A Raman spectroscopy study on the effects of intermolecular hydrogen bonding on water molecules absorbed by borosilicate glass surface

Fabing Li, Zhanlong Li, Ying Wang, Shenghan Wang, Xiaojun Wang, Chenglin Sun, Zhiwei Men

ABSTRACT

The structural forms of water/deuterated water molecules located on the surface of borosilicate capillaries have been first investigated in this study on the basis of Raman spectral data obtained at different temperatures and under atmospheric pressure for molecules in bulk and also for molecules absorbed by borosilicate glass surface. The strongest two fundamental bands locating at 3063 cm\(^{-1}\) (2438 cm\(^{-1}\)) in the recorded Raman spectra are assigned here to the O\(\cdot\)H (O\(\cdot\)D) bond stretching vibrations and they are compared with the corresponding bands observed at 3124 cm\(^{-1}\) (2325 cm\(^{-1}\)) in the Raman spectrum of ice Ih. Our spectroscopic observations have indicated that the structure of water and deuterated water molecules on borosilicate surface is similar to that of ice Ih (hexagonal phase of ice). These observations have also indicated that water molecules locate on the borosilicate surface so as to construct a bilayer structure and that strong and weak intermolecular hydrogen bonds are formed between water/deuterated molecules and silanol groups on borosilicate surface. In accordance with these findings, water and deuterated water molecules at the interface of capillary have a higher melting temperature.

1. Introduction

Water is one of the most important and basic materials in living systems. Despite its apparent molecular simplicity, it has long been considered as complex nature [1]. Water interfaces play an essential role in many surface science phenomena. Examples range from electrochemistry [2,3] and micelle formation [4] to biological processes, such as protein activity [5] and membrane stability [4]. In the recent years, the structural properties of water molecules absorbed on a surface have been intensively investigated both experimentally and theoretically. In the experimental investigations, the small-angle X-ray scattering [6], neutron scattering [7], nuclear magnetic resonance methods [8], and the nonlinear spectroscopic methods, such as optical second harmonic generation [9] and sum-frequency generation [10,11] have been utilized. In the theoretical investigations, molecular simulation methods [12,13] and Ab-initio types of calculation methods [14] have been utilized. Normally, the obtained calculation results need to be confirmed by experimentally, however, the experimental techniques previously used are rather difficult to survey the interactions of water molecules. At this point, Raman spectroscopy, which can provide the data that can be used in analysing the fundamental vibrations of water molecules, their structural properties as well as their interactions with each other and with the other molecules in the medium [15,16], proves its benefit and efficiency. As also reported in earlier studies, Raman bands are sensitive to the structural changes or phase transitions under specific conditions (high or low temperature, high pressure and interface) [17], and they can be used in the elucidation of the structural properties of water molecules under different conditions.

In our study, we report the results of our investigations on water and deuterated water molecules located at the interfaces between the water/deuterated water sample and the borosilicate capillary (primarily \(\text{SiO}_2\)) surface. The results indicate that the interaction of hydrogen bond (O\(\cdot\)H \(\equiv\) O and O\(\cdot\)D \(\equiv\) O) [18] and electric field on borosilicate surface leads to the structure of water and deuterated water molecules similar to that of ice Ih, and water at the interface of capillary melts at about 333 K. Determination of the strong and weak intermolecular hydrogen bonds indicates that the water molecules adsorbed on the capillary surface are located in a bilayer structure, and this is very important in understanding the structural properties of water molecules at the interfaces between water and absorbing surface.

2. Experimental Measurements

The water sample in liquid form we used in the spectroscopic measurements was obtained by deionizing a triple distilled water sample. The deuterated water sample used in the measurements was of 99.8%...
purity. First, the water and deuterated water samples were put into two separated borosilicate capillaries with 0.3 mm radius, the main component of which is SiO₂ (about 80%), Na₂O and B₂O₃, and then, their Raman spectra were recorded by using a Renishaw InVia model micro Raman spectrometer equipped with an argon laser of 5145 Å wavelength and an output power of 10.7 mW. The spectra in backscattering configuration were obtained by using an objective lens with 50× long working distance and numerical aperture (N.A.) of 0.45 mm. In recording the spectra, the objective lens was focused first on the liquid water/deuterated water and then on the interfaces between the water/deuterated water and borosilicate capillary surface. The axial resolution reached in these spectroscopic measurements was 5 μm, as previously reported in ref. [20]. At the first stage of the measurement process, the high precision Raman spectra were recorded from the surfaces of the prepared water and deuterated water samples. At the next stage, the focal point of the objective lens was moved step by step towards the interface between the water/deuterated water sample and the borosilicate capillary surface (see Fig. 1), and during this operation, a new Raman spectrum was recorded from each point on which the objective was focused. When the measurements were completed, we obtained a series of Raman spectra from both the liquid water and deuterated water samples and the interfaces between the water/deuterated water samples and borosilicate capillary surface. At the final stage of the measurement process, we recorded the Raman spectrum of the borosilicate capillary used in the measurement process. The spectra were recorded with a scanning speed of 10 cm⁻¹/s and a spectral resolution of 4 cm⁻¹ by using a grating of 1200 lines/mm. During the measurement process, a Linkam PE95 heating-freezing stage with 0.1 K accuracy was utilized to control the position and temperature of the ice Ih (at 253 K), H₂O and D₂O samples investigated at different temperatures.

