}{\pi} \sum_{i=0}^{\infty} \frac{\tilde{\nu}_a k(\tilde{\nu})}{\tilde{\nu}_a^2 - \tilde{\nu}_i^2}$$

$n_{\infty}$ is taken as $n$ values at 590 nm without absorption for each sample suspension. $P$ is the Cauchy principal value. These values were determined by the following equation [36]:

$$n = n_1 + (m_2 - m_1)v,$$

where $n_1$ is the refractive index of the medium (water: 1.333) [37], $m_2$ is the refractive index of a silica particle (fused silica: 1.458) [38], and $v$ is the volume fraction of colloidal particles. The validity of this equation was confirmed by the measurements of sample solutions by an Abbé refractometer (TGK, ER-2S).

These obtained sample refractive index $n(\tilde{\nu})$ are used to calculate the apparent absorbance. The calculated apparent spectrum can be described by the following equation including reflections at different interfaces (Fig. 1b):
\[
Abs_{\text{cal}}(\tilde{\nu}) = -\log \left[ \frac{\cos^4(\theta_0 - \theta_1) T_S(\tilde{\nu})(1 + 2R_S(\tilde{\nu}) R'_S(\tilde{\nu}) + T_P(\tilde{\nu})(1 + 2R_P(\tilde{\nu}) R'_P(\tilde{\nu})))}{\cos^4(\theta_0 - \theta_1) + 1} \right].
\]

The expression of reflection and transmission are developed by the Fresnel amplitude coefficients of the reflected and transmitted radiations:

\[
\begin{align*}
    r_{i,j,s} &= \frac{n_i \cos \theta_i - n_j \cos \theta_j}{n_i \cos \theta_i + n_j \cos \theta_j} \\
    t_{i,j,s} &= \frac{2n_i \cos \theta_j}{n_i \cos \theta_i + n_j \cos \theta_j} \\
    r_{i,j,p} &= \frac{n_j \cos \theta_i - n_i \cos \theta_j}{n_j \cos \theta_i + n_i \cos \theta_j} \\
    t_{i,j,p} &= \frac{2n_j \cos \theta_i}{n_j \cos \theta_i + n_i \cos \theta_j}
\end{align*}
\]

where

\[
\begin{align*}
    \cos \theta_1 &= \sqrt{1 - \frac{1}{n_1^2} \sin \theta_0} \\
    \cos \theta_2 &= \sqrt{1 - \frac{1}{n_2^2} \sin \theta_0}
\end{align*}
\]

The reflection at plate/sample interface \(R(1 \to 2)\), the sample transmission \(T(1 \to 2 \to 1)\) and the reflection at plate/air interface \(R'(1 \to 0)\) (Fig. 1b) can be written as the followings reported by Hawranek et al. [39], respectively:

\[
\begin{align*}
    R &= \frac{2r^2(1 - \cos 2\delta)}{1 + r^4 - 2r^2 \cos 2\delta} \\
    T &= \frac{t_1^2 t_2^2}{1 + r^4 - 2r^2 \cos 2\delta} \\
    R' &= t_1^{10}
\end{align*}
\]

where

\[
\begin{align*}
    \delta &= 2\pi \tilde{\nu} d n_2 \cos \theta_2 \\
    r_{12} &= r_{21} = r
\end{align*}
\]

The value of refractive index \(n_1\) for CaF₂ at the IR wavenumber range was calculated from the dispersion formula [40].

These equations (4-14) are substituted in the equation (3) and \(Abs_{\text{cal}}\) could be obtained. The \(k(\tilde{\nu})\) is replaced by the following relation:

\[
k_{\text{new}}(\tilde{\nu}) = k_{\text{old}}(\tilde{\nu}) \times \frac{Abs_{\text{meas.}}}{Abs_{\text{cal}}}. \tag{15}
\]

The above procedures are repeated until the root mean square of \([Abs_{\text{meas.}} - Abs_{\text{cal}}]\) is less than \(10 \times 10^{-5}\).

FIG. 2. Absorption index \(k\) spectra of the colloidal silica suspensions for different volume fractions (0–31.1 vol.%).

### III. RESULTS

#### A. Absorption index \(k\) spectra for colloidal silica suspensions

The absorption index spectra (Fig. 2) were obtained from the transmission IR spectra for colloidal silica suspensions sandwiched between two CaF₂ plates by the above calculation procedures. A broad absorption band around 3400 cm\(^{-1}\) and a small band at 1640 cm\(^{-1}\) are assigned to OH stretching and H–O–H bending vibrations of water molecules, respectively [41]. A sharp band at 1120 cm\(^{-1}\) can be assigned to Si–O stretching vibration of colloidal silica particles [42]. A small band at 2350 cm\(^{-1}\) is due to atmospheric CO₂.

