

# Hydrogen Bonding, H-D Exchange, and Molecular Mobility in Thin Water Films on TiO<sub>2</sub>(110)

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Hydrogen bonding, H-D exchange, and molecular mixing in water films on TiO<sub>2</sub>(110) have been studied using water electron-stimulated desorption. For  $T < 70$  K, films with different water isotopes adsorbed on the Ti<sup>4+</sup> and bridging oxygen rows can be prepared. For  $T > 70$  K, H-D and molecular exchange between these “layers” occur with a distribution of activation energies and is surprisingly efficient. The results demonstrate that all the water molecules that are directly bound to TiO<sub>2</sub>(110)—i.e., in the first and second monolayers—are also hydrogen bonded to each other.

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The interaction of water with TiO<sub>2</sub> is important for a variety of areas ranging from photocatalysis [1] to self-cleaning surfaces [2]. Scientifically, water on rutile TiO<sub>2</sub>(110) is considered to be the most important “benchmark” system for metal oxides [3–5]. Thus, the interactions of water with TiO<sub>2</sub>(110) for coverages,  $\theta$ , of 1 monolayer (ML) and less have been extensively studied [4–13]. On TiO<sub>2</sub>(110),  $\theta = 1$  ML is defined with respect to the fivefold-coordinated Ti<sup>4+</sup> sites ( $5.2 \times 10^{14}$  cm<sup>-2</sup>) [3,7,8] and is approximately half the amount in a “bilayer” of crystalline ice ( $1.14 \times 10^{15}$  cm<sup>-2</sup>) [14]. Surprisingly, there have been few investigations for  $\theta > 1$  ML despite the fact that the “second” ML of water also binds directly to the surface [7,8,10,12]. However, understanding the water structure for  $\theta > 1$  ML is important since the corrugated structure of TiO<sub>2</sub>(110) and the strong binding of the first water ML are both likely to influence the transition to bulk water further from the surface, and thus the chemistry of H<sub>2</sub>O/TiO<sub>2</sub>(110) interfaces [7,10].

Since water in the first and second layers nominally adsorbs at Ti<sup>4+</sup> and bridge bonded oxygen (BBO) sites, respectively [7,8], we will designate these as H<sub>2</sub>O<sub>Ti</sub> and H<sub>2</sub>O<sub>BBO</sub> (see Fig. 1, schematic). High resolution electron energy loss spectroscopy experiments suggest that H<sub>2</sub>O<sub>BBO</sub> does not hydrogen bond with H<sub>2</sub>O<sub>Ti</sub> [7]. In contrast, work function measurements suggest that H<sub>2</sub>O<sub>BBO</sub> adsorbs with its dipole parallel to the surface and is hydrogen bonded to H<sub>2</sub>O<sub>Ti</sub> [8]. X-ray scattering measurements for liquid water on TiO<sub>2</sub>(110), density functional theory (DFT), and molecular dynamics (MD) simulations also suggest hydrogen bonding between H<sub>2</sub>O<sub>BBO</sub> and H<sub>2</sub>O<sub>Ti</sub> [10,12,15]. MD simulations found that H<sub>2</sub>O<sub>Ti</sub> did not exchange with the rest of the film even at room temperature, and that the structure of the third and higher layers had converged to bulk liquid water [10].

In this Letter, we use electron-stimulated desorption (ESD) of water from films of D<sub>2</sub>O, H<sub>2</sub><sup>16</sup>O, and H<sub>2</sub><sup>18</sup>O to investigate hydrogen bonding, H-D exchange, and molecular mixing between H<sub>2</sub>O<sub>Ti</sub> and H<sub>2</sub>O<sub>BBO</sub> on TiO<sub>2</sub>(110). By depositing H<sub>2</sub>O<sub>BBO</sub> at  $\leq 70$  K, isotopically layered films

