

# Initial Growth of the Water Layer on (1 × 1)-Oxygen-Covered Ru(0001) in Comparison with that on Bare Ru(0001)

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The initial growth of a water (D<sub>2</sub>O) layer on (1 × 1)-oxygen-covered Ru(0001) has been studied in comparison with that on bare Ru(0001) by means of temperature-programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS). Although water molecules adsorbed on both bare and (1 × 1)-oxygen-covered Ru(0001) commonly tend to form hydrogen bonds with each other when mobility occurs upon heating, the TPD and IRAS measurements for the two surfaces exhibit distinct differences. On (1 × 1)-oxygen-covered Ru(0001), most of the D<sub>2</sub>O molecules were desorbed with a peak at 160 K, even at submonolayer coverage, as condensed water desorption. The vibration spectra of adsorbed D<sub>2</sub>O also showed broad peaks such as a condensed water phase, from the beginning of low coverage. For submonolayer coverage, in addition, we found a characteristic O–D stretching mode at around 2650 cm<sup>−1</sup>, which is never clearly observed for D<sub>2</sub>O on bare Ru(0001). Thus, we propose a distinctive water adsorption structure on (1 × 1)-oxygen-covered Ru(0001) and discuss its influence on water layer growth in comparison with the case of D<sub>2</sub>O on bare Ru(0001).

## 1. Introduction

The comparison and characterization of interactions between water and several solid surfaces still attract our interest relating not only to the fundamental aspects but also to numerous practical phenomena in electrochemistry, atmospheric chemistry, geochemistry, corrosion, wetting, and surface modification for products. A great number of studies have been performed using well-defined single-crystal substrates and many properties of the water layers have been characterized on the atomic scale.<sup>1,2</sup> Regarding the flexibility of hydrogen-bonding interactions of water molecules, significant property changes by atom or molecule coadsorption have been reported. In particular, oxygen adatoms on metal surfaces strongly affect the stability and structures of water layers. Here, we show new results that compare initial water layer growth on bare Ru(0001) and on well-ordered (1 × 1)-oxygen-covered Ru(0001), viz., (1 × 1)-O/Ru(0001), where oxygen adatoms fully cover the Ru(0001) substrate.<sup>3–5</sup>

Because of the close match in lattice constants between Ru(0001) (4.68 Å) and the basal plane of I<sub>h</sub>-phase crystal water ice (4.50 Å), an overlayer structure based on  $p(\sqrt{3} \times \sqrt{3})R30^\circ$  was observed and depicted using the basal water bilayer in I<sub>h</sub> ice, in early investigations.<sup>6–8</sup> Lately, a com-

mensurate  $p(\sqrt{3} \times \sqrt{3})R30^\circ$  structure assigned to the first D<sub>2</sub>O bilayer was clearly detected, and the separation between two vertically different D<sub>2</sub>O layers in the bilayer was estimated to be  $0.10 \pm 0.02$  Å (nearly coplanar), by low-energy electron diffraction (LEED) intensity analysis.<sup>9</sup> However, details of the water layer structures on the Ru(0001) surface are still under debate. In fact, a more energetically stable structure consisting of a partially dissociated bilayer has been proposed by recent theoretical calculations.<sup>10–13</sup>

A new view on very recent experimental reports<sup>14–16</sup> may solve this inconsistency. At more than 150 K, H<sub>2</sub>O dissociates and forms a stable mixed overlayer (H + OH + H<sub>2</sub>O) on Ru(0001), whereas D<sub>2</sub>O scarcely dissociates, even above the desorption temperature, e.g., 180 K, as its activation barrier is slightly higher than that of H<sub>2</sub>O.<sup>14,15</sup> The structure of the mixed overlayer has been reassigned to a longer range superstructure as  $p(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ .<sup>16</sup> Consequently, the mixed overlayer theoretically proposed is basically pertinent in the sketch of H<sub>2</sub>O on Ru(0001), but probably not for D<sub>2</sub>O. The difference in dissociation activity between H<sub>2</sub>O and D<sub>2</sub>O well-explains their anomalous isotope effects on bare Ru(0001), i.e., the higher-temperature desorption species for H<sub>2</sub>O in temperature-programmed desorption (TPD) measurements<sup>14,19</sup> and the long-range superstructures for H<sub>2</sub>O in LEED observations.<sup>18,20</sup>

The structure of the first water layer on Ru(0001) is yet under debate and the new view above-mentioned is a speculation. However, a quite recent theoretical study<sup>21</sup> has claimed the nondissociative D<sub>2</sub>O overlayer on Ru(0001), solving the discrepancies in both work function changes<sup>18</sup> and vibrational spectrum deviation<sup>22</sup> with theoretical predictions.<sup>10,13</sup> In addition, our recent study by precise TPD examination has shown a small reactivity for D<sub>2</sub>O dissociation on Ru(0001). If it is accepted

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that the dissociation of water molecules on Ru(0001) is an activated process<sup>12,15</sup> and the activation barriers for H<sub>2</sub>O and D<sub>2</sub>O dissociation differ, i.e., D<sub>2</sub>O has a higher activation barrier that is comparable to that for water molecule desorption from clean Ru(0001) as the conclusion in ref 15, the influence of thermal dissociation is regarded as little for the initial D<sub>2</sub>O layer growth on Ru(0001) below 162 K, which is the maximum temperature for the main discussion of water layer growth here. Therefore, we have inferred that the D<sub>2</sub>O molecules on Ru(0001) form an intact molecular layer probably based on the bilayer structure.

