

## Investigations of the Structure of H<sub>2</sub>O Clusters Adsorbed on TiO<sub>2</sub> Surfaces by Near-Infrared Absorption Spectroscopy

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The overtone and combination bands of the fundamental vibration modes ( $\nu_1$ , symmetric stretching;  $\nu_2$ , bending; and  $\nu_3$ , asymmetric stretching) attributed to the H<sub>2</sub>O molecules adsorbed on a TiO<sub>2</sub> surface could be observed in the near-infrared (NIR) region. Especially, two absorption bands attributed to the combination ( $\nu_2 + \nu_3$ ) and ( $\nu_1 + \nu_3$ ) modes of the H<sub>2</sub>O molecules adsorbed on the TiO<sub>2</sub> surface were observed at around 1940 and 1450 nm, respectively. From detailed investigations on the ( $\nu_2 + \nu_3$ ) combination band, it was found that H<sub>2</sub>O molecules adsorbed on a TiO<sub>2</sub> surface aggregate to form clusters due to the high surface tension of H<sub>2</sub>O arising from the intermolecular hydrogen bonds, and the hydrogen-bonded H<sub>2</sub>O in the bulk part of the cluster and the hydrogen-bond-free H<sub>2</sub>O in the outside spherical part of the cluster could be easily distinguished. Furthermore, it was quantitatively confirmed that the relaxation of the surface energy accompanying the adsorption of H<sub>2</sub>O on the TiO<sub>2</sub> surface stabilized the adsorption states of the hydrogen-bonded H<sub>2</sub>O molecules, while on the other hand, the hydrogen-bond-free H<sub>2</sub>O molecules became unstable as compared to the liquid-phase H<sub>2</sub>O molecules.

### Introduction

FT-IR [middle infrared (MIR), 2.5–25  $\mu\text{m}$ ] measurement is generally one of the most powerful and useful methods in the investigation of adsorption states of H<sub>2</sub>O molecules on solid surfaces.<sup>1–9</sup> However, MIR beams are so sensitive, not only to the H<sub>2</sub>O molecules adsorbed on the surface of samples but also to the H<sub>2</sub>O vapor in instruments, that the FT-IR instruments, especially the optical part, detector, and sample chamber, should be dried as well as possible during measurements. Furthermore, to obtain the spectra with sufficient signal-to-noise ratios in the OH stretching modes of the surface hydroxyls and H<sub>2</sub>O molecules adsorbed on solid surface, the samples should be outgassed under at least 10 kPa in an in situ FT-IR cell. On the other hand, the near-infrared (NIR, 800–2500 nm) absorption spectra are hardly affected by H<sub>2</sub>O vapor under ambient conditions due to the much smaller molar absorption coefficient of H<sub>2</sub>O in NIR regions as compared to that for MIR regions. This advantage makes it possible to measure the spectra of H<sub>2</sub>O molecules adsorbed on powder samples under ambient atmospheres and to provide useful information on the adsorption states of H<sub>2</sub>O and the characters of solid surfaces, such as hydrophilicity or hydrophobicity. It is well-known that the overtone and combination bands of the fundamental vibration modes attributed to H<sub>2</sub>O molecules can be obtained in the NIR region. The NIR adsorption spectra of liquid water, ice, and water vapor have widely been investigated in order to clarify the structures of complicated hydrogen-bonded H<sub>2</sub>O molecules;<sup>10–17</sup> however, the structures of H<sub>2</sub>O clusters adsorbed on a solid surface under ambient conditions have yet to be clarified.

In this study, diffuse reflectance NIR (DR-NIR) measurements of TiO<sub>2</sub> powder were carried out under ambient conditions in order to qualify and quantify the intermolecular hydrogen bonds of H<sub>2</sub>O clusters adsorbed on a TiO<sub>2</sub> surface. Furthermore, the adsorption states of H<sub>2</sub>O molecules on a TiO<sub>2</sub> surface are discussed from the standpoint of the hydrogen bonds.