can be prepared. When H<sub>2</sub>O<sub>BBO</sub> is deposited at  $T > 70$  K, partial or complete mixing with H<sub>2</sub>O<sub>Ti</sub> occurs depending on the temperature and time. H-D exchange between H<sub>2</sub>O<sub>Ti</sub> and H<sub>2</sub>O<sub>BBO</sub> occurs at  $\sim 15$  K lower temperatures than H<sub>2</sub><sup>16</sup>O-H<sub>2</sub><sup>18</sup>O exchange. The mixing occurs with a distribution of activation energies,  $E_0$ , centered on  $E_0 = 0.29$  eV with a full width at half maximum ( $\Delta E_{FWHM}$ ) of 0.07 eV for H<sub>2</sub><sup>16</sup>O-H<sub>2</sub><sup>18</sup>O, and  $E_0 = 0.26$  eV and  $\Delta E_{FWHM} = 0.07$  eV for H-D exchange. The results show that H<sub>2</sub>O<sub>BBO</sub> is hydrogen bonded to H<sub>2</sub>O<sub>Ti</sub> and that H<sub>2</sub>O<sub>Ti</sub> rapidly exchanges with H<sub>2</sub>O<sub>BBO</sub> at  $T > 120$  K. Since the lateral distance for atop adsorption at these sites is too large for hydrogen bonding, one or both of the adsorbates must

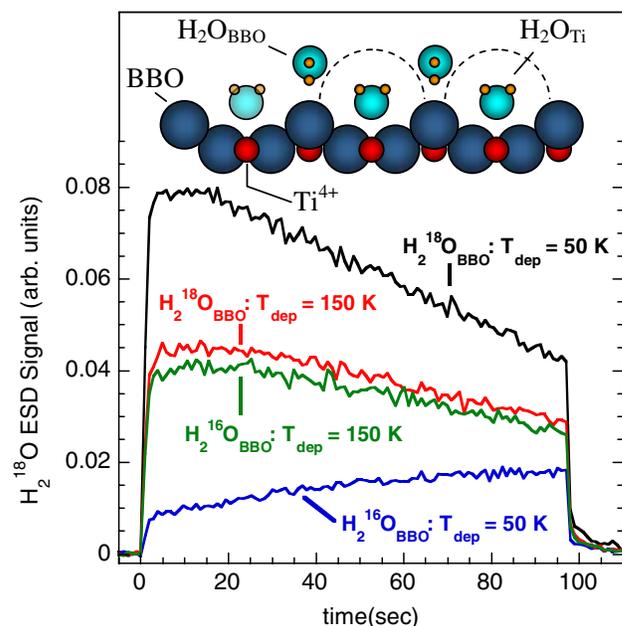


FIG. 1 (color online). ESD of H<sub>2</sub><sup>18</sup>O vs irradiation time from 2 ML films of H<sub>2</sub><sup>18</sup>O and H<sub>2</sub><sup>16</sup>O. The total electron fluence is  $8 \times 10^{15}$  e<sup>-</sup>/cm<sup>2</sup>. The schematic shows the nominal adsorption sites for H<sub>2</sub>O<sub>Ti</sub> and H<sub>2</sub>O<sub>BBO</sub> on TiO<sub>2</sub>(110) (side view). The dashed line shows the O-O distance (0.275 nm) in ice.

be displaced toward the other in agreement with theoretical predictions [10,12].

The experiments were performed in ultrahigh vacuum on sputtered and vacuum annealed (at 950 K for 2 minutes)  $\text{TiO}_2(110)$ . Water temperature programmed desorption indicated the annealed surface had  $8 \pm 1\%$  bridging oxygen vacancies [7]. Water ESD due to scanning a 100 eV electron beam over the sample was measured with a quadrupole mass spectrometer. The experimental details have been described previously [16,17].

