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PAPER

# Atomic scale characterization of interfacial water near an oxide surface using molecular dynamics simulations

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Atomic scale characterization of the structure and dynamics of confined water molecules located near the metal oxide–aqueous interface is carried out using molecular dynamics simulations. Proximity effects on water molecules ( $\text{H}_2\text{O}$ ) near a magnesium oxide surface ( $\text{MgO}(100)$ ) at room temperature are evaluated based on various structural and dynamical correlation functions. Translational and orientational order parameters are used to quantify the extent of ordering of water molecules near the oxide surface. There is significant ordering of water molecules in the two layers close to the oxide interface and the extent of ordering decreases with increasing distance from the oxide–water interface. The characteristic structural features of proximal water molecules near oxide–aqueous interfaces are strongly correlated to their vibrational densities of states. Systematic trends in libration, bending, and stretching bands are correlated with local ordering of water molecules and the hydrogen-bonding network. We find that restricted transverse oscillations result in larger blue shifts in O–O–O bending and O–O stretching bands for water molecules having increased proximity to the interface. The O–H stretching band is red-shifted whereas the libration bands for proximal water are blue shifted with respect to bulk water; the extent of shifts are sensitive to the interface proximity, their local confinement and their hydrogen bonding status.

## I. Introduction

The behavior of confined water molecules located at the metal oxide–aqueous solution interfaces has been a subject of immense scientific interest owing to their importance in a variety of fields, including heterogeneous catalysis, photo catalysis, atmospheric chemistry, corrosion science, environmental chemistry, geochemistry, metal oxide crystal growth, chemical sensing and energy technologies to name a few.<sup>1–6</sup> The physical and chemical interactions occurring at the interface of metal-oxide and aqueous media are extremely complex and a fundamental atomic scale understanding of these phenomena is still lacking.<sup>1–5</sup> Of particular importance is the influence of oxide surfaces and interfaces on the highly directional hydrogen-bond network, whose structure and dynamics dictate the unique chemical and physical properties of liquid water.<sup>7</sup> For example, interfacial water molecules can control ion adsorption and transport, which are relevant in several applications ranging from catalysis to emerging energy technologies.<sup>3,8,9</sup> In general, the structure and dynamics of interfacial water near an oxide surface such as magnesium oxide play an important role in controlling and initiating numerous physical, chemical, and biological processes.<sup>3</sup>

Although several experiments and theories have revealed the pathways and time scales associated with different aspects of

the structure and vibrational dynamics of bulk water, our understanding of water molecules at surfaces and interfaces has not reached the level of bulk.<sup>3,9,10</sup> Experimentally, spectroscopic techniques such as surface-specific sum-frequency vibrational spectroscopy (SFVS)<sup>9,11–13</sup> and total internal reflection (TIR) sum-frequency vibrational spectroscopy (VSFS)<sup>10</sup> have been employed to gain insights into the structure of water near oxide surfaces and interfaces. These methods have helped identify ice-like, liquid-like, and dangling O–H structures in the terminated hydrogen-bonding network of the water layer located in close proximity to water–alumina, water–silica and water–quartz interfaces.<sup>9,10,12</sup> For example, Shen *et al.* have used sum-frequency vibrational spectroscopy to study water/quartz interfaces with different bulk pH values.<sup>13</sup> Their study suggested that spectra for interfacial water molecules display an ice-like peak which suggests that water molecules at a crystalline oxide surface form a more ordered hydrogen-bonding network. Similarly, Paulidou and Nix have used reflection IR spectroscopy to study the adsorption of water on ordered epitaxial layers of lanthanum oxide.<sup>14</sup> Their study suggests the formation of two distinct types of hydroxyl groups, which differ in their coordination to the lanthanum ions thereby suggesting that adsorption is accompanied by surface reconstruction. Spectroscopic studies by Eftekhari-Bafrooei and Borguet have employed time-resolved sum frequency generation (tr-SFG) to understand the effect of hydrogen-bond strength on the vibrational relaxation of interfacial water near a silica surface.<sup>15</sup> Compared to bulk water, their

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study suggests a shorter vibrational lifetime of O–H stretching for interfacial water at the charged surface than in the bulk whereas the same is longer at the neutral surface.

Atomistic molecular dynamics (MD) simulations and first principles studies have been used in the past to understand the structure, dynamics and energetics of interfacial water molecules adsorbed onto the oxide surfaces. For example, Argyris *et al.* have investigated interfacial water properties at the alumina surface using classical molecular dynamics simulations.<sup>16</sup> They observed that the interfacial water exhibits preferential orientation and delayed dynamics compared to bulk water. Předota *et al.* have modeled rutile ( $\alpha$ -TiO<sub>2</sub>) surfaces in contact with aqueous solution and presented results on the structure of water and ions at the interface.<sup>17,18</sup> Their MD simulation results on the ordering of water molecules agree very well with experimental data obtained by X-ray standing wave (XSW) and X-ray reflectivity (*e.g.*, crystal truncation rod (CTR)) analysis of surface structures. The molecular configurations and wetting properties of water at the interface of silica surfaces have already been investigated in a number of classical force-field-based simulations.<sup>13,20–24</sup> Skelton *et al.* have studied interactions between two different terminations of the (10 $\bar{1}$ 0) surface of quartz ( $\alpha$  and  $\beta$ ) and water using MD simulations and have compared the results with X-ray reflectivity (XR) experiments.<sup>19</sup> They concluded that the interfacial water structure at the two terminations of quartz (10 $\bar{1}$ 0),  $\alpha$  and  $\beta$ , is very different because of differences in connectivity and intra-surface hydrogen bonding. Similarly, there have been a number of experimental works on understanding the behavior of water near silica surfaces.<sup>7,9,25</sup>