### Experimental Section

The diffuse reflectance near-infrared (DR-NIR) absorption spectra of H<sub>2</sub>O adsorbed on TiO<sub>2</sub> (P-25, Degussa) were recorded in air at ambient temperature on a UV–vis–NIR spectrophotometer equipped with an integrating sphere (Varian, Cary 5). The NIR absorption spectra of distilled liquid H<sub>2</sub>O in quartz cells with different path lengths (10, 2, and 1 mm) and a FT-IR cell equipped with CaF<sub>2</sub> windows (thickness of spacer ca. 80  $\mu\text{m}$ ) were recorded as references in the transmittance mode at room temperature on a UV–vis–NIR spectrophotometer (Perkin-Elmer, Lambda 19). The CaF<sub>2</sub> crystal is highly transparent in the NIR region (800–2500 nm). The background for the NIR measurements was calibrated with BaSO<sub>4</sub> powder in the diffuse reflectance mode and with air in the transmittance mode, respectively. The FT-IR absorption spectra of the TiO<sub>2</sub> self-supporting pellet were measured at room temperature by a FT-IR spectrometer (Bruker, IFS-28) equipped with a MCT detector. The background for the FT-IR measurements was calibrated with a blank IR cell equipped with CaF<sub>2</sub> windows.

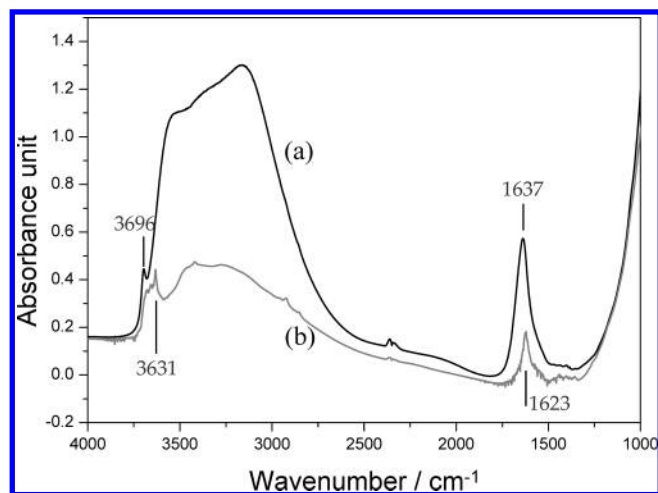
### Results and Discussion

Figure 1 shows the typical FT-IR (MIR, middle infrared) absorption spectra of the TiO<sub>2</sub> powder sample measured in air and after degassing at room temperature. For the spectrum of P-25 measured in air, a broad absorption band at around 3600–2800 cm<sup>−1</sup> and a small peak at 3696 cm<sup>−1</sup> were observed. The

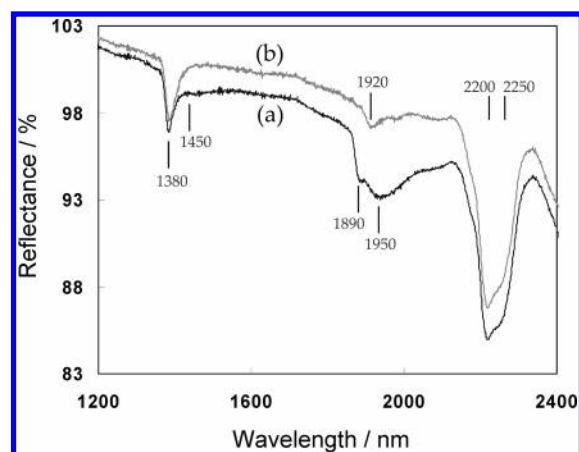
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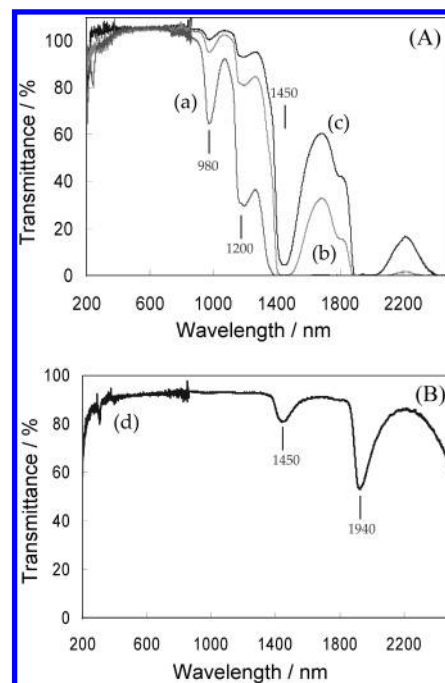
**Figure 1.** FT-IR (MIR) absorption spectra of TiO<sub>2</sub> (P-25) in air (a) and after evacuation at room temperature for 1 h (b).