3. Theoretical Calculations

In all the theoretical calculations performed in this study, Gaussian09 [21]. On the other hand, in visualizing the intermolecular hydrogen bonding interactions between water molecules and silanol (SiOH) groups, Gaussian VIEW software [22], which is a utility software providing graphical interfaces for visualizing the output data of Gaussian and similar software, was used. The model used in the calculations is the “Self-Consistent Isodensity polarizable Continuum Model” (SC-PCM) [23]. In calculation of the vibrational spectral data, which are used in predicting the observed Raman spectra, the harmonic oscillator approach was used.

4. Results and Discussion

Fig. 2(a) and Fig. 2(d) show the spectra of bulk H₂O and D₂O, respectively. In these spectra, three water bands locate at 3256, 3412, and 3622 cm⁻¹, while the corresponding three deuterated water bands locate at 2390, 2521 and 2630 cm⁻¹. We assign the bands at 3256 (2390) and 3412 cm⁻¹ (2521 cm⁻¹) to the symmetric and antisymmetric O-H (O-D) bond stretching vibrations, respectively. On the other hand, the bands at 3622 cm⁻¹ (2630 cm⁻¹) are the corresponding assignments for the OH (OD) bond stretching vibrations of free water and deuterated water molecules.

Fig. 2(b) and Fig. 2(e) show the Raman spectra recorded at room temperature and under atmospheric pressure from the interface between water/deuterated water molecules and borosilicate surface. In these spectra, the strongest bands locate at 3063 cm⁻¹ (2348 cm⁻¹) and the corresponding bands in the Raman spectra of ice Ih locate at 3124 cm⁻¹ (2325 cm⁻¹).

The water bands at 3063 and 3160 cm⁻¹ (2348 and 2466 cm⁻¹) are our corresponding assignments for the antisymmetric and symmetric O-H (O-D) bond stretching vibration of tetrahedrally coordinated water molecules [24–28]. It has been previously reported by Dr. Du et al. [11] that the intensity of the band at 3160 cm⁻¹ can be seen as an indication of the molecular arrangement of water molecules [11]. In the literature, the Raman band at 3398 cm⁻¹ has been assigned to the stretching vibrations of the water molecules coordinated through bifurcated hydrogen bonds [29] and the intensity of this band has been shown as an indication of the disorder at the molecular arrangement of water molecules [11]. On the other hand, the Raman band at 3576 cm⁻¹ has been assigned to the antisymmetric O-H stretching vibration of asymmetrically bonded water molecules [11].

As can be seen from Fig. 2c and f, the spectra that we recorded at 253 K under atmospheric pressure for ice Ih of H₂O and D₂O include the spectral regions 2800–4000 cm⁻¹ and 2200–2700 cm⁻¹. In these spectra, the Raman bands due to the stretching vibrations of water molecules locate at 3124, 3237 and 3347 cm⁻¹ and the corresponding bands for deuterated water molecules locate at 2325, 2452 and 2450 cm⁻¹. In the literature, the Raman bands located at 3347 cm⁻¹ (2450 cm⁻¹) have been assigned to the symmetric O-H (O-D) stretching vibrations of water and deuterated water molecules [30]. In the Raman spectra given here, the bands at 3124 cm⁻¹ (2325 cm⁻¹) have the maximum intensity, and we assign them to the antisymmetric
O—H (O—D) stretching vibrations of water and deuterated water molecules. To our view, the shoulder band at 3237 cm\(^{-1}\) (2452 cm\(^{-1}\)) is an overtone band due to bending vibration of water and deuterated water, and a Fermi resonance is observed between the overtone band (around 3347 cm\(^{-1}\)) due to the bending vibration and the fundamental band (around 3347 cm\(^{-1}\)) due to the symmetric O—H stretching vibration, all of which locate in the high frequency region of the observed spectra [31,32]. The fundamental and overtone bands observed in our Raman spectra and their assignments are given in comparison in Table 1.