Figure 1 shows the  $\text{H}_2^{18}\text{O}$  ESD yields versus time for several  $\text{H}_2^{18}\text{O}$ - $\text{H}_2^{16}\text{O}$  films for  $\theta = 2$  ML. The surface was first exposed to  $6.5 \times 10^{14}$  molecules/ $\text{cm}^2$  of either  $\text{H}_2^{16}\text{O}$  or  $\text{H}_2^{18}\text{O}$  at 190 K (where the  $\text{H}_2\text{O}_{\text{BBO}}$  desorption rate is large) to produce a saturation coverage of  $\text{H}_2\text{O}_{\text{Ti}}$  without any  $\text{H}_2\text{O}_{\text{BBO}}$ . Next, 1 ML was deposited at either 50 K or 150 K using the other isotope and the films were irradiated with electrons at 50 K. For  $\text{H}_2^{18}\text{O}_{\text{BBO}}$  deposited at 50 K, the  $\text{H}_2^{18}\text{O}$  ESD yield was initially high and then decreased with increasing time (Fig. 1, black line). For  $\text{H}_2^{16}\text{O}_{\text{BBO}}$  deposited at 50 K, the  $\text{H}_2^{18}\text{O}$  ESD was initially small, but increased with time (Fig. 1, blue line). For  $\text{H}_2^{18}\text{O}_{\text{BBO}}$  or  $\text{H}_2^{16}\text{O}_{\text{BBO}}$  deposited at 150 K, the ESD yields were almost independent of the ordering of the isotopes and intermediate in magnitude (Fig. 1, green and red lines).

The results in Fig. 1 show that the  $\text{H}_2^{18}\text{O}$  ESD yield depends on the deposition order of the isotopes and the  $\text{H}_2\text{O}_{\text{BBO}}$  deposition temperature. The changes in the ESD yields versus time are due to electron-stimulated processes, including electron-driven mixing of the water films. However, the results also show that the *initial* ESD yields can be used to probe the water structure *prior* to irradiation: since the ESD yields change very little for irradiation times less than  $\sim 12$  s, the signal during this time is characteristic of the structure prior to electron-driven processing of the films. For  $\text{H}_2\text{O}_{\text{BBO}}$  deposited at 50 K, the large differences in the ESD yields arise for three reasons: first, for isotopically pure water films, the ESD yield for  $\theta = 2$  ML is 4.5 times greater than for  $\theta = 1$  ML [18]. Second, for  $1 < \theta \leq 2$  ML energy transfer from  $\text{H}_2\text{O}_{\text{Ti}}$  to  $\text{H}_2\text{O}_{\text{BBO}}$  also enhances the  $\text{H}_2\text{O}_{\text{BBO}}$  ESD signal. Third, there is little or no molecular exchange between water in the first and second layers at 50 K. In contrast, substantial mixing occurs at 150 K and the ESD yield is nearly independent of the order in which the isotopes were deposited.

Figure 2 shows the initial integrated water ESD yields from isotopically labeled films using combinations of  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{18}\text{O}$ , and  $\text{D}_2^{16}\text{O}$  versus the  $\text{H}_2\text{O}_{\text{BBO}}$  deposition temperature,  $T_{\text{dep}}$ . For  $\text{H}_2^{18}\text{O}$ - $\text{H}_2^{16}\text{O}$  films with  $\theta = 2$  ML, the  $\text{H}_2^{18}\text{O}$  ESD yield is small (large) for  $T_{\text{dep}} < 90$  K when  $\text{H}_2^{16}\text{O}$  ( $\text{H}_2^{18}\text{O}$ ) is deposited second and monotonically increases (decreases) at higher temperatures (Fig. 2, circles). For these experiments, the midpoint of the transition from unmixed to mixed is at  $112 \pm 3$  K.