**Figure 2.** Diffuse reflectance NIR absorption spectra of H<sub>2</sub>O adsorbed on TiO<sub>2</sub> (P-25) in air (a) and after evacuation at room temperature (b).

assignments of these two absorption bands are well-known to be the stretching vibration modes of the H<sub>2</sub>O molecules, which have complex interactions by hydrogen bonds, and the end part of the polymeric chained H<sub>2</sub>O molecules without hydrogen bonds, respectively.<sup>2–4,7,9</sup> This broad absorption band at around 3600–2800 cm<sup>−1</sup> corresponding to the polymeric chained H<sub>2</sub>O molecules contains not only the components of the H<sub>2</sub>O molecules with different numbers of hydrogen bonds but also the Fermi resonance attributed to the overtone absorption of the bending mode of the H<sub>2</sub>O molecule at 1637 cm<sup>−1</sup>. The difficulty in excluding the effect of the Fermi resonance from the components of the hydrogen-bonded H<sub>2</sub>O molecules makes it difficult to analyze the detailed adsorption state and the structure of the polymeric chained H<sub>2</sub>O molecules on solid surfaces by FT-IR (MIR) measurement. Furthermore, as the MIR beams are quite sensitive to H<sub>2</sub>O molecules, the FT-IR absorption spectra of the H<sub>2</sub>O molecules adsorbed on solid surfaces measured under ambient conditions are generally in saturation.

The absorption coefficient of the combination bands observed in the NIR region is too small; however, the resolution of each peak in the NIR absorption spectra is much higher as compared to the absorption spectra in the MIR region. This indicates that detailed investigations of the combination bands can reveal the structure of complex hydrogen-bonded H<sub>2</sub>O molecules adsorbed on solid surfaces under ambient conditions. Figure 2 shows the diffuse reflectance NIR (DR-NIR) absorption spectrum of the TiO<sub>2</sub> powder under ambient conditions. The typical absorption band attributed to the band gap excitation of the TiO<sub>2</sub> semi-



**Figure 3.** UV-Vis-NIR absorption spectra (transmittance) of liquid H<sub>2</sub>O. (A) Quartz cells, path length (a) 10, (b) 2, and (c) 1 mm. (B) FT-IR cell (CaF<sub>2</sub> window), path length (spacer) (d) ca. 80 μm.