#### B. Difference Absorption index \(k\) spectra from pure bulk water

In order to examine changes of O–H stretching band shape, difference absorption index \(k\) spectra from the pure water spectrum for each silica colloid volume fraction were calculated (Fig. 3). The \(k\) spectra were first normalized to the peak height at H–O–H bending band (1640 cm\(^{-1}\)) of colloidal silica suspensions in order to eliminate the bulk water and extract the spectroscopic feature of the interfacial water. The bending band has been often used as an indicator of bulk water because of its less sensitivity for the hydrogen bond structure than the stretching band [43].

These difference \(k\) spectra show the following changes with increasing silica colloid volume fraction (Fig. 3):

1. Decrease in the intensity around 3380 cm\(^{-1}\)
2. Increase in the intensity around 3620 cm\(^{-1}\)
3. Increase in the intensity around 3060 cm\(^{-1}\)
The decreasing intensity at around 3380 cm\(^{-1}\) in the difference \(k\) spectra for increasing silica colloid volume fraction (Fig. 3) may correspond to a loss of the bulk water feature in the interfacial water. On the other hand, the increasing intensity at around 3620 and 3060 cm\(^{-1}\) for increasing silica colloid volume fraction can be attributed to characteristics of the surface and interfacial species. The 3620 and 3060 cm\(^{-1}\) components correspond to OH species with longer and shorter H bonds, respectively, based on the relation of O–H band frequency and H bond distance [10].

C. 3620, 3060 and 3380 cm\(^{-1}\) band components

The band areas of these interfacial water components at the different volume fractions of silica were calculated (Fig. 4). The band area of the 3380 cm\(^{-1}\) component (3455–3220 cm\(^{-1}\)) decreases with the silica volume fraction. On the other hand, the band areas of the 3620 cm\(^{-1}\) (4000–3455 cm\(^{-1}\)) and the 3060 cm\(^{-1}\) (3220–2500 cm\(^{-1}\)) components increase with the silica volume fraction.

The increase of the 3060 cm\(^{-1}\) component appears to be proportional to the silica volume fraction. However, the increase of the 3620 cm\(^{-1}\) component and the decrease of the 3380 cm\(^{-1}\) component show less linearities. Although data are somewhat scattered, these two components might show some saturations at higher silica volume fractions.

IV. DISCUSSION

A. Interfacial and surface OH components

The obtained results showed increase/decrease of three OH components at 3620, 3380 and 3060 cm\(^{-1}\) in the difference spectra from bulk water with increasing silica volume fractions (Fig. 4). Since the 3380 cm\(^{-1}\) component decrease with silica volume fraction, this component can correspond to the bulk water. In fact, OH band for pure water has a band maximum around 3400 cm\(^{-1}\) (Fig. 2). This bulk component is corresponding to “liquid-like” water component around 3400 cm\(^{-1}\) with random orientations observed in SFG measurements of water at silica/water interfaces [15, 16].

The 3620 cm\(^{-1}\) component is considered to be longer H bond water molecules than the bulk “liquid-like” water. The band position is somewhat lower than the 3690 cm\(^{-1}\) component observed by SFG, which is called “free OH” [15].

The 3060 cm\(^{-1}\) component corresponds to shorter H bond water molecules than the bulk. This component was not clearly observed in SFG spectra but can be obscured by the intense band around 3200 cm\(^{-1}\) due to “ice-like” water at the silica surface [15, 16]. The absence of 3200 cm\(^{-1}\) component in our transmission spectra might be due to the general presence of this “ice-like” component throughout the silica/water system. On the other hand, oriented “ice-like” water molecules on the silica surface were selectively observed in SFG spectra.

Sulpizi et al. (2012) calculated IR spectra for interfacial water by density functional theory molecular dynamics simulations (DFTMD) [29]. Two bands around 3080 and 3200 cm\(^{-1}\) were found for surface silanol groups, which are strongly hydrogen bonded each other. They reported also that water molecules bonded to out-of-plane and in-plane surface silanols are located at 3160 cm\(^{-1}\) (ice-like) and 3400 cm\(^{-1}\) (liquid-like)
3300 cm$^{-1}$ (liquid-like), respectively. Subsequent water layers show absorption bands around 3280 cm$^{-1}$ with a shoulder around 3550 cm$^{-1}$ [29]. Therefore, the 3060 cm$^{-1}$ component observed in our study can correspond to surface silanol component around 3080 cm$^{-1}$ reported by Sulpizi et al. (2012) [29]. On the other hand, the 3620 cm$^{-1}$ component might correspond to weakly hydrogen bonded subsequent water layers after the first water layers strongly hydrogen bonded to the surface silanols.