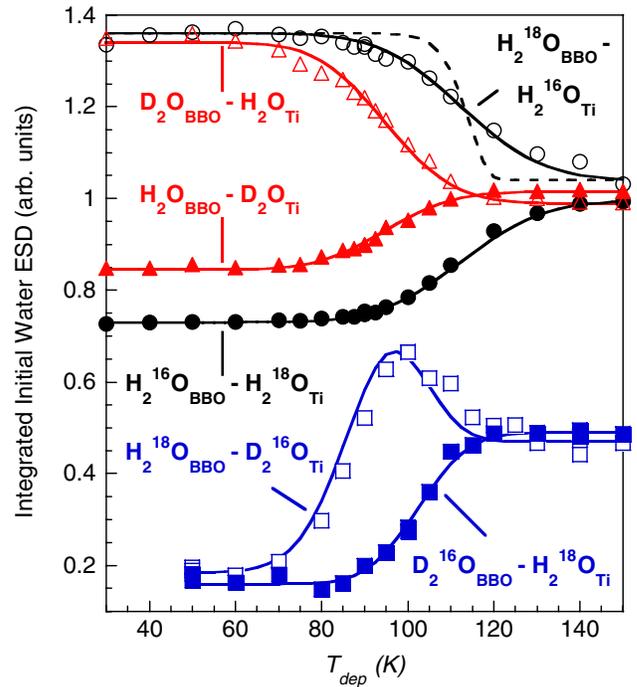


FIG. 2 (color online). Integrated  $\text{H}_2^{18}\text{O}$  (circles),  $\text{D}_2\text{O}$  (triangles), and  $\text{D}_2^{18}\text{O}$  (squares) ESD yields from  $\text{H}_2^{16}\text{O}$ - $\text{H}_2^{18}\text{O}$ ,  $\text{H}_2\text{O}$ - $\text{D}_2\text{O}$ , and  $\text{H}_2^{18}\text{O}$ - $\text{D}_2^{16}\text{O}$  films, respectively, vs  $T_{\text{dep}}$ . One ML water films were prepared at 190 K and more water of another isotope was deposited at  $T_{\text{dep}}$ . The integrated ESD yields (first 10 s corresponding to a fluence of  $\sim 8 \times 10^{14} e^-/\text{cm}^2$ ) were then measured. The results have been offset for clarity. Layered films (i.e., unmixed) are produced for  $T_{\text{dep}} < 70$  K. At higher temperatures, interlayer mixing and H-D exchange occurs and the ESD yields increase or decrease depending on the starting configuration. The solid lines are model fits to the data (see text).

For  $\text{D}_2\text{O}$ - $\text{H}_2\text{O}$  films with  $\theta = 2$  ML, the  $\text{D}_2\text{O}$  ESD yields versus  $T_{\text{dep}}$  (Fig. 2, triangles) are similar to the  $\text{H}_2\text{O}^{16}$ - $\text{H}_2^{18}\text{O}$  films, except the H-D exchange occurs at lower temperature (midpoint =  $95 \pm 2$  K). We also measured the  $\text{D}_2^{18}\text{O}$  ESD from  $\text{D}_2^{16}\text{O}$ - $\text{H}_2^{18}\text{O}$  films (Fig. 2, squares) which permits measurement of H-D and molecular exchange in the same experiment. For  $T_{\text{dep}} \leq 70$  K, very little mixing occurs and the  $\text{D}_2^{18}\text{O}$  ESD yield is small for *both*  $\text{H}_2^{18}\text{O}_{\text{Ti}}$ - $\text{D}_2^{16}\text{O}_{\text{BBO}}$  (Fig. 2, solid squares) and  $\text{D}_2^{16}\text{O}_{\text{Ti}}$ - $\text{H}_2^{18}\text{O}_{\text{BBO}}$  (Fig. 2, open squares). For  $70 \text{ K} < T_{\text{dep}} < 90$  K, H-D exchange is significant while molecular mixing is slow. Therefore, when  $\text{H}_2^{18}\text{O}$  is deposited second, H-D exchange leads to the formation  $\text{D}_2^{18}\text{O}$  in the second layer and the signal increases (Fig. 2, open squares). Above 90 K, molecular exchange leads to a *decrease* in the concentration of  $^{18}\text{O}$  in the second layer and a *maximum* in the  $\text{D}_2^{18}\text{O}$  ESD yield at 100 K. In contrast, when  $\text{D}_2^{16}\text{O}$  is deposited second, H-D exchange does not lead to an appreciable increase in the  $\text{D}_2^{18}\text{O}$  ESD signal for  $T_{\text{dep}} < 90$  K since those molecules are formed in the first layer where the ESD yield is low (Fig. 2, solid