Similar experimental and theoretical studies have also been performed on the MgO surfaces. For example, Włodarczyk *et al.* have utilized global *ab initio* structure optimizations combined with statistical thermodynamics to probe local ordering of a single monolayer of water close to the MgO(001).<sup>5</sup> Their first principles calculations suggest the existence of two stable surface structures: a  $c(4 \times 2)$  structure containing ten water molecules per unit cell stable at low temperature and a  $p(3 \times 2)$  structure containing six water molecules per unit cell stable at high temperature. Finocchi *et al.* have looked at the interaction of a water molecule with a neutral oxygen vacancy on the MgO(100) surface and find that the dissociation of the water molecule is energetically favored at the vacancy site.<sup>26</sup> Jug *et al.* have performed Born–Oppenheimer MD simulations and shown that a temperature increase from 0 to 300 K can cause drastic changes in the adsorption behavior of water layers on the stoichiometric MgO(100) surface.<sup>27</sup> Their study indicated that amongst the various investigated configurations, the  $p(3 \times 2)$  structure was the most stable at room temperature. Karl *et al.* have used MD techniques to study the structure and stability of  $c(4 \times 2)$ ,  $p(3 \times 2)$ , and  $(1 \times 1)$  overlayers of water on the MgO(100) surface.<sup>28</sup> Spagnoli *et al.* have used molecular dynamics simulations to examine the structure of water around the nanoparticles, and they find highly ordered layers of water at the interface.<sup>29</sup> Fox *et al.* have used MD simulations to predict the desorption rate of an isolated water molecule on the MgO(001) surface at low coverages.<sup>30</sup> Soetens *et al.* have looked at the structure of ice ad-layers on MgO(100).<sup>31</sup> They find that the centers of mass of the H<sub>2</sub>O molecules adopt a square arrangement commensurate

with the substrate network, which leads to weak hydrogen bonds between adjacent water molecules. Similarly, Johnson *et al.* have studied the energetics of adsorption of molecular water on the MgO(001) surface and its interface with water.<sup>32</sup> McCarthy *et al.* have used atomistic simulations such as Monte-Carlo to compute the structural and dynamical properties of an isolated water molecule as well as water multi-layers on defect-free MgO(001) and observed significant differences in the interfacial water structure compared to bulk.<sup>33</sup> Likewise, there have been some limited studies that have probed the influence of the MgO surface on the layering in interfacial water molecules. For example, de Leeuw *et al.* have developed the shell potential model and investigated the interaction of liquid water with MgO surfaces. They find that the adsorption of the first monolayer to the surfaces disrupts ordering in the next few layers. McCarthy *et al.* have studied the water–MgO interaction and looked at structures of 2-dimensional water over-layers. Their study reveals a densely packed first layer and a more diffuse second layer. Although the above studies have looked at the structure of water near MgO interfaces, systematic studies into atomic scale characterization of water molecules as a function of their distance from the oxide surface is still lacking.

Furthermore, despite the advances in experimental measurements and computational techniques, there are a number of fundamental unanswered questions concerning water's interactions and their dynamics near oxide surfaces.<sup>34</sup> These include questions such as how much does the interaction of water with an oxide surface influence water dynamics? Does the geometry of the interface or crystal orientation of the oxide surface matter? Is there a substantial difference between the dynamics of water interacting with a charged interface *versus* bulk water? What are the changes in the structure and dynamics of the hydrogen-bonding network? It is therefore not surprising that the studies on atomic scale characterization of interfacial water near oxide surfaces continue to be a subject of immense scientific interest.<sup>1,8,9,14,16,34</sup> A detailed understanding of the molecular scale structure is necessary to exercise control over the dynamical processes occurring in the interfacial water near oxide surfaces.

In this work, we choose to simulate a MgO–water system as a representative model to study the structure and dynamics of water near an oxide interface. We perform an all atom molecular dynamics simulation employing a Buckingham potential model of oxide and flexible SPC/E (termed SPC/EF henceforth) model of water to probe the local structure and dynamics of interfacial water near an oxide surface. The structural and dynamical analyses of interfacial water are based on the calculated radial distribution functions, the oxygen and hydrogen density profiles of water close to the oxide interface and the hydrogen bonding lifetimes of interfacial and bulk water molecules. We have also derived translational and orientational order parameters to quantify the extent of ordering of water molecules near the oxide surface. The atomic scale characterization of interfacial water molecules was carried out by calculating their vibrational density of states. The vibrational spectra calculated by Fourier transforming the velocity auto-correlation function obtained from the MD simulation trajectories provide information on the various inter and intra-molecular vibrational modes. Comparisons to available experimental and theoretical studies are also made where possible.