The preadsorption of a small amount of oxygen atoms strongly influences the structures and the kinetics of water layers on Ru(0001).<sup>7,8,14,23,24</sup> The strong interaction due to hydrogen bonds between water molecules and oxygen adatoms inhibits the ordered structure of the adsorbed water layer. In these previous studies, because precovered oxygen coverage was less than 0.5 ML {1 ML =  $1.6 \times 10^{15}$  cm<sup>-2</sup>, which is the same as the number of topmost Ru atoms on Ru(0001)}, the oxygen adatoms should form the (2 × 2)-O structure at near 0.25 ML or the (2 × 1)-O structure at near 0.5 ML and then induce a lattice misfit for the water bilayer formation. To remove the lattice misfit effect and to extract the actual interaction between oxygen adatoms and water molecules, we performed a study using (1 × 1)-O/Ru(0001) for comparison with that on bare Ru(0001).

In this paper, we show TPD and infrared reflection absorption spectroscopy (IRAS) results in order to delineate the initial D<sub>2</sub>O layer growth on bare Ru(0001) and on (1 × 1)-O/Ru(0001). The results clearly demonstrate the interaction differences of the water layers with bare or (1 × 1)-O-covered Ru(0001). In contrast to the fact that D<sub>2</sub>O molecules in the first layer on Ru(0001) desorb between 165 and 210 K, most of the D<sub>2</sub>O molecules on (1 × 1)-O/Ru(0001) desorb with a peak at about 160 K like condensed water desorption, even at submonolayer coverage. The IRAS results also show the interaction difference on bare and (1 × 1)-O-covered Ru(0001) in the coverage range of the submonolayer. In particular, we found an OD stretching mode at 2650 cm<sup>-1</sup> for D<sub>2</sub>O on (1 × 1)-O/Ru(0001), which has never been observed for D<sub>2</sub>O on bare Ru(0001). Then, we discuss the initial growth of water layers on bare Ru(0001) and on (1 × 1)-O/Ru(0001).

## 2. Experimental Section

The experiments were carried out in a UHV chamber (base pressure;  $2.0 \times 10^{-11}$  Torr) equipped with a quadrupole mass spectrometer for TPD, a Fourier transform infrared spectrometer for IRAS, and a gas delivery system. Details of the apparatus have been described elsewhere.<sup>25,26</sup> A Ru(0001) single-crystal was cooled to 25 K using a cryogenic refrigerator. It can be heated to 1560 K by electron bombardment of its back surface. The substrate temperature was monitored using a W5%Re–W26%Re thermocouple spot-welded at the crystal edge. The observed temperature was calibrated in comparison with the previous TPD results.<sup>17,19</sup> The Ru(0001) surface was cleaned by repeated cycles of Ar<sup>+</sup> sputtering, annealing, oxidation, and flashing up to 1560 K. Water (D<sub>2</sub>O) vapor was introduced through a pulse gas doser. Substantial predosing of the gas line with D<sub>2</sub>O was required to reduce the H<sub>2</sub>O background and to prevent D<sub>2</sub>O recombination to HDO on the walls of the gas line.

The (1 × 1)-O/Ru(0001) surface was prepared as follows, using a known procedure.<sup>3–5</sup> The Ru(0001) sample was kept at a temperature of 600 K and simultaneously exposed to NO<sub>2</sub> at

$1 \times 10^{-6}$  Torr for 10 min. The quality of the surface was confirmed by LEED, where the sharp (1 × 1) spots were observed. Heating of (1 × 1)-O/Ru(0001) up to 600 K was sufficient to repeat the water adsorption experiments, where no difference between the first and repeated measurements was confirmed.

The IRAS spectra were collected at a sample temperature of 25 K using 1500 scans at a resolution of 4 cm<sup>-1</sup>. The intensity of the IRAS spectra is shown as the ratio  $\Delta R/R$ , where  $\Delta R$  and  $R$  are the reflected intensities from the water-deposited surface and from the substrate surface, respectively. The TPD spectra were obtained at a heating rate of 1 K/s.