Also, for the bands observed for water/deuterated water molecules in ice Ih, in bulk, and also on the borosilicate capillary surface, some parameters such as “wavenumber”, “half-maximum (FWHM)” and “difference of intensities (\(\Delta I\))” are shown in the Table 2. As can be seen from this table, the spectral data of water/deuterated water in bulk form considerably differ from the spectral data obtained from the interface between the water/deuterated water molecules the capillary surface. This situation clearly indicates to the difference between the molecular arrangements of water/deuterated water molecules in bulk form and those on the capillary surface. From their band characteristics, one can confidently say that the three bands observed at 3063, 3160, and 3398 cm\(^{-1}\) in the spectra obtained from the water-capillary interface and the other three bands observed at 3124, 3237, and 3347 cm\(^{-1}\) in the spectra obtained for ice Ih are corresponding bands. If these bands (see Fig. 2(b), (c)) are compared, it is seen that their characteristics are very similar and this situation indicates to the similarity between the molecular arrangements of water molecules located on the borosilicate surface and the ones in ice Ih (hexagonal phase of ice). The same conclusion is obtained also for deuterated water molecules when the corresponding bands in Fig. 2(e) and (f) are compared.

The Raman spectra of water and deuterated water which were recorded at 323 and 333 K are shown in Fig. 3. These spectra have shown that the observed bands will shift to higher wavenumber values when the temperature of the sample is increased. Also, they also show that the band at 3063 cm\(^{-1}\) (2348 cm\(^{-1}\)) gradually decreases in intensity, and eventually, completely disappears if the temperature continues to increase. This situation indicates to a change in the molecular arrangement of water molecules located at the water-capillary interface. It should also be noted here that the Raman spectrum of deuterated water molecules located at the interface differs from that of the deuterated water in bulk form at 333 K. These results reveal that water at the interface of capillary melts at a higher temperature (about 333 K).

The chemical structure of SiO\(_2\) surface has been previously reported in the literature [33]. When a cleaned silica surface is covered by bulk...

---

**Table 1**

Comparison of the Raman bands observed for water/deuterated water molecules in ice Ih and in bulk with those observed for water/deuterated water molecules absorbed by borosilicate surface.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>H(_2)O (bulk)</th>
<th>H(_2)O (surface)</th>
<th>Ice Ih</th>
<th>D(_2)O (bulk)</th>
<th>D(_2)O (surface)</th>
<th>Ice Ih</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetric</td>
<td>3256</td>
<td>3160</td>
<td>3347</td>
<td>2390</td>
<td>2466</td>
<td>2450</td>
</tr>
<tr>
<td>Antisymmetric</td>
<td>3412</td>
<td>3063</td>
<td>3124</td>
<td>2521</td>
<td>2348</td>
<td>2325</td>
</tr>
<tr>
<td>Free OH</td>
<td>3622</td>
<td>3398</td>
<td>2360</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The bifurcated hydrogen bond</td>
<td>3237</td>
<td>2515</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overtone</td>
<td>3237</td>
<td>2515</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. The antisymmetric O—H (O—D) stretching vibrational mode of tetrahedrally coordinated water molecules.

b. The antisymmetric O—H stretching vibrational mode of asymmetrically bonded water molecule.

d. H\(_2\)O in bulk; e: H\(_2\)O on the capillary surface; f: H\(_2\)O in ice Ih.

d. Difference between the intensities of the first and second peaks (from low to high wavenumber).

**Table 2**

The fundamental Raman bands observed for the O—H bond stretching vibrations of water molecules (in bulk, in ice Ih and on the surface of capillary).

<table>
<thead>
<tr>
<th>H(_2)O (bulk)</th>
<th>H(_2)O (surface)</th>
<th>Ice Ih</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu^0) (cm(^{-1}))</td>
<td>3256 3412 3622 3063 3160 3398 3576 3124 3237 3347</td>
<td></td>
</tr>
<tr>
<td>FWHM (cm(^{-1}))</td>
<td>241 210 126 176 65 270 56 150 50 236</td>
<td></td>
</tr>
<tr>
<td>(\Delta I) (a.u.)</td>
<td>(-50 \quad 600 \quad 609)</td>
<td></td>
</tr>
</tbody>
</table>

a. Wavenumber.

b. Difference between the intensities of the first and second peaks (from low to high wavenumber).
SiOH groups (silanol groups), the water molecules are adsorbed on the surface of silica through hydrogen bonding interactions with silanol groups (see Fig. 4) [14]. The Raman spectrum of SiOH and those of the water molecules coordinated with SiOH groups have been simulated by Gaussian software in Fig. 5, where two new bands at 3520 and 3578 cm$^{-1}$ resulting from water molecules are shown. The band located at 3578 cm$^{-1}$ in the theoretical spectra obtained for H$_2$O + SiOH is associated with the band at 3576 cm$^{-1}$ in the experimental Raman spectra obtained from the water-capillary interface. On the other hand, the theoretical band at 3520 cm$^{-1}$ is attributed to the OH stretching vibrations of water molecules coordinated with SiOH groups through hydrogen bonding interactions.