## II. Computational details

### (a) Potential model

Atomistic simulations are based on the Born model which assumes that ionic interactions occur *via* long-range electrostatic forces and short-range forces which can be described using simple analytical functions.<sup>35</sup> The potential energy is thus a function of the distance between ions. In addition to the Coulomb term to describe the long-range electrostatic interactions between the ions of MgO, a Born–Meyer–Buckingham (BMB) potential is used to describe the short-ranged interactions between the ions.<sup>36–41</sup> The potential energy between ions *i* and *j* separated by the distance  $r_{ij}$  due to the charges  $q_i$  and  $q_j$  between the pairs of ions is given by.

$$V(r) = A \exp\left(-\frac{r}{\rho}\right) - Cr^{-6} + \frac{q_i q_j}{r_{ij}} \quad (2.1)$$

The exponential term of the short-range potential takes into account Pauli repulsion and the  $r^{-6}$  term accounts for any attractive dispersion or van der Waal's interactions. The details of the potential model, and the parameters used for Buckingham potentials for the MgO substrate employed in this study are discussed in detail in the work of McCarthy *et al.*<sup>33</sup> The charges on the magnesium, oxide oxygen, water oxygen and water hydrogen atoms are  $+1.966e$ ,  $-1.966e$ ,  $-0.8476e$  and  $+0.4238e$ , respectively (Table 1).

In this study, we have used the SPC/EF water model.<sup>42,43</sup> Recently, López-Lemus *et al.* and Yuet and Blankshtein have shown that the flexible SPC/EF water model fairs better than other force-fields in predicting the structure and dynamical properties of interfacial water.<sup>42,43</sup> The flexible SPC/EF potential model contains both intra- and intermolecular contributions. The intra-molecular interaction between two bonded atoms at a distance  $r$  is

$$U_b(r) = K_b (r - r_0)^2 \quad (2.2)$$

where  $K_b$  is the spring constant and  $r_0$  is the equilibrium bond-length.

The bending interaction is given by:

$$U_\theta(r) = K_\theta (\theta - \theta_0)^2 \quad (2.3)$$

where  $K_\theta$  is also a spring constant and  $\theta = 109.4$  is the HOH angle at equilibrium. The interaction between two atoms at a distance  $r$  in different molecules is given by a LJ model and a Coulomb potential:

$$U(r) = 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r} \quad (2.4)$$

**Table 1** Potential energy parameters for the MgO substrate derived from the work of McCarthy *et al.*<sup>33</sup>

	$A/\text{kcal mol}^{-1}$	$1/(\rho)/\text{\AA}^{-1}$	$C/\text{kcal mol}^{-1} \text{\AA}^6$
Mg–Mg	22 645	4.24	1224
O <sub>oxide</sub> –O <sub>oxide</sub>	95 810	4.36	252
Mg–O <sub>w</sub>	86 651	4.30	434
Mg–H <sub>w</sub>	3981	3.81	148
Mg–O <sub>oxide</sub>	46 579	4.30	555
H <sub>w</sub> –O <sub>oxide</sub>	8189	3.87	67
O <sub>w</sub> –O <sub>oxide</sub>	178 234	4.36	197

where  $\sigma$  and  $\epsilon$  are the scaling parameters for distance and energy, respectively,  $q_i$  and  $q_j$  are the charges of atoms *i* and *j*. The charges on the oxygen and hydrogen atoms are  $-0.8476e$  and  $+0.4238e$ , respectively. The LJ parameters are used only for the interaction of oxygen atoms and the values are  $\sigma = 3.166 \text{\AA}$  and  $\epsilon = 0.1554 \text{ kcal mol}^{-1}$ .

We would additionally like to point that although the SPC/EF water model is non-polarizable, our comparison of the SPC/EF water model with the polarizable shell model<sup>44</sup> suggested that the SPC/EF water model predicts the ordering of water molecules more accurately than the polarizable shell model. Hence, the SPC/EF water model appears more suitable for the study of local ordering, adsorption behavior, modeling solvent effect, and hydration behavior of oxides such as MgO or as aqueous solvent in more complex simulations of oxide materials. Hence, this potential model was chosen to model the MgO–water interaction in this study (Table 2).

### (b) MD simulation details

The simulations were carried out on a periodic system comprised of MgO(100) slabs containing 1024 Mg<sup>2+</sup> ions and 1024 O<sup>2-</sup> ions. The thickness of the MgO slabs was  $\sim 14 \text{\AA}$ . The center of the unit-cell (between two exposed MgO(100) slabs) was filled with water molecules. A simulation cell of  $\sim 34 \times 17 \times 72 \text{\AA}$  with a water thickness of  $\sim 44 \text{\AA}$  was used. The number of water molecules filled (836 molecules) was chosen to initially equal the bulk density of water and were taken from NPT equilibrated bulk water. The simulations were performed at room temperature (300 K) using a NPT (constant number of particles, pressure and temperature) ensemble. The equilibration of the system was carried out for  $\sim 500$  ps and the remaining 500 ps in the 1 ns simulation run were treated as production run for calculating the time-averaged properties. The equations of motion were integrated using the Verlet leap-frog scheme with a time step of 0.5 femto-second. The temperature and pressure was held at 300 K and 1 atm using a Nose–Hoover thermostat and a barostat, respectively. The Nose–Hoover parameters were set at 0.5 for both the thermostat and barostat relaxation times ps.<sup>44</sup> All the simulations were carried out using the DLPOLY code.<sup>45</sup>