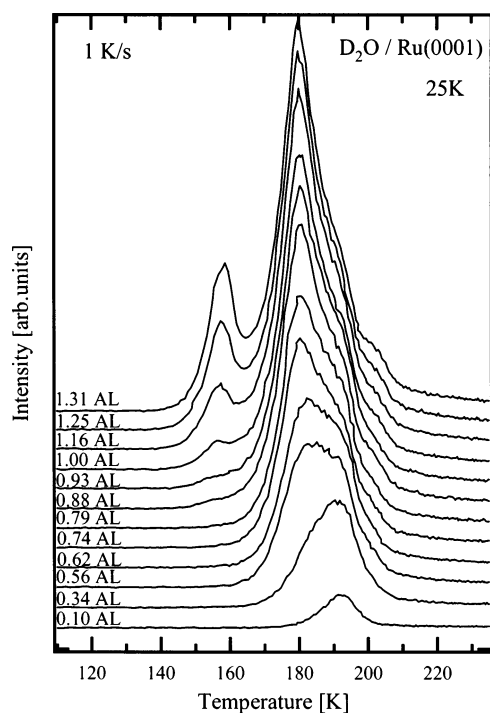
In this paper, the coverage of the saturated first D<sub>2</sub>O layer on Ru(0001) is defined as 1 AL (adsorption layer). If the saturated first D<sub>2</sub>O layer is regarded as the commensurate bilayer,<sup>9</sup> 1 AL corresponds to 0.67 ML. We used the following procedure to prepare the saturated first D<sub>2</sub>O layer: condensation of water multilayer at 25 K followed by annealing up to 162 K to remove the multilayer. This procedure led to a TPD spectra similar to that reported in the literature, in terms of desorption peak position and shape. The relative coverage was estimated from the D<sub>2</sub>O TPD integral between 130 and 230 K, since recent reports<sup>14,15,19</sup> have shown a very small thermal-dissociation probability for D<sub>2</sub>O on Ru(0001). For D<sub>2</sub>O on (1 × 1)-O/Ru(0001), the coverage is also given in the absolutely same unit “AL” for comparison with the results on bare Ru(0001) {the unit does not correspond to the first-layer saturation coverage on (1 × 1)-O/Ru(0001)} and is estimated using the same procedure for bare Ru(0001), since we also confirmed little D<sub>2</sub>O dissociation on (1 × 1)-O/Ru(0001).

## 3. Results

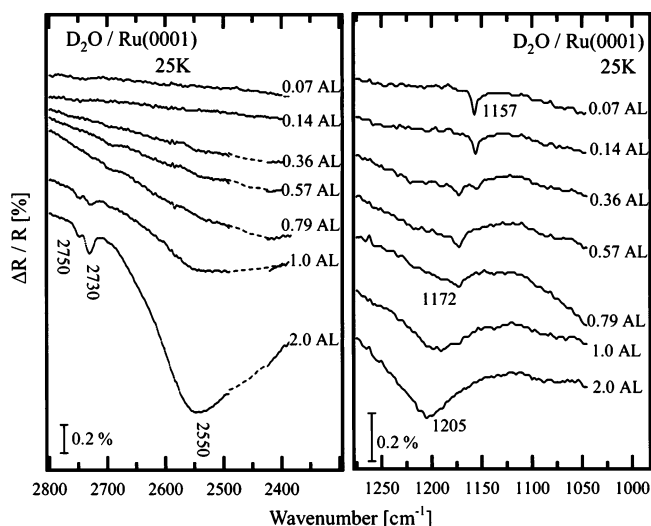
### 3.1. D<sub>2</sub>O on Ru(0001).

**3.1.1. TPD of D<sub>2</sub>O on Ru(0001).** To investigate the adsorptive properties of D<sub>2</sub>O on the Ru(0001) surface, TPD spectra were acquired for various initial D<sub>2</sub>O coverages, as shown in Figure 1, and exhibited the same features as previously reported.<sup>1,2,17–19</sup> At a low coverage, a peak at about 190 K in a typical first-order desorption appeared. We assigned it to the desorption of intact D<sub>2</sub>O molecules interacting strongly with bare Ru(0001). For a higher coverage of up to 1 AL, a growing broader peak consisting of a peak at 180 K and a shoulder at 190 K was observed. For a coverage of more than 1 AL, a multilayer desorption peak at 160 K was measured. These obtained results suggest that the binding of the first D<sub>2</sub>O layer with the substrate is much stronger than that with the condensed upper D<sub>2</sub>O layers.

**3.1.2. IRAS of D<sub>2</sub>O on Ru(0001).** Many features in the IRAS spectra of D<sub>2</sub>O on Ru(0001) shown here well-reproduce the previous reports by careful IRAS observations.<sup>27,28</sup> Figure 2 shows the coverage dependence of IRAS spectra for D<sub>2</sub>O on Ru(0001) measured immediately after deposition at 25 K. At a coverage of below 0.14 AL, only a sharp absorption peak appeared at 1157 cm<sup>-1</sup> in the region of the DOD scissoring mode,  $\delta_{\text{DOD}}$ , while no absorption peak was detected in the region of the O–D stretching mode,  $\nu_{\text{OD}}$ , in our detection limit. The peak at 1157 cm<sup>-1</sup> has been assigned to  $\delta_{\text{DOD}}$  of a molecular water monomer adsorbed on Ru(0001).<sup>28</sup> The frequency of the monomer  $\delta_{\text{DOD}}$  peak at 1157 cm<sup>-1</sup> is much lower than the one for its gas phase (1176 cm<sup>-1</sup>).<sup>29</sup> This indicates a strong interaction between adsorbed water molecules and bare Ru(0001), which is consistent with the higher temperature desorption peak at about 190 K in TPD spectra below 0.36 AL. The main bonding interaction is through an oxygen lone-pair orbital 1b<sub>1</sub> rehybridized with Ru 4d<sub>z<sup>2</sup></sub> states,<sup>12</sup> where the water