As also simulated in Fig. 4, each adsorbed water molecule, which has two acceptor and two donor parts for hydrogen bonding interactions, can form four hydrogen bonds with one surface-hydroxyl (in SiOH group) and three neighbour water molecules. The adsorption energy is about 712 meV/H$_2$O [14], which is close to adhesive energy reported for bulk ice, 720 meV/H$_2$O [34]. Besides, for a sufficiently low proton concentration of water (high pH values), silanol groups can be negatively charged by deprotonation. The pH values higher than or equal to 10 indicate to the presence of fully ionized silanol groups on the surface [35]. It has been reported that the surface negative charges can generate a strong electric field near the surface, which depends on the dielectric saturation [36]. The pH value of distilled water is about 7.
and the borosilicate capillaries with Na$_2$O enhance the pH value of water molecules at the water-capillary interface. The solubility of borosilicate glasses in the ultrapure water is around 1.5 and 2.5 ppm, and a sufficient amount of hydrogen is dissolved so as to enhance the pH value, which generates a strong electric field. It has been reported that, under such an electric field, the molecular arrangement of water molecules is ice-like [11]. In agreement with this determination, the molecular arrangement of water molecules at the water-borosilicate capillary interface is similar to the arrangement of water molecules in ice Ih. By supporting our results, Dr. Hu et al. [37] have reported that the molecular arrangement of water molecules at mica (primarily SiO$_2$) surface is similar to that in ice Ih.

The OH stretching modes of water molecules coordinated with the others through hydrogen bonding interactions have been previously studied by Wang et al. [38]. According to their view, one of these stretching modes (its energy is 388 eV) indicates to the presence of a strong hydrogen bonding interaction, while the other (its energy is 432 eV) indicates to the presence of a weak hydrogen bonding interaction. Our spectroscopic observations (see Fig. 2) have shown that one of the Raman bands due to the OH stretching vibrations of water molecules at the water-capillary interface locates at 3063 cm$^{-1}$ (or 378 MeV), which is quite close to the value (388 MeV) indicating the presence of a strong hydrogen bonding interaction. On the other hand, the other Raman band resulting from the OH bond stretching vibrations of water molecules at the interface locates at 3398 cm$^{-1}$ (or 419 MeV), which is quite close to the value (432 MeV) indicating to the presence of a weak hydrogen bonding interaction. Similarly, in the Raman spectra of ice Ih (see Fig. 2 c), the bands at 3124 and 3237 cm$^{-1}$ can be associated with the presence of a strong hydrogen bonding and with the presence of a weak hydrogen bonding interaction, respectively [25,31,39–41]. In the Raman spectra of water molecules absorbed by borosilicate surface, the corresponding bands locate at 3063 and 3160 cm$^{-1}$. While the former indicates to the presence of a strong hydrogen bonding interaction, the later indicates to the presence of a weak hydrogen bonding interaction. As a conclusion, the hydrogen bonds formed between water molecules at the water-borosilicate interface can be classified into two types. As simulated in Fig. 4, the presence of one strong hydrogen bond (confirmed by the band at 3063 cm$^{-1}$) and the presence of two weak hydrogen bonds (confirmed by the bands at 3160 and 3398 cm$^{-1}$), indicate that the molecular arrangement of water molecules adsorbed by borosilicate surface is of bilayer structure [38]. By supporting our results, Doering et al. [42] have reported that the water molecules of bilayer structure construct a puckered hexagonal network as in the bulk ice.

5. Conclusions

Our spectroscopic observations have shown that the strongest two bands in the Raman spectra of water/deuterated water molecules absorbed by the borosilicate capillary surface locate at 3063 cm$^{-1}$ (2438 cm$^{-1}$) and these two bands can be associated with the other two strong bands observed at 3124 cm$^{-1}$ (2325 cm$^{-1}$) in the Raman spectrum of ice Ih. The obtained results have confirmed that hydrogen bonding interactions and electric field around the borosilicate capillary surface form the molecular arrangement of water and deuterated water absorbed by the surface and make it similar to that of ice Ih. The results have also revealed that water/deuterated water molecules adsorbed on the borosilicate capillary surface construct a bilayer structure depending on the strong and weak intermolecular hydrogen bonding interactions between the water molecules and silanol groups. These findings are important in understanding the structural properties of water/deuterated molecules located on the borosilicate surface. In agreement with our spectroscopic observations, water/deuterated water molecules absorbed by borosilicate surface lead to a higher melting point (at about 333 K) with respect to that of liquid water.

Acknowledgement

This work was supported by National Natural Science Foundation of China (NSFC) (11574113, 11604024 and 11374123).

References