## III. Results and discussion

### 3.1 Structural analysis of water molecules

**I. Radial distribution function.** Fig. 1 shows the radial distribution function (RDF) for oxygen–oxygen (ow–ow) (Fig. 1 (a1)), oxygen–hydrogen (ow–hw) (Fig. 1 (a2)), and hydrogen–hydrogen (hw–hw) (Fig. 1 (a3)) atom pairs of

**Table 2** Potential parameters for the SPC/EF water model<sup>42</sup>

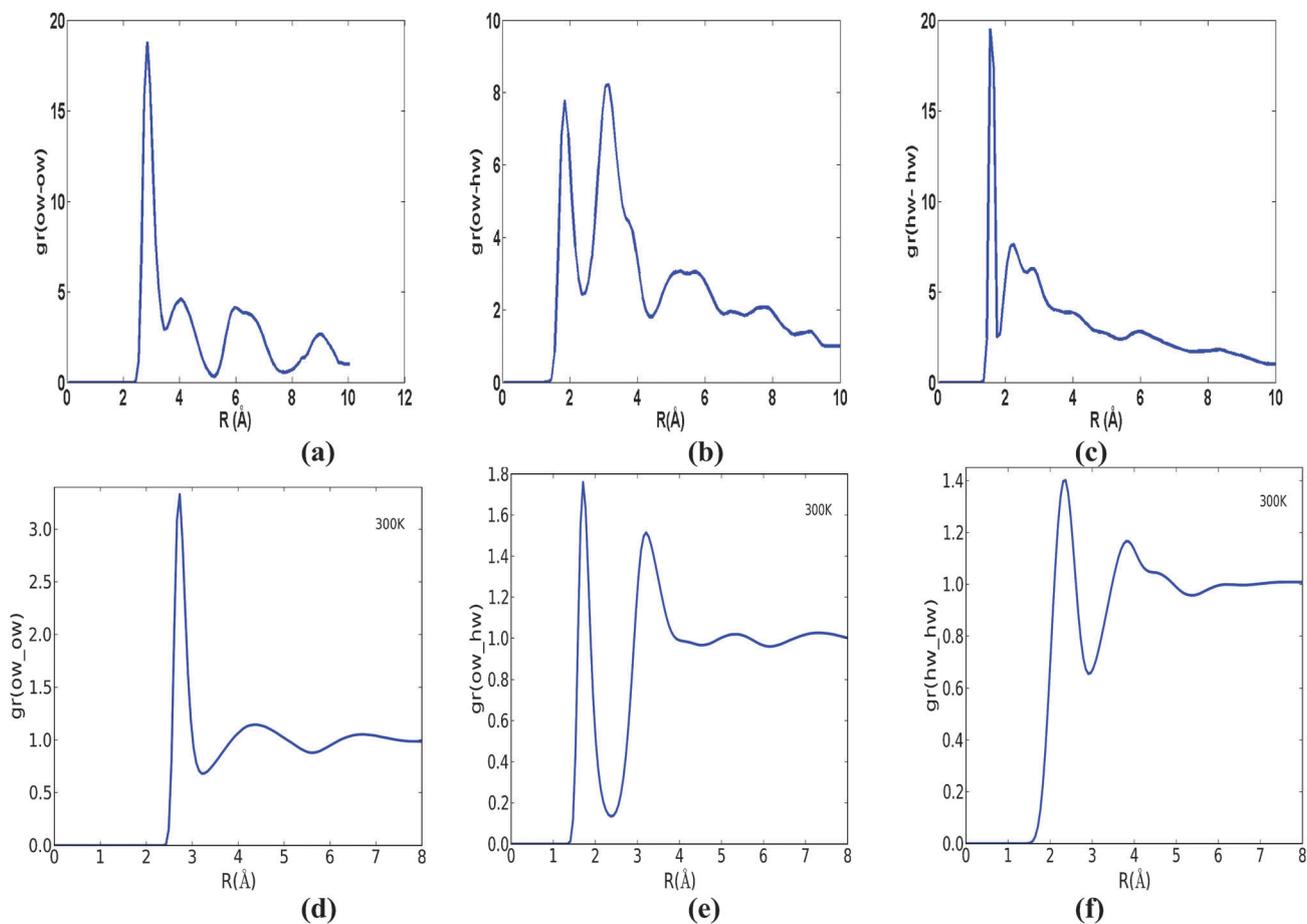
Parameter	SPC/EF water model
$q_o$ (e)	$-0.8476$
$q_H$ (e)	$0.4238$
$\epsilon/\text{kcal mol}^{-1}$	$0.1554$
$\sigma/\text{\AA}$	$3.166$
$K_b/\text{kcal mol}^{-1} \text{\AA}^{-2}$	$1108.27$
$r_0/\text{\AA}$	$1.0$
$K_\theta/\text{kcal mol}^{-1} \text{rad}^{-2}$	$91.54$
$\theta_0$	$109.47$