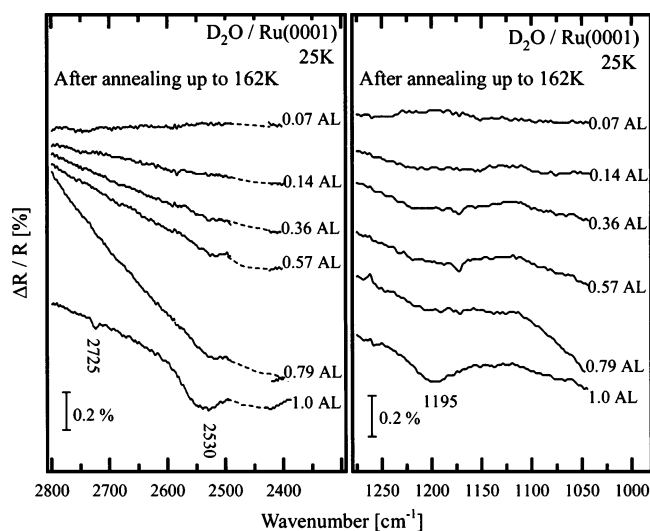
**Figure 1.** D<sub>2</sub>O TPD spectra for various initial coverages of D<sub>2</sub>O on Ru(0001). The substrate was exposed to D<sub>2</sub>O at 25 K and heated linearly at a heating rate of 1 K/s.



**Figure 2.** IRAS spectra for various coverages of D<sub>2</sub>O on Ru(0001) measured at 25 K, in which unwanted signals at around 2450 cm<sup>-1</sup> due to imperfection in reference spectrum subtraction were removed.

molecular plane lies almost parallel to the surface. This configuration inhibits the vibration excitation of both  $\nu_{OD}$  and  $\delta_{DOD}$ , according to the selection rule of IRAS on metal surfaces.<sup>30</sup> Since the inactive vibrational mode can be detected in spectra via a coupling with the other active vibrational mode, the clear observation of only the  $\delta_{DOD}$  peak at 1157 cm<sup>-1</sup> is probably due to the coupling of the DOD scissoring mode with the D<sub>2</sub>O–Ru stretching mode.

With increasing coverage, the peak at 1157 cm<sup>-1</sup> became smaller and disappeared above 0.57 AL, whereas a broad  $\delta_{DOD}$  absorption band peaked at 1172 cm<sup>-1</sup> was detected at 0.36 AL and increased. At more than 1 AL, the broad  $\delta_{DOD}$  band gradually shifts to a higher frequency. These  $\delta_{DOD}$  frequency changes have been attributed to the formation of hydrogen bonds with additional D<sub>2</sub>O molecules.<sup>27,28</sup> This characterization is



**Figure 3.** IRAS spectra for various initial coverages of D<sub>2</sub>O on Ru(0001) after annealing up to 162 K. The sample was heated at 1 K/s and quenched immediately to 25 K. The spectra were obtained at 25 K. Unwanted signals at around 2450 cm<sup>-1</sup> due to imperfection in reference spectrum subtraction were removed.

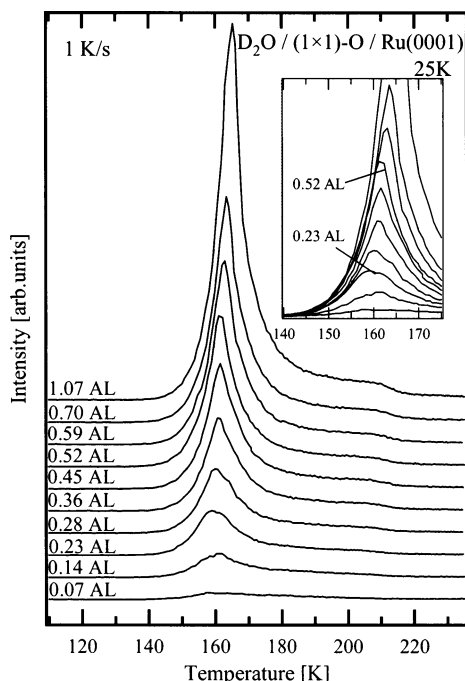
consistent with the observation of a broad  $\nu_{OD}$  absorption band at around 2550 cm<sup>-1</sup> above 0.36 AL, because this  $\nu_{OD}$  absorption band has been assigned to the O–D stretching mode of hydrogen-bonding waters.<sup>31,32</sup>

The water multilayers adsorbed on Ru(0001) at 25 K form an amorphous phase because of water's low mobility.<sup>33</sup> In contrast, the water molecules become mobile and make stable structures on the surface during annealing below the desorption temperature.<sup>27</sup> Figure 3 shows the annealing temperature dependence of the IRAS spectra measured at 25 K after annealing up to 162 K with a heating rate of 1 K/s followed by quenching immediately to 25 K, for each coverage. The sharp peak of the monomer  $\delta_{DOD}$  at 1157 cm<sup>-1</sup> obtained below 0.36 AL in Figure 2 disappeared after annealing. The water molecules are not dissociated during annealing, because the simple first-order desorption peak at about 190 K is observed below 0.36 AL as shown in Figure 1. Thus, the  $\delta_{DOD}$  peak should be shifted and broadened by cluster formation<sup>28</sup> as the spectrum changes upon increasing coverage (Figure 2), even though the broad  $\delta_{DOD}$  absorption band is not clear at that coverage in the obtained spectra (Figure 3). The sharp  $\delta_{DOD}$  peak at 0.07 AL in Figure 2 disappeared after annealing up to 93 K (not shown here), which implies that almost all of the monomers form hydrogen bonds with other molecules and make islands until the annealing temperature.