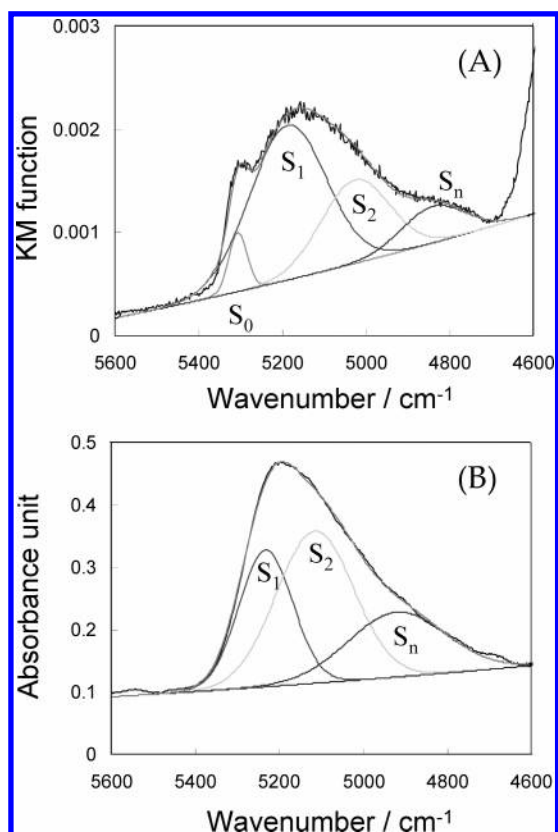
conductor was observed at around 390 nm (spectra not shown here). Small adsorption bands could be observed at around 1950, 1890 (as a shoulder), and 1450 nm. The former two peaks can be assigned to the combination ( $\nu_2 + \nu_3$ ) band of the bending ( $\nu_2$ ) and asymmetric stretching ( $\nu_3$ ) of the fundamental vibration modes of the H<sub>2</sub>O molecules,<sup>13,15–17</sup> while, the latter is assigned to the combination ( $\nu_1 + \nu_3$ ) band of the symmetric ( $\nu_1$ ) and asymmetric ( $\nu_3$ ) stretching vibration modes.<sup>12,16,17</sup> Furthermore, sharp peaks could also be observed at 2200, 2250 (as a shoulder), and 1380 nm. The former two bands are due to the combination ( $\nu + \delta$ ) bands of the stretching ( $\nu$ ) and bending ( $\delta$ ) modes of the nonbonded and bonded silanol groups of the quartz cell, and the latter is due to the overtone ( $2\nu$ ) absorption band of the stretching ( $\nu$ ) of silanol groups.<sup>16</sup> These absorption bands attributed to the silanol groups of the quartz cell did not change even after evacuation at 1073 K, indicating that these silanol groups exist in the bulk of the SiO<sub>2</sub> matrices and do not affect the NIR absorption spectra of the powder samples. The most part of the combination ( $\nu_2 + \nu_3$ ) band at around 1950 nm was found to disappear and a small absorption band at 1920 nm remained after evacuation at room temperature. Moreover, this small absorption band at 1920 nm disappeared completely after evacuation at 473 K. These results clearly show that these combination bands due to H<sub>2</sub>O molecules observed in the NIR region are attributed to the physisorbed H<sub>2</sub>O molecules rather than the hydroxyl groups of the TiO<sub>2</sub> surface. Detailed explanations of these absorption bands will be discussed from the standpoint of the hydrogen bonds in H<sub>2</sub>O clusters.

As shown in Figure 3, the NIR absorption spectra of liquid H<sub>2</sub>O in quartz cells with different path lengths (10, 2, and 1 mm) and in a FT-IR cell equipped with CaF<sub>2</sub> window and thin spacer (thickness ca. 80 μm) were measured in the transmittance mode at room temperature as references. Investigations on the NIR absorption spectra of various chemical states of H<sub>2</sub>O have been intensively carried out since the 1960s in order to clarify the hydrogen bonds of liquid- or solid-phase H<sub>2</sub>O clusters. The assignments of the combination bands of the H<sub>2</sub>O molecules were extracted from refs 10–17 and are summarized in Table