proximal water confined between MgO(100) surfaces. The corresponding RDF graph for pure bulk water are also shown in Fig. 1(b1)–(b3). Note that the RDF for bulk water agrees very well with that predicted by previously reported experiments.<sup>46</sup> In the case of ow–ow RDF for pure bulk water, we observe a peak at  $\sim 2.73$  Å and a broader peak between  $\sim 4.41$  and  $\sim 6.51$  Å. The RDF for the ow–ow pair of water molecules in the presence of MgO shows well-defined and distinct peaks at  $\sim 2.8$  Å and  $\sim 4.05$  Å, which correspond to the first and second hydration shell. Additionally, we also observe peak splitting between  $\sim 5$  and  $\sim 7$  Å (at  $\sim 5.85$  Å and  $\sim 6.45$  Å). Similarly, the ow–hw pair in pure bulk water show peaks at  $\sim 1.71$  Å,  $\sim 3.21$  Å, and  $\sim 5.6$  Å whereas in the presence of the oxide, they show peaks at  $\sim 1.85$  Å,  $\sim 3.05$  Å,  $\sim 5.05$  Å and  $\sim 5.65$  Å. Thus, the first nearest neighbor distance in ow–ow and ow–hw RDFs, which corresponds to the intra-molecular bond remains mostly unaffected whereas the second and third neighbor peaks that are representative of inter-molecular bonding are significantly shortened in the presence of the oxide surface. Similarly, we find that the hw–hw pair of pure bulk water shows peaks at  $\sim 2.31$  Å and  $\sim 3.6$  Å and the same in the presence of MgO displays peaks at  $\sim 1.55$  Å and at  $\sim 2.25$  Å, respectively. The shortening in the first neighbor peak of hw–hw that corresponds to the

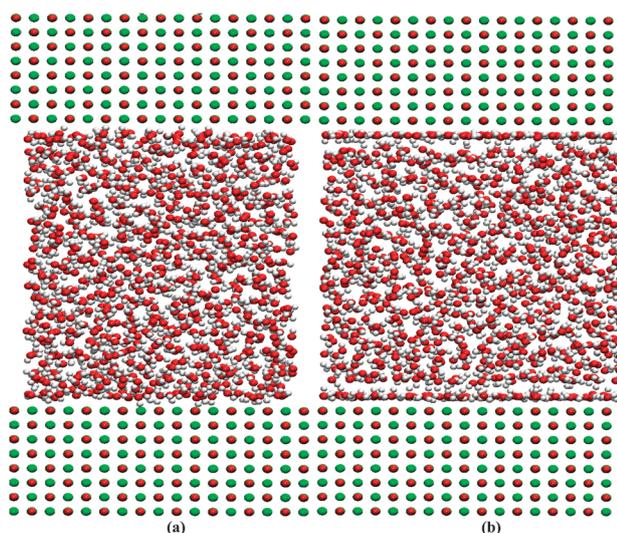
intra-molecular bond suggests constrained degrees of freedom. The above results also suggest a possible ordering of the water molecules confined between the MgO(100) slabs.

To confirm this, we analyze the snapshots obtained from the simulated MD atomic trajectories. Fig. 2 (a) and (b) shows the initial configuration and configuration after 1 ns of simulation time, respectively, of the MgO–water system at 300 K. Fig. 2(a) suggests that water molecules are randomly distributed on the MgO slab at the start of the simulation. Fig. 2(b), however, clearly indicates layering/ordering of the interfacial water molecules after 1 ns of simulation run at 300 K. The water molecules above the ordered monolayers of interfacial water molecules display a liquid-like behavior. A similar behavior was observed in earlier studies carried out at 300 K by Marmier *et al.*<sup>47</sup>

**II. Atomic density profiles.** To further confirm the ordering of water, we computed the atomic density profiles of water molecules normal to the MgO(100) surfaces at the beginning and end of the simulation as shown in Fig. 3 (a) and (b), respectively. The density distribution of water in the case of initial configuration is very broad. The broadening and merging of the peaks in the atomic density profile is a result of integration of the atomic density for all the various