The other clear difference between IRAS spectra before annealing (Figure 2) and after annealing (Figure 3) is the change in the O–D stretching mode of hydrogen-bond-free D,  $\nu_{OD}$ -(dangling-D), at around 2740 cm<sup>-1</sup>. Before annealing and at more than 1 AL, two types of  $\nu_{OD}$ -(dangling-D) were observed at 2750 and 2730 cm<sup>-1</sup> assigned to that of two-coordinated and three-coordinated water molecules, respectively.<sup>31,32</sup> After annealing, in contrast, only the  $\nu_{OD}$ -(dangling-D) peak at 2725 cm<sup>-1</sup> for the three-coordinated D<sub>2</sub>O was observed. These clearly show that the hydrogen-bonding network is improved during the annealing procedure, and all of the water molecules are placed in three or four coordination.

In Figure 3, the species showing a  $\nu_{OD}$ -(dangling-D) peak at 2725 cm<sup>-1</sup> after annealing is attributed to that forming dangling-D toward the vacuum, namely, the D-up configuration. Since we observed this signal at the D<sub>2</sub>O coverage very closed





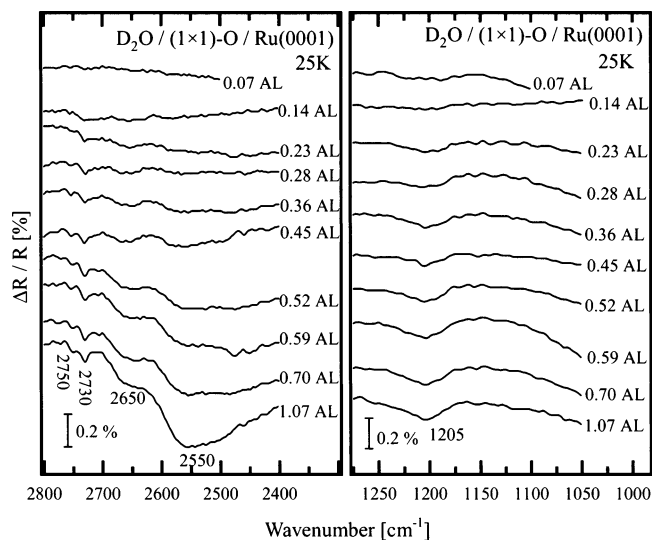
**Figure 4.** D<sub>2</sub>O TPD spectra for various initial coverages of D<sub>2</sub>O on (1 × 1)-O/Ru(0001). The substrate was exposed to D<sub>2</sub>O at 25 K and heated linearly at a heating rate of 1 K/s. In the inset, the spectra are overlapped to clarify the order of desorption kinetics.

to or above 1 AL, corresponding to the appearance of the multilayer desorption peak at about 155 K in TPD (Figure 1), the D-up species are considered to be in the second layer. This observation is in good agreement with the recent study using sum-frequency generation measurements.<sup>22</sup>

### 3.2. D<sub>2</sub>O on (1 × 1)-O/Ru(0001).

**3.2.1. TPD of D<sub>2</sub>O on (1 × 1)-O/Ru(0001).** The coverage dependence of TPD spectra for D<sub>2</sub>O on (1 × 1)-O/Ru(0001) is shown in Figure 4. The TPD results were obtained with the same measurement conditions as for bare Ru(0001); the (1 × 1)-O/Ru(0001) surface was exposed to D<sub>2</sub>O at 25 K and heated linearly with a heating rate of 1 K/s. The initial D<sub>2</sub>O coverage was estimated from the D<sub>2</sub>O TPD integral between 130 and 230 K, since we observed no difference in the TPD spectra in repeated TPD cycles using the maximum annealing temperature of 245 K, where a TPD spectrum change was expected if some portion of D<sub>2</sub>O were dissociated and its fragments remained.

The TPD spectra of D<sub>2</sub>O on (1 × 1)-O/Ru(0001) show a simple shape: a sharp desorption peak at about 160 K and a broad tail up to 215 K. The tail components possibly consist of not only residual signals of the sharp peak at 160 K but also desorption from some defect sites on (1 × 1)-O/Ru(0001). The temperature of the main peak is similar to the desorption temperature of multilayer D<sub>2</sub>O on Ru(0001), as shown in Figure 1. The main peak intensity increased in the first-order desorption process until 0.23 AL, which implies the desorption of intact single D<sub>2</sub>O molecules in the submonolayer regime. With a further increase in the coverage, the desorption kinetics changed to a fractional order (in between the first- and zero-orders), as shown in the inset of Figure 4. The fractional-order kinetics implies the desorption of D<sub>2</sub>O from three-dimensional (3D) islands, which should be induced by heating during TPD measurements. Since the main peak was observed at 160 K, even at submonolayer coverage, and did not show any significant temperature change at the desorption from condensed phase, the interaction between D<sub>2</sub>O and the (1 × 1)-O/Ru(0001) surface