squares). Above 90 K, molecular exchange increases the  $^{18}\text{O}$  (and  $\text{D}_2^{18}\text{O}$ ) concentration in the second layer causing the  $\text{D}_2^{18}\text{O}$  ESD yield to increase. The observed H-D exchange (Fig. 2) indicates water adsorbed on the  $\text{Ti}^{4+}$  rows is hydrogen bonded to water adsorbed “on” the BBO rows.

The activation energy for interlayer exchange can be determined using the data in Fig. 2. If the rate  $\frac{d\theta_j^i}{dt}$  at which isotope  $i$  diffuses out of layer  $j$  is proportional to the coverage in that layer  $\theta_j^i$  times the fraction of unoccupied sites in the other layer, then:

$$\frac{d\theta_1^i}{dt} = -\frac{d\theta_2^i}{dt} = -k_{12}\theta_1^i(1 - \theta_2) + k_{21}\theta_2^i(1 - \theta_1), \quad (1)$$

where  $\theta_j$  is the total coverage in layer  $j$  ( $\theta_j = \sum_i \theta_j^i$ ) and  $k_{jm}$  is the rate at which particles hop from layer  $j$  to layer  $m$  [19]. Since it only takes a few hops to create the steady state concentration of vacancies in either layer, the “blocking” terms  $(1 - \theta_j)$  are approximately constant and can be obtained from the steady state solutions to Eq. (1). Assuming an Arrhenius form for  $k_{12}(T)$ , i.e.,  $k_{12}(T) = \nu \exp(-E_{12}/k_B T)$ , where  $E_{12}$  is the activation energy for diffusing from layer 1 to layer 2 and  $\nu$  is the prefactor, the ESD signal versus temperature should have the following form:

$$Y^i(T) = A + B \exp[-\nu t_c \exp(-E_{12}/kT)\theta(1 - \theta_2)/\theta_2], \quad (2)$$

where  $\theta$  is the total water coverage,  $t_c$  is the (constant) time at temperature  $T$ , and  $A$  and  $B$  are constants that include sensitivity factors for the ESD signal from each layer and coverage terms that are of order unity [20].

For any normal value of  $\nu$  (i.e.,  $10^{12 \pm 1} \text{ s}^{-1}$ ), Eq. (2) predicts a transition from unmixed to mixed that is too abrupt (Fig. 2, dotted line). Using  $\nu \sim 10^3 \text{ s}^{-1}$  and  $E_{12} = 0.085 \text{ eV}$ , the data in Fig. 2 can be fit very well (not shown). However, such a small value of the prefactor is unphysical. Alternatively, if the interlayer exchange is governed by a distribution of activation energies, then Eq. (2) needs to be convolved with the probability distribution for the energies. The solid red lines in Fig. 2 show the results assuming a “normal” prefactor ( $\nu = 10^{12} \text{ s}^{-1}$ ) and a Gaussian distribution centered on  $E_0 = 0.29 \text{ eV}$  with  $\Delta E_{\text{FWHM}} = 0.07 \text{ eV}$ . A similar analysis applies for H-D exchange: for the  $\text{H}_2\text{O}-\text{D}_2\text{O}$  films shown in Fig. 2, a distribution with  $E_0 = 0.26 \text{ eV}$  and  $\Delta E_{\text{FWHM}} = 0.07 \text{ eV}$  fits the data very well (Fig. 2, solid black lines). The activation energies for molecular and H-D exchange are comparable to the strength of hydrogen bonds. The distributions of energies suggest that lateral inhomogeneities—arising, for example, from steps or BBO vacancies—are important. The factors responsible for the observed distributions are currently under investigation.