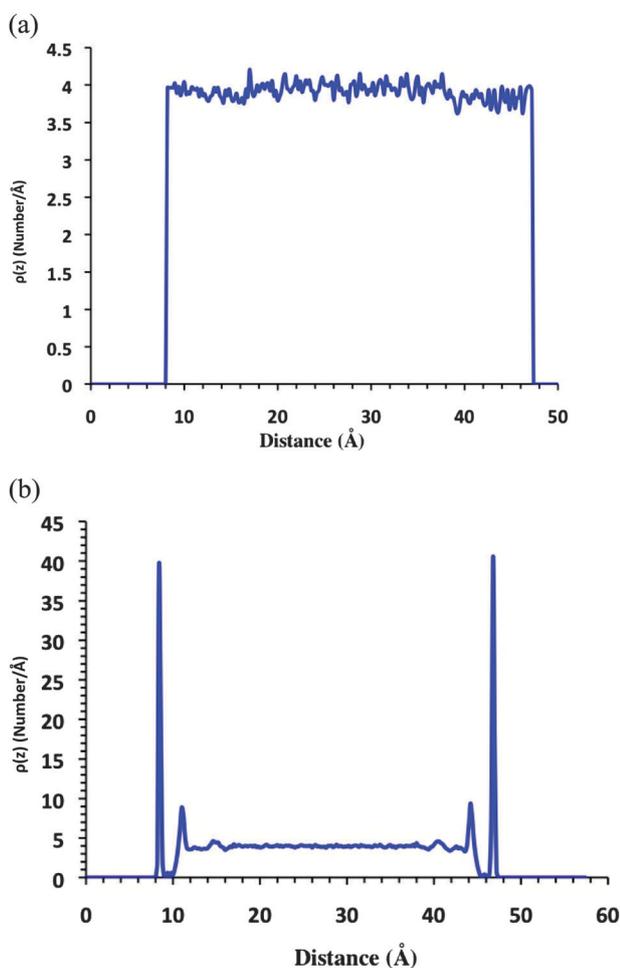


**Fig. 1** Radial distribution function (RDF) for water near a magnesium oxide surface using the SPC/EF water model: oxygen–oxygen (ow–ow) of (a1) proximal water and (a2) bulk water; oxygen–hydrogen (ow–hw) of (a3) proximal water and (b1) bulk water; and hydrogen–hydrogen (hw–hw) of (b2) proximal water and (b3) bulk water.



**Fig. 2** Snapshots showing the MgO–water system using the SPC/EF water model. (a) Initial configuration at the start of the simulation. (b) Configuration obtained after 1 ns at 300 K.

randomly oriented water molecules and hence the peaks are not fully resolved. On the other hand, the atomic density

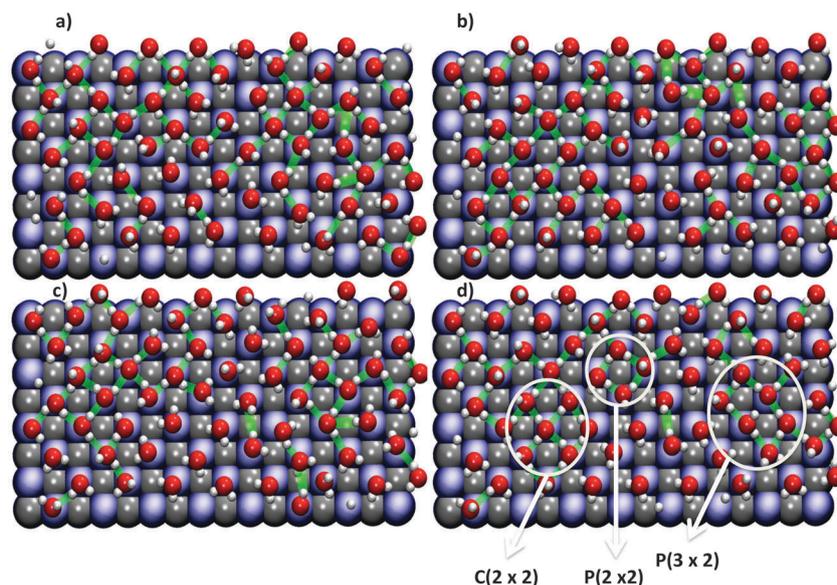


**Fig. 3** Density profiles of water molecules perpendicular to the oxide surface; (a) starting configuration (time = 0 ns); (b) final configuration (time = 1 ns) at 300 K.

profile of water molecules in the final configuration exhibits characteristic peaks that correspond to the various ordered layers of water close to the oxide interface. The interface proximity effect is clearly evident from the density profile of the final configuration. There is ordering of water molecules in the two layers close to the oxide interface and the extent of ordering decreases with increasing distance from the oxide–water interface. Similar ordering of water molecules was found in the case of alumina and silica surfaces in the MD simulations of Argyris *et al.*<sup>16,23,24</sup>

**III. Analysis of simulation snapshots.** Fig. 4 [I] (a)–(d) shows the snapshots of water molecules located near the MgO(100) surface. The 1st layer comprises of water molecules that are in direct contact with the MgO(100) surface. We define a cluster of water molecules based on the hydrogen bonds formed between the adjacent water molecules. Two water molecules were defined to be hydrogen bonded if the distance between donor oxygen and acceptor oxygen is  $\leq 3.6$  Å (based on the radial distribution function of the oxygen–oxygen pair of water (see Fig. 1 (b2))) and the angle between acceptor oxygen–donor oxygen–hydrogen atom is  $\leq 30^\circ$ . Based on this hydrogen bonding criteria, we observe that water molecules form clusters of different sizes. This observation is in good agreement with previous theoretical and experimental studies by Heidberg *et al.*<sup>8</sup> Heidberg *et al.* investigated water adsorption on a cleaved MgO(001) single crystal using transmission Fourier transform infrared (FTIR) spectroscopy as well as low energy electron diffraction (LEED).<sup>8</sup> They concluded that water forms an ordered monolayer with the molecular H<sub>2</sub>O plane nearly parallel to the surface.<sup>8</sup> Fig. 4 [I] (a)–(d) also suggest that water molecules in these clusters are nearly parallel to the MgO(100) surface. The observation of clustering of water molecules is in good agreement with previous theoretical study by Marmier *et al.*<sup>47</sup> They performed MD simulations at various temperatures (150–300 K) and coverages (1–3 layers) to study the adsorption of water on a clean MgO(100) surface using semi-empirical potentials. They observed that water forms a very stable, planar monolayer on MgO(100) with weak hydrogen bonds between molecules at all studied temperatures (150–300 K). They also observed that at 300 K, water molecules in the upper layer of the planar monolayer breaks up and aggregates in a 3D liquid-like structure.<sup>47</sup> In our simulations as well, we find a similar structuring of water in the planar monolayer with the cluster size varying from  $\sim 2$  to 14 water molecules. In particular, our simulations suggest that structures resembling  $p(2 \times 2)$ ,  $p(3 \times 2)$  and  $c(2 \times 2)$  patterns are stable at room temperature (see Fig. 4 I(d)). A similar observation was made by Jug *et al.* whose study indicated that amongst the various investigated configurations, the  $p(3 \times 2)$  structure was the most stable at room temperature.<sup>27</sup>