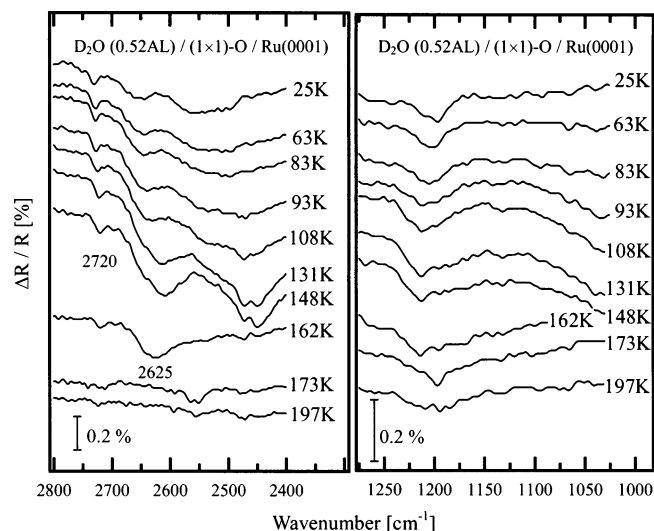
**Figure 5.** IRAS spectra for various coverages of D<sub>2</sub>O on (1 × 1)-O/Ru(0001) measured at 25 K.

is comparable to that of hydrogen bonds between water molecules and is much weaker than that of D<sub>2</sub>O with bare Ru(0001).

**3.2.2. IRAS of D<sub>2</sub>O on (1 × 1)-O/Ru(0001).** Figure 5 shows the coverage dependence of the IRAS spectra for D<sub>2</sub>O on (1 × 1)-O/Ru(0001) measured immediately after deposition at 25 K. While it was difficult to find any reliable absorption peaks at 0.07 AL, we observed several adsorption signals above 0.14 AL, where the spectra commonly show a broad  $\delta_{\text{DOD}}$  absorption band at around 1205 cm<sup>-1</sup>, two broad  $\nu_{\text{OD}}$  absorption bands at around 2650 and 2550 cm<sup>-1</sup>, and two sharp  $\nu_{\text{OD}}$ (dangling-D) absorption peaks at 2750 and 2730 cm<sup>-1</sup>. These broad adsorption bands imply a variety of adsorption structures in a geometrical distribution. Since the obtained frequencies of D<sub>2</sub>O did not depend on coverage, the distribution of the adsorption structures on (1 × 1)-O/Ru(0001) at 25 K should be uniform within the utilized coverage range.

The broad absorption peaks at 1205 and 2550 cm<sup>-1</sup> are attributed to typical  $\delta_{\text{DOD}}$  and  $\nu_{\text{OD}}$  for condensed D<sub>2</sub>O in the amorphous phase, as shown in Figure 2. The broad peak at 2650 cm<sup>-1</sup> is a characteristic mode for D<sub>2</sub>O on (1 × 1)-O/Ru(0001) and is never observed for D<sub>2</sub>O on bare Ru(0001). According to the theoretical calculation for water clusters,<sup>31,32</sup> this vibration mode is assigned to the O–D stretching mode of hydrogen-bond-free O,  $\nu_{\text{OD}}$ (dangling-O), of D<sub>2</sub>O. Because the  $\nu_{\text{OD}}$ (dangling-O) was observed even at submonolayer coverage, it is obvious that the interaction between D<sub>2</sub>O and (1 × 1)-O/Ru(0001) clearly differs from that between D<sub>2</sub>O and bare Ru(0001).

The significant difference in IRAS results for D<sub>2</sub>O on (1 × 1)-O/Ru(0001) is probably due to the lack of rehybridization between the water oxygen lone-pair orbital and the Ru atom orbital, because the Ru surface is fully covered by oxygen adatoms. In contrast to that the water molecules on partially oxidized Ru(0001) interact with both Ru and O atoms,<sup>7,8,14,23,24</sup> D<sub>2</sub>O on (1 × 1)-O/Ru(0001) interacts with only the surface O atoms through the hydrogen bonds. This hypothesis is in good agreement with the observation of the D<sub>2</sub>O TPD peak at 160 K at submonolayer coverage, since the temperature is close to that for the desorption from condensed water. Therefore, the characteristic adsorption structure of the first layer is considered one in which the D<sub>2</sub>O molecule forms hydrogen bonds between two heavy-water D atoms and surface O adatoms. Consequently,



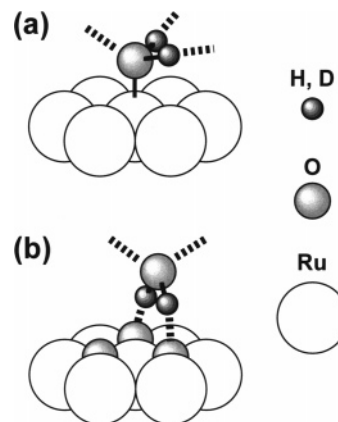
**Figure 6.** Evolution of IRAS spectra after annealing at various desired temperatures from 25 to 197 K with a heating rate of 1 K/s followed by quenching immediately to 25 K.