The distribution of activation energies for interlayer mixing has a significant affect on the kinetics. Figure 3

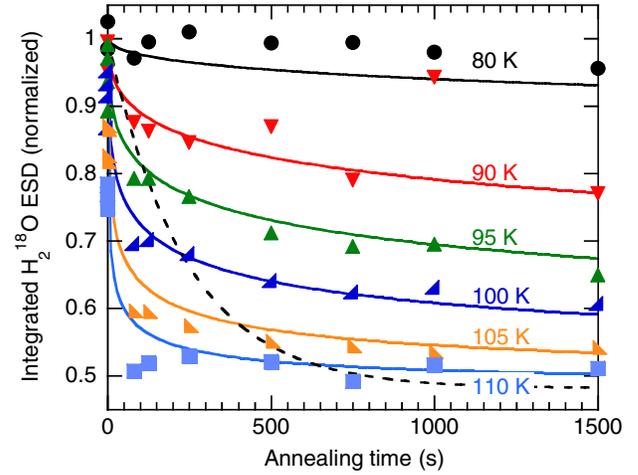


FIG. 3 (color online). Integrated  $\text{H}_2^{18}\text{O}$  ESD (symbols) and model results including a distribution of activation energies (solid lines) vs time. The dashed line is for a single activation energy at 80 K.

shows the  $\text{H}_2^{18}\text{O}$  ESD signal versus annealing time for different annealing temperatures when 1 ML of  $\text{H}_2^{16}\text{O}$  was deposited at 190 K and 0.5 ML of  $\text{H}_2^{18}\text{O}$  was subsequently deposited at 40 K. The films were then isothermally annealed prior to measuring the ESD signal at 30 K. The decrease in the ESD signal versus time cannot be described by a single exponential. The dotted line shows the expected interlayer exchange at 80 K using a single activation energy and prefactor (with values that fit the results in Fig. 2). In contrast, using a distribution of activation energies with a normal prefactor fits the data very well (Fig. 3, solid lines).

Figure 4 shows the  $\text{H}_2^{18}\text{O}$  ESD from 1 ML  $\text{H}_2^{18}\text{O}$  deposited on  $\text{TiO}_2(110)$  (circles) and a smooth [21], 40 ML amorphous solid water film (ASW) (triangles) versus the coverage of a  $\text{H}_2^{16}\text{O}$  “cap” deposited on top. Since 100 eV electrons efficiently excite all the molecules

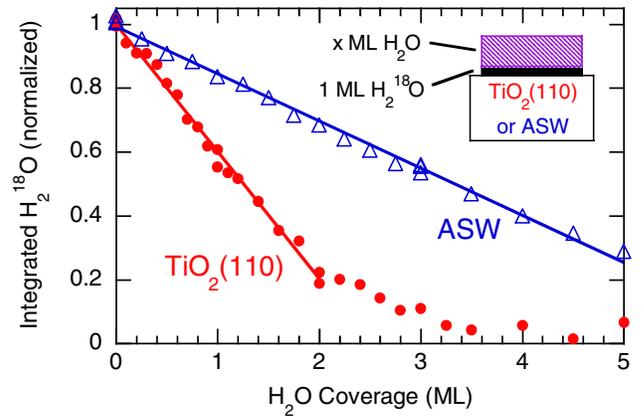


FIG. 4 (color online). Integrated  $\text{H}_2^{18}\text{O}$  ESD, measured at 30 K, from 1 ML  $\text{H}_2^{18}\text{O}$  on  $\text{TiO}_2(110)$  (circles) and 40 ML ASW (triangles) vs  $\text{H}_2^{16}\text{O}$  coverage deposited on top at 80 K.