**TABLE 1: List of the Combination Bands Due to Different States of H<sub>2</sub>O Molecules Observed in the Near IR Region**

ice, cm <sup>-1</sup> (nm)	liquid near freezing point, cm <sup>-1</sup> (nm)	liquid near boiling point, cm <sup>-1</sup> (nm)	vapor, cm <sup>-1</sup> (nm)	assignments <sup>a</sup>
9760 (1025)	10 210 (979)	10 340 (967)	10 613 (942)	2ν <sub>1</sub> + ν <sub>3</sub>
7990 (1250)	8310 (1200)	8640 (1160)	8807 (1135)	ν <sub>1</sub> + ν <sub>2</sub> + ν <sub>3</sub>
6700 (1492)	6880 (1453)	7020 (1425)	7252 (1380)	ν <sub>1</sub> + ν <sub>3</sub>
5620 (1780)	5620 (1780)	5600 (1786)		ν <sub>2</sub> + ν <sub>3</sub> + ν <sub>L</sub>
5030 (1988)	5160 (1938)	5220 (1920)	5332 (1875)	ν <sub>2</sub> + ν <sub>3</sub>

<sup>a</sup> ν<sub>1</sub>, symmetric stretching (3657 cm<sup>-1</sup>); ν<sub>2</sub>, bending (1595 cm<sup>-1</sup>); ν<sub>3</sub>, asymmetric stretching (3756 cm<sup>-1</sup>); ν<sub>L</sub>, hindered rotation (600 cm<sup>-1</sup>).

**Figure 4.** Deconvoluted spectra of the combination band (ν<sub>2</sub> + ν<sub>3</sub>) at around 1950 nm. (A) H<sub>2</sub>O adsorbed on TiO<sub>2</sub> surface; (B) liquid H<sub>2</sub>O.

1. Liquid H<sub>2</sub>O showed four main absorption bands at 980, 1200, 1450, and 1940 nm in NIR region, depending on the path length. H<sub>2</sub>O in a 1-mm-thick quartz cell showed the absorption bands at 1450, 1200, and 980 nm. These bands are well-known to be assigned to the combination bands (ν<sub>1</sub> + ν<sub>3</sub>),<sup>12,16,17</sup> (ν<sub>1</sub> + ν<sub>2</sub> + ν<sub>3</sub>),<sup>10,17</sup> and (2ν<sub>1</sub> + ν<sub>3</sub>),<sup>10,14,17</sup> respectively. As the path length of the quartz cell increases, the absorbance of the H<sub>2</sub>O in the NIR region increases, meaning that the transparency of the H<sub>2</sub>O in the NIR region becomes lower. Furthermore, H<sub>2</sub>O in a FT-IR cell (thickness of spacer ca. 80 μm) showed absorption bands at 1940 and 1450 nm, similar to the H<sub>2</sub>O molecules adsorbed on the TiO<sub>2</sub> surface. From these results, the assignments of the small peaks observed in the NIR absorption spectra of the TiO<sub>2</sub> powder could be justified. To obtain detailed absorption states of the H<sub>2</sub>O molecules, the deconvoluted spectra of the combination (ν<sub>2</sub> + ν<sub>3</sub>) band of H<sub>2</sub>O adsorbed on TiO<sub>2</sub> and liquid H<sub>2</sub>O at around 1950 nm are shown in Figure 4. The NIR absorption bands of H<sub>2</sub>O adsorbed on the TiO<sub>2</sub> surface and liquid H<sub>2</sub>O could be deconvoluted into four and three components, respectively. The wavenumbers (wavelengths) of these components

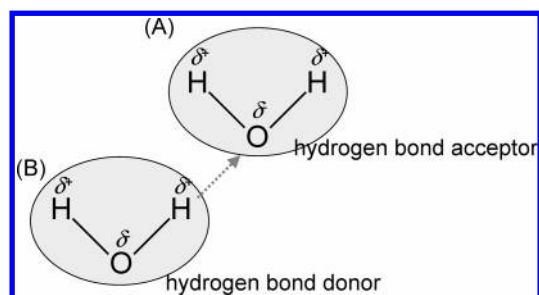
**TABLE 2: Components Determined by the Deconvolution of the Combination Band (ν<sub>2</sub> + ν<sub>3</sub>) at 1950 nm in the Near IR Region**