If the 3060 cm$^{-1}$ component is due to in-plane surface silanol which is strongly H bonded to adjacent out-of plane surface silanol, in-plane Si–OH vibrations could not be observed by SFG, because of its selectivity to the OH dipole moments normal to the surface plane.

### B. Evaluation of closest distance among silica particles

In order to discuss origins of increase/decrease of the 3620, 3380 and 3060 cm$^{-1}$ band areas with increasing silica volume fraction, these might be related to overlapping electrical double layer (EDL) developed around colloidal silica particles. The spreading length of the diffuse layer, the outer layer of EDL, can be characterized by the Debye length [24]. Since the initial colloidal silica suspension (16.5 vol.%) includes Na$_2$SO$_4$ as a stabilizing agent, the Debye length equation for a salt with cation : anion molar ratio of 2 : 1 is:

$$\kappa^{-1} = 1.76 \times 10^{-10} (C_{\text{salt}})^{-1/2} [\text{m}]$$

The concentration of Na$_2$SO$_4$ ($C_{\text{salt}}$ [mol/L]) can be calculated for each volume fraction of the colloidal silica solutions based on the initial concentration at 16.5 vol.% ($\sim$0.02 wt.%). The obtained Debye length is plotted against the silica volume fraction in Fig. 5.

Since the diffuse layer spreads from each silica particle surface, the closest distance of silica particles (Fig. 4) should be divided by 2 to compare with the Debye length. The half closest distance among silica colloids is plotted in Fig. 5. The Debye length (red curve) crosses the half closest distance (blue curve) at 5 nm for about 13 vol.% of silica. Therefore, electrical double layers around silica particles can start overlapping from about 13 vol.% with the closest distance of about 5 nm. This overlap might explain the attenuation of increase/decrease of 3060 and 3380 cm$^{-1}$ components at larger silica volume fractions (Fig. 5).

### C. Electrical double layer model

The different behavior of 3620 cm$^{-1}$ and 3060 cm$^{-1}$ components with increasing colloidal silica concentrations observed in this study (Fig. 4) can be explained by the following model: The lower wavenumber component (3060 cm$^{-1}$) are confined near the silica surface and can increase with increasing colloidal silica concentrations (Fig. 5). This can correspond to surface silanol component around 3080 cm$^{-1}$ reported by Sulpizi et al. (2012) [29]. On the other hand, the higher wavenumber water component (3620 cm$^{-1}$) would extend into the diffuse layer over the Debye length and would be saturated by the overlapping of diffuse layer among silica particles (Fig. 5). Therefore, this 3620 cm$^{-1}$ component might correspond to weakly hydrogen bonded subsequent water layers after the first water layers strongly hydrogen bonded to the surface silanols.

In the overlapping electrical double layers, high concentrations of H$^+$ and Na$^+$ cations can be attained and these can be adsorbed on the negatively charged silica surface at slightly alkaline environment of the present study (pH=8.2). Water molecular structures might be then modified according to the surface species of silica [15]. The confinement of water molecules in small nanometer-scale pore spaces may cause structural modification of water associated with the electrical double layer developing on the material surfaces. These models can be discussed more precisely and quantitatively by more experimental data by controlling the electrical double layers and surface species together with the simulation such as molecular dynamics (MD) calculation.
V. CONCLUSIONS

The difference absorption index $k$ spectra from the pure water were extracted from transmission infrared spectra on silica colloid suspensions with varying volume fractions (0–31.1 vol.%) sandwiched between two CaF$_2$ plates of 1 mm thick under an infrared microscope. The difference spectra in the O–H stretching region have three components showing different behavior with increasing silica volume fraction: the 3060 cm$^{-1}$ component increased linearly with the silica volume fraction, while the 3620 cm$^{-1}$ and 3380 cm$^{-1}$ components increased/decreased with less lineairities. The attenuation of these increase/decrease appears to correspond to the half closest distance of about 5 nm indicating overlapping electrical double layers. The 3060 cm$^{-1}$ and 3620 cm$^{-1}$ components are considered to be characteristic to the surface silanol and interfacial water and affected by overlapping electrical double layers among silica particles.