in a 3 ML film on  $\text{TiO}_2(110)$ , the rapid decrease in the  $\text{H}_2^{18}\text{O}$  ESD indicates that energy is transferred from  $\text{H}_2^{18}\text{O}_{\text{Ti}}$  to  $\text{H}_2^{16}\text{O}$  in the cap layer. Simple momentum transfer due to  $\text{H}_2^{16}\text{O}$  adsorbing “on top” of  $\text{H}_2^{18}\text{O}$ , or possibly transfer of electronic excitations to the “surface”  $\text{H}_2\text{O}_{\text{BBO}}$  molecules [17], could be responsible. In either case,  $\text{H}_2\text{O}_{\text{BBO}}$  must be close enough to form hydrogen bonds with  $\text{H}_2\text{O}_{\text{Ti}}$ . The *faster* decrease for the  $\text{H}_2^{18}\text{O}$  ESD on  $\text{TiO}_2(110)$  as compared to ASW indicates that hydrogen bonding between  $\text{H}_2\text{O}_{\text{BBO}}$  and  $\text{H}_2\text{O}_{\text{Ti}}$  is the *preferred* arrangement. Water molecules cannot be simultaneously adsorbed directly on top of the  $\text{Ti}^{4+}$  and BBO sites and still form a bond since the distance (0.325 nm laterally) is too large (Fig. 1, schematic). Therefore, one or both of the adsorbates must be laterally displaced in agreement with theoretical predictions [10,12].

The similarity of the H-D and molecular exchange (Fig. 2) suggests that these processes are coupled. Thus mechanisms which explain only one process are unlikely (e.g., H atom diffusion, which could explain H-D exchange but not molecular exchange). Hydrogen bonding—which is important in H-D exchange—is known to influence molecular diffusion. For example, water dimers on Pd(111) diffuse faster than monomers [22]. On  $\text{TiO}_2(110)$ , diffusion of isolated water monomers *across* BBO rows occurs preferentially at sites with bridging hydroxyl groups,  $\text{OH}_{\text{Br}}$  [11]. These STM results and DFT calculations [9,12] indicate that  $\text{OH}_{\text{Br}}$  form hydrogen bonds with  $\text{H}_2\text{O}_{\text{Ti}}$ . Similar hydrogen bonding interactions could also foster molecular exchange between the layers when more water is present. The STM experiments also suggest that hydrogen bonding can result in H-D exchange between  $\text{OH}_{\text{Br}}$  and  $\text{H}_2\text{O}_{\text{Ti}}$  [11].

The results herein demonstrate that H-D and molecular exchange between  $\text{H}_2\text{O}_{\text{Ti}}$  and  $\text{H}_2\text{O}_{\text{BBO}}$  on  $\text{TiO}_2(110)$  are facile at low temperatures compared to molecular diffusion in crystalline ice or ASW where, for example, water should (on average) diffuse much less than 1 lattice site in 100 s at 120 K [14,23]. In contrast to MD simulations [10,15], our results suggest that  $\text{H}_2\text{O}_{\text{Ti}}$  will readily exchange with the rest of a liquid water film at room temperature. Furthermore, STM results indicate that diffusion of isolated water monomers on  $\text{TiO}_2(110)$  is also slow at 120 K [11]. A possible explanation for the enhanced exchange within thin water films on  $\text{TiO}_2(110)$  is that the substrate provides a poor template for forming a water film with its preferred structure, thus facilitating rearrangement.

In summary, the results presented here demonstrate that isotopically “layered” films can be prepared by depositing the second monolayer of water at temperatures below 70 K. At higher temperatures, hydrogen bonding between the layers leads to H-D and molecular exchange with a distribution of activation energies. A simple model reproduces

the observed molecular mixing and H-D exchange. The results demonstrate the importance of hydrogen bonding interactions between  $\text{H}_2\text{O}_{\text{Ti}}$  and  $\text{H}_2\text{O}_{\text{BBO}}$  on  $\text{TiO}_2(110)$ , and will further the development of a comprehensive picture of the structure and chemistry of  $\text{H}_2\text{O}/\text{TiO}_2$  interfaces.

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