the heavy-water O atom points toward the vacuum (O-up configuration). This structure is consistent with the observation of  $\nu_{\text{OD}}$ (dangling-O) in IRAS. Since the  $\nu_{\text{OD}}$ (dangling-O) absorption band was observed with the  $\nu_{\text{OD}}$ (dangling-D) peaks simultaneously, some portion of  $\text{D}_2\text{O}$  takes a D-up configuration. Therefore, the adsorption layer for  $\text{D}_2\text{O}$  on  $(1 \times 1)\text{-O/Ru(0001)}$  at 25 K consists of several adsorption structures.

Figure 6 shows the annealing dependence of the IRAS spectrum at the initial coverage of 0.52 AL. The spectra were measured at 25 K after annealing up to various desired temperatures with a heating rate of 1 K/s followed by quenching immediately to 25 K. With increasing annealing temperature up to 131 K, the  $\delta_{\text{DOD}}$  and  $\nu_{\text{OD}}$  signals showed frequency shifts. In particular, the red-shifts of  $\nu_{\text{OD}}$  vibrations from 2550 to 2450  $\text{cm}^{-1}$  are considered as a transition from an amorphous ice phase to a dense ice phase with an improvement in their hydrogen-bonding network, as observed in a previous IRAS study of thermal  $\text{D}_2\text{O}$  thin layer evolution.<sup>33</sup> As can be seen from the  $\text{D}_2\text{O}$  TPD features shown in Figure 4, the 3D-island formation possibly takes place under this thermal evolution. In the annealing temperature range between 131 and 148 K, the spectra were basically the same, in which the water layer is in a stable phase on  $(1 \times 1)\text{-O/Ru(0001)}$ .

After annealing up to 162 K ( $\text{D}_2\text{O}$  molecules partially desorbed in this annealing procedure), the IRAS spectrum was markedly changed, as shown in Figure 4, and the remaining  $\text{D}_2\text{O}$  coverage was estimated to be 0.24 AL (46% of initial coverage) from TPD measurement. Here, the main  $\nu_{\text{OD}}$  absorption band at around 2450  $\text{cm}^{-1}$  disappeared and the characteristic  $\nu_{\text{OD}}$ (dangling-O) band at 2625  $\text{cm}^{-1}$  selectively remained. This clearly indicates that the O-up configuration is a stable structure for  $\text{D}_2\text{O}$  on  $(1 \times 1)\text{-O/Ru(0001)}$ .

After further annealing up to 173 and 197 K, only a small amount of  $\text{D}_2\text{O}$  remained at defect sites on the surface. The remaining  $\text{D}_2\text{O}$  did not show the characteristic  $\nu_{\text{OD}}$ (dangling-O) band on  $(1 \times 1)\text{-O/Ru(0001)}$ , and it only exhibited a small  $\nu_{\text{OD}}$  peak at 2550  $\text{cm}^{-1}$  and a  $\delta_{\text{DOD}}$  peak at 1200  $\text{cm}^{-1}$ . Since these frequencies are the same as those of amorphous ice, the hydrogen-bonding networks of remained water molecules ought to be imperfect.



**Figure 7.** Schematic view of preferred structures of water (a) on Ru(0001) and (b) on  $(1 \times 1)\text{-O/Ru(0001)}$ .

#### 4. Discussion

Even on bare Ru(0001), the details of the first water layer structures are still under debate, related to the theoretical prediction of a partially dissociated bilayer structure.<sup>10–13</sup> Very recent experimental studies have elucidated a large isotope effect for water dissociation on Ru(0001),<sup>14,15</sup> in which only a small amount of  $\text{D}_2\text{O}$  is dissociated slightly above desorption temperature. Our recent study has also shown the small thermal dissociation probability for  $\text{D}_2\text{O}$  on Ru(0001). We have, therefore, inferred that the  $\text{D}_2\text{O}$  molecules on Ru(0001) below 162 K form an intact molecular layer, probably based on the  $I_h$  ice bilayer structure.

In this study, we successfully observed the interaction difference of water with bare Ru(0001) and  $(1 \times 1)\text{-O/Ru(0001)}$ . Whereas the adsorbed  $\text{D}_2\text{O}$  molecules commonly tend to form hydrogen bonds with each other when they can be mobile during annealing, the formation of the first water layer is quite different, depending on whether it is on bare Ru(0001) or  $(1 \times 1)\text{-O/Ru(0001)}$ , as observed by TPD and IRAS.