H <sub>2</sub> O adsorbed on TiO <sub>2</sub>	liquid H <sub>2</sub> O	no. of active H-bonds	state of H <sub>2</sub> O
5308 cm <sup>-1</sup> (1884 nm)	nd	0	S <sub>0</sub> ; H <sub>2</sub> O without active H-bonds
5188 cm <sup>-1</sup> (1928 nm)	5233 cm <sup>-1</sup> (1955 nm)	2	S <sub>2</sub> ; H <sub>2</sub> O with one active H-bond
5027 cm <sup>-1</sup> (1989 nm)	5116 cm <sup>-1</sup> (1955 nm)	2	S <sub>2</sub> ; H <sub>2</sub> O with active H-bonds
4841 cm <sup>-1</sup> (2066 nm)	4921 cm <sup>-1</sup> (2032 nm)	2	S <sub>n</sub> ; H <sub>2</sub> O with two active and one (or two) passive H-bond(s) (polymeric chained H <sub>2</sub> O molecules)

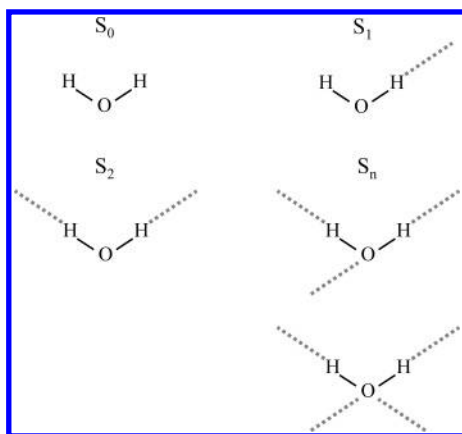
are summarized in Table 2. In the case of H<sub>2</sub>O adsorbed on the TiO<sub>2</sub> surface, these four components can be assigned to the different structures of the H<sub>2</sub>O molecules, which depend on the number of intermolecular hydrogen bonds (S<sub>0</sub>, S<sub>1</sub>, S<sub>2</sub>, and S<sub>n</sub>).

When intermolecular hydrogen bonds are involved, two kinds of hydrogen bonds, such as a hydrogen-bond donor and a hydrogen-bond acceptor, should be considered. When one H<sub>2</sub>O molecule interacts with the other by a hydrogen bond, as illustrated in Figure 5, molecule A works as a hydrogen-bond acceptor and molecule B works as a hydrogen-bond donor. The O atom of molecule A strongly attracts not only the H atom of molecule A but also the H atom of the neighbor molecule B due to high electron affinity. The polarization of the H<sub>2</sub>O molecule arises from the former interaction, and the latter works as the driving force for intermolecular hydrogen bonds. In this case, the OH bond of molecule B is strongly affected but the OH bond of molecule A is less affected. This means that the hydrogen bond as a donor may show a large shift in the chemical states of the H<sub>2</sub>O molecule as compared to a hydrogen bond as an acceptor. The hydrogen bond donors/acceptors can be expressed to be “active hydrogen bonds” and “passive hydrogen bonds”. From these considerations, concrete models of the H<sub>2</sub>O molecules with different numbers of hydrogen bonds are illustrated in Figure 6. One H<sub>2</sub>O molecule can possess four hydrogen bonds (two active and two passive) at the maximum, but the active hydrogen bond is much more important than the passive one. It is actually quite difficult to distinguish these two types of hydrogen bonds, which work between the H<sub>2</sub>O molecules; however, in this work, the effect of the passive hydrogen bond as an acceptor is considered negligible.

Component S<sub>0</sub> of the H<sub>2</sub>O adsorbed on the TiO<sub>2</sub> surfaces observed at 5308 cm<sup>-1</sup> (1884 nm) was found to show a similar wavenumber as H<sub>2</sub>O vapor, 1875 cm<sup>-1</sup>, and component S<sub>2</sub> observed at 5027 cm<sup>-1</sup> (1989 nm) showed almost the same wavenumber as ice, 1988 cm<sup>-1</sup>, as summarized in Table 2. These results clearly indicate that the physicochemical properties of the H<sub>2</sub>O molecules in the S<sub>0</sub> and S<sub>2</sub> structures are quite similar

**Figure 5.** Interaction between two H<sub>2</sub>O molecules by hydrogen bonds. (A) Hydrogen-bond acceptor; (B) hydrogen-bond donor.