In our simulations of the MgO(100) surface, the water molecule is adsorbed on the MgO(100) surface with its molecular plane more or less parallel to the surface. This is in good agreement with the experimental studies of Xu and Goodman, who used reflection absorption infrared spectroscopy (RAIRS) and low energy electron diffraction (LEED) to find that the water molecule is adsorbed with its plane nominally parallel to the surface.<sup>64</sup> The oxygen of the water molecule



**Fig. 4** (I) Different water clusters, defined based on the hydrogen bond formation (shown in green), observed on the MgO surface (Mg shown in blue and O shown in silver) during simulations (a), (b), (c) and (d) top view of the surface at different time intervals. (II) Probable hydrogen bond networks formed between water and water and between water and oxide surface observed during this study. Green dots show the hydrogen bonds between water and water and the red dash shows the hydrogen bonds between hydrogen of water and oxygen in the oxide.

prefers to adsorb on top of the magnesium of the oxide surface. Similar conclusions were also drawn from the *ab initio* density-functional studies of Alavi *et al.*<sup>65</sup> There have been some limited studies that have probed the effect of crystal orientation on the MgO surfaces. The effect of adsorption of water molecules on the (100) and (310) crystal surfaces has been studied by de Leeuw and Parker.<sup>44</sup> On the (310) surface, the water molecules preferred to adsorb with their oxygen atom in the interstitial lattice oxygen site on the interface edge. It was found to be doubly coordinated to magnesium ions on both the edge and the plane below. In the case of the (100) surface, they observed that the adsorption pattern on the surface forces the water molecules in subsequent layers to form an intermolecular configuration which is more open than in the system of pure water. In this work, we have not explored the effect of crystal orientation on the interfacial dynamics of water and focus primarily on proximity effects near an MgO(100) surface.

### 3.2 Orientational and translational order of water molecules

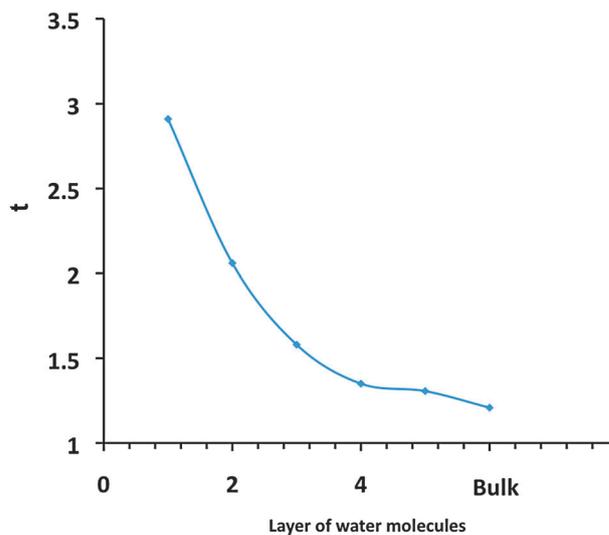
The translational order parameter ( $t$ ) is given by:<sup>48</sup>

$$t \equiv \int_0^{s_c} |g_{OO}(s) - 1| ds \quad (3.1)$$

where the dimensionless variable  $s = r\rho^{1/3}$  is the radial distance  $r$  scaled by the mean intermolecular distance  $\rho^{-1/3}$  ( $\rho = N/V$ ),  $g_{OO}(r)$  is the oxygen–oxygen radial distribution function and  $s_c$  usually corresponds to distances which are large enough to have  $g(s_c) \approx 1$ . In this work,  $s_c \sim 10 \text{ \AA}$  was chosen. In an ideal gas, the RDF is equal to 1 and  $t = 0$ . In a crystal, there is a long-range order and  $g_{OO}(r) = 1$  over long distances, and the order parameter  $t$  is large. The physical meaning of  $t$  is such that both positive and negative

oscillations of  $g_{OO}(r) = 1$  and contribute equally to this quantity. In a system with a long-range order *e.g.*, a crystal, these oscillations persist over long distances, and hence  $t$  is large. The translational order in the case of liquids is expected to be smaller than that for ordered systems.