On bare Ru(0001),  $\text{D}_2\text{O}$  directly attached to Ru(0001) desorbs at about 190 K. The  $\text{D}_2\text{O}$  molecules are strongly bonded to the surface through an oxygen lone-pair orbital rehybridized with Ru.<sup>12</sup> In this adsorption state, the water molecule can form three hydrogen bonds with other water molecules,<sup>1,12</sup> as shown in Figure 7a. Consequently, the water molecule acts as a member of the  $I_h$  ice bilayer on Ru(0001), according to the modified Bernal–Fowler–Pauling (BFP) rules proposed by Doering and Madey.<sup>8</sup>

In contrast to the case of  $\text{D}_2\text{O}$  on Ru(0001), the  $\text{D}_2\text{O}$  molecules at submonolayer coverage on  $(1 \times 1)\text{-O/Ru(0001)}$  exhibit the desorption peak at 160 K like that of condensed water, as shown in Figure 4. The weak adsorption is probably due to the lack of the bond through the oxygen lone-pair orbital. Only hydrogen bonds between heavy-water D and precovered O are made on  $(1 \times 1)\text{-O/Ru(0001)}$ , so that the desorption temperature is similar to that of condensed water. In fact, we observed the dominant  $\nu_{\text{OD}}$ (dangling-O) band at 2625  $\text{cm}^{-1}$  after annealing up to 162 K, in which the  $\text{D}_2\text{O}$  molecules ought to be in a thermally stable geometry. Therefore, we propose the O-up configuration shown in Figure 7b as a preferred structure for  $\text{D}_2\text{O}$  on  $(1 \times 1)\text{-O/Ru(0001)}$ .

In the O-up configuration, the  $\text{D}_2\text{O}$  molecules deviate from the modified BFP rules, because the molecule does not maintain the tetrahedral bonding configuration for additional water molecules.<sup>8</sup> As a result, the  $\text{D}_2\text{O}$  molecules in the O-up configuration no longer behave as a member of the  $I_h$  ice bilayer,

even though the (1 × 1)-O phase does not disturb the close match in lattice constants between the  $I_h$  ice bilayer and Ru(0001).

When one of the hydrogen bonds is broken in the O-up configuration, the water molecule will form the tetrahedral bonding configuration with additional water molecules. Because the strength of the bond between heavy-water D and precovered O is probably comparable to that of the water–water hydrogen bond, the water–substrate bond is easily rearranged to the water–water bond, where 3D-island formation is expected in order to maximize the number of hydrogen bonds. This prediction is in good agreement with our observation of the fractional-order desorption shown in Figure 4.

In a helium atom diffraction study of water layers on (1 × 1)-O/Rh(111),<sup>34</sup> a dense (1 × 1)-H<sub>2</sub>O adsorption phase has been proposed. The model structure consists of water molecules bonding to the substrate via one hydrogen bond between water H and precovered O. Another water H bonds to the neighboring water O in that model, without H-up configuration species. In the case of D<sub>2</sub>O on (1 × 1)-O/Ru(0001), however, we observed the  $\nu_{OD}$ (dangling-O) band always together with the  $\nu_{OD}$ -(dangling-D) absorption peak, as shown in Figures 5 and 6, which has exhibited a mixture layer including the D-up configuration species. In addition, D<sub>2</sub>O molecules prefer to form 3D islands at higher coverages on (1 × 1)-O/Ru(0001). These facts indicate that the proposed dense (1 × 1)-H<sub>2</sub>O model for the (1 × 1)-O/Rh(111) substrate is probably not the general stable structure for the fully oxygen covered metal surfaces, because all water molecules are not in a four-coordinated configuration, according to the modified BFP rules.

## 5. Summary

The initial growth of adsorbed water (D<sub>2</sub>O) layers on (1 × 1)-O/Ru(0001) has been studied in comparison with that on bare Ru(0001) using TPD and IRAS, focusing on the interaction difference of D<sub>2</sub>O with those substrates. Although the water molecules on both bare and (1 × 1)-oxygen-covered Ru(0001) commonly tend to form hydrogen bonds with each other when surface mobility occurs, quite different results of TPD and IRAS measurements for the two surfaces were obtained.

On bare Ru(0001) at 25 K and at a very low D<sub>2</sub>O coverage, a sharp single absorption peak at 1157 cm<sup>-1</sup> attributed to the DOD scissoring mode for monomer D<sub>2</sub>O was detected. As the coverage was gradually increased, the sharp absorption peak disappeared by formation of hydrogen bonds. A similar change was observed after the procedure of annealing up to 162 K and quenching, which implies that the adsorbed water molecules prefer to cluster, as they can be mobile. The D<sub>2</sub>O molecules at the very low coverage desorbed with the peak at 190 K in the first-order desorption process.

On (1 × 1)-O/Ru(0001), most of the D<sub>2</sub>O molecules desorbed at about 160 K as condensed water desorption, even at submonolayer coverage. The vibration spectra at low coverage also showed broad peaks, reflecting a variety of hydrogen-bonding interactions and configurations. In particular, we found the characteristic O–D stretching mode at around 2650 cm<sup>-1</sup>, which was assigned to that of the D<sub>2</sub>O molecules in a hydrogen-

bond-free O situation. This D<sub>2</sub>O molecule is probably adsorbed on (1 × 1)-O/Ru(0001) with hydrogen bonds between two heavy-water D atoms and precovered O adatoms (O-up configuration). Consequently, the D<sub>2</sub>O molecules cannot take the four-coordinate structure while maintaining the O-up configuration in the adsorbed water layer and therefore cannot make a single  $I_h$ -ice bilayer on (1 × 1)-O/Ru(0001).

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