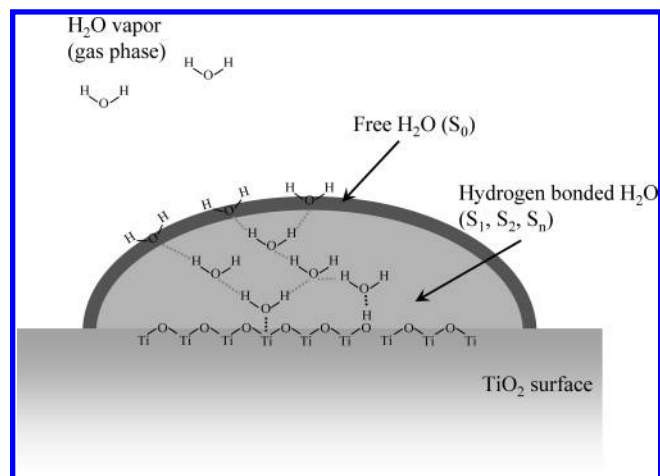




**Figure 6.** Component models of H<sub>2</sub>O molecules with different numbers of hydrogen bonds: (—) covalent bonds; (---) hydrogen bonds.

to those of H<sub>2</sub>O vapor without active hydrogen bonds and ice (solid-phase H<sub>2</sub>O) interacting with the complex hydrogen bonds, respectively. H<sub>2</sub>O molecules in S<sub>n</sub> structure are expected to contain two active hydrogen bonds as donors and one (or two) additional passive hydrogen bond(s) as acceptors. Furthermore, H<sub>2</sub>O molecules in S<sub>n</sub> structure are thought to be rigid due not only to the intermolecular hydrogen bonds but also to the strong interaction with the solid surface. On the other hand, the combination ( $\nu_2 + \nu_3$ ) band of liquid-phase H<sub>2</sub>O was deconvoluted into three components of the hydrogen-bonded H<sub>2</sub>O molecules (S<sub>1</sub>, S<sub>2</sub>, and S<sub>n</sub>). An absorption band due to the S<sub>0</sub> structure, such as gas-phase-like H<sub>2</sub>O molecules without hydrogen bonds, was not observed in liquid-phase H<sub>2</sub>O. Each component attributed to the hydrogen-bonded H<sub>2</sub>O (S<sub>1</sub>, S<sub>2</sub>, and S<sub>n</sub>) was found to shift toward lower wavenumber regions after adsorption on the TiO<sub>2</sub> surface. Generally, the driving force for the adsorption of various molecules on solid surfaces is the relaxation of the surface energy. These red shifts observed in the hydrogen-bonded H<sub>2</sub>O molecules clearly indicate that the chemical states of the H<sub>2</sub>O molecules on the surface are stabilized by the adsorption process. Furthermore, the ratio of S<sub>1</sub> to S<sub>2</sub> for H<sub>2</sub>O adsorbed on the TiO<sub>2</sub> surface was found to be larger than that for liquid-phase H<sub>2</sub>O, meaning that the degree of the hydrogen bonds in H<sub>2</sub>O on the TiO<sub>2</sub> surface is smaller when compared to liquid H<sub>2</sub>O; that is, the structure of the H<sub>2</sub>O clusters adsorbed on a TiO<sub>2</sub> surface is more flexible as compared to liquid H<sub>2</sub>O.

From these considerations, the structural model of an H<sub>2</sub>O cluster on a solid surface composed by H<sub>2</sub>O multilayers could be proposed as shown in Figure 7. The H<sub>2</sub>O molecules, which directly interact with the solid surface such as surface cations or surface hydroxyls, form a monolayer as chemisorbed H<sub>2</sub>O molecules and then the hydrogen-bonded H<sub>2</sub>O molecules form multilayers as physisorbed H<sub>2</sub>O molecules (S<sub>1</sub>, S<sub>2</sub>, and S<sub>n</sub>). Finally, H<sub>2</sub>O molecules without active hydrogen bonds cover the polymeric chained H<sub>2</sub>O molecules to form the outermost shell of the H<sub>2</sub>O cluster (S<sub>0</sub>). These polymeric chained H<sub>2</sub>O molecules (S<sub>1</sub>, S<sub>2</sub> and S<sub>n</sub>) are called “hydrogen-bonded water”, while on the other hand, the hydrogen-bond-free H<sub>2</sub>O molecules (S<sub>0</sub>) in the outermost shell are called “free water”. Nosaka et al.<sup>18</sup> have observed one sharp and two broad signals attributed to the H<sub>2</sub>O molecules adsorbed on a TiO<sub>2</sub> thin film sample by <sup>1</sup>H NMR measurements. They have discussed these three kinds of H<sub>2</sub>O as a layer model due to their different molecular mobilities; however, the different chemical properties of these H<sub>2</sub>O molecules have not yet been discussed in terms of the number of hydrogen bonds. It is well-known that <sup>1</sup>H NMR



**Figure 7.** Structural model of H<sub>2</sub>O cluster adsorbed on the solid surface.

spectra due to H<sub>2</sub>O molecules in nonpolar solvents, such as deuterium-labeled benzene (C<sub>6</sub>D<sub>6</sub>) or toluene (C<sub>7</sub>D<sub>8</sub>), show a sharp peak with a small chemical shift, while on the other hand, H<sub>2</sub>O molecules in polar solvents, such as deuterium-labeled methanol (CD<sub>3</sub>OD) or D<sub>2</sub>O, show broad spectra with a large chemical shift. These differences can be correctly explained by the degree of hydrogen bonds that work between the H<sub>2</sub>O molecules.

Many FT-IR (MIR) studies on the adsorption of H<sub>2</sub>O on solid surfaces have already revealed that the polymeric chained H<sub>2</sub>O molecules with hydrogen bonds and the end part of polymeric chained H<sub>2</sub>O molecules without hydrogen bonds can be clearly distinguished.<sup>2–4,7,9</sup> However, as the effect of Fermi resonance attributed to the overtone absorption of the vending mode of the H<sub>2</sub>O molecule cannot be inevitable, it is difficult to obtain quantitative information on the hydrogen bonds of H<sub>2</sub>O molecules by FT-IR measurements.

## Conclusions

Combination bands attributed to the fundamental vibration modes of the H<sub>2</sub>O molecule ( $\nu_1$ , symmetric stretching;  $\nu_2$ , bending; and  $\nu_3$ , asymmetric stretching) adsorbed on a TiO<sub>2</sub> surface and liquid H<sub>2</sub>O could be observed in the near-infrared (NIR) absorption spectra. From detailed investigations on the combination band ( $\nu_2 + \nu_3$ ), quantitative and qualitative information about the intermolecular hydrogen bonds could be obtained. Moreover, the structural model of the H<sub>2</sub>O clusters adsorbed on solid surfaces could be proposed depending on the number of hydrogen bonds. In the multilayer H<sub>2</sub>O structure model, the H<sub>2</sub>O layer on the outermost shell was found to work as hydrogen-bond-free H<sub>2</sub>O-like gas-phase H<sub>2</sub>O molecules, while on the other hands, H<sub>2</sub>O molecules in the bulk part of the H<sub>2</sub>O clusters interact with each other rigidly by complex hydrogen bonds. Furthermore, relaxation of the surface energy, by which the chemical states of H<sub>2</sub>O molecules on a TiO<sub>2</sub> surface are stabilized by the adsorption as compared to liquid-phase H<sub>2</sub>O, could be quantitatively observed with the NIR absorption spectra attributed to the combination bands of H<sub>2</sub>O molecules.

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