Fig. 5 shows the translational order calculated for the various water layers away from the oxide–water interface. A comparison with bulk water is also shown. The order parameter  $t$  has a much larger value  $\sim 2.9$  for the 1st layer of interfacial water molecules which is typical of ordered water molecules.<sup>49</sup> The magnitude of the translational order parameter decreases to  $\sim 2.1$  for the second layer, which suggests a less ordered structure. Beyond the 2nd layer of water molecules, the  $t$  value



**Fig. 5** Translational order parameters for SPC/EF water models as a function of various water layers away from the oxide interface. Comparison with bulk water is also shown.

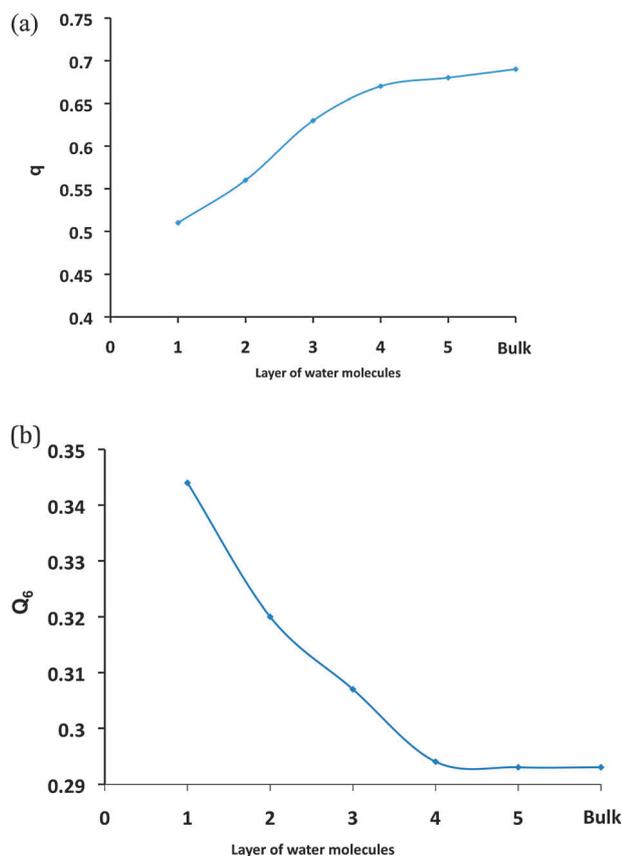
falls rapidly ( $\sim 1.3$ – $1.5$ ) and approaches that of bulk water ( $\sim 1.2$ ). Note that Yan *et al.* also obtained a value of  $\sim 1.2$  for the translational order parameter for liquid water at 300 K.<sup>49</sup> The predictions of the SPC/EF water model thus suggest that the first two water layers near the oxide surface are strongly ordered with the layers (3rd and beyond) farther away being much less affected by the oxide surface.

Furthermore, one can define orientational order ( $q$ ) to quantify the tetrahedrality of the first shell. Thus, the ability of the water to produce tetrahedral arrangements is described by the orientational parameter  $q$ , which is defined as follows:<sup>50</sup>

$$q \equiv 1 - \frac{3}{8} \sum_{j=1}^3 \sum_{k=j+1}^4 \left[ \cos \theta_{jik} + \frac{1}{3} \right]^2 \quad (3.2)$$

where  $\theta_{jik}$  is the angle formed by the lines joining the oxygen atom of a given molecule with that of each of the four nearest neighboring molecules. In this study, the ensemble average is obtained over not only all the molecules but also the time-frames of the simulation. The value of  $q$  would effectively range from 0, in a random distribution of molecules (such as ideal gas), to 1, in a perfect tetrahedral arrangement. Note that the value of this order parameter is not subjected to the choice of any particular local coordinate system in the reference molecule.

Fig. 6(a) shows the variation in the  $q$  parameter with distance of the layers from the oxide interface. The order



**Fig. 6** Orientational order parameters (a)  $q$  and (b)  $Q_6$  for the SPC/EF water model as a function of various water layers away from the oxide interface. Comparison with bulk water is also shown.

parameter  $q$  is a measure of tetrahedrality in the distribution of the four nearest oxygen around a central oxygen. Compared to bulk water, the interfacial water molecules located near an oxide surface have constrained transverse and longitudinal degree of freedom. Hence, the resulting hydrogen bond network between water–water can be significantly different from that of bulk water. In particular, one can expect a distortion of the tetrahedral order in interfacial water caused by the lateral diffusion being reduced and also by changes in the distribution of hydrogen bonds near an interface. This is indeed manifested in the low  $q$  values for water layers close to the oxide interface ( $\sim 0.52$ ). As the distance from the interface increases, the 2-D layering of water molecules evolves into a more 3-D network. The hydrogen-bonding network becomes more and more three-dimensional and approaches the hydrogen-bonding network of bulk water. Accordingly, the values of the order parameter  $q$  increases and  $q$  for layers of water molecules farther away from the oxide surface (beyond 3rd) approach that for bulk water ( $\sim 0.69$ ). Note that a  $q$  value of 0.69 for ambient water is in good agreement with those reported previously.<sup>49–51</sup>

We can also define a bond orientational order parameter ( $Q_6$ ) for the second shell of water which quantifies the extent to which a molecule  $i$  and twelve of its neighbors adopt the local ordered (typically fcc, bcc, or hcp) structures. We have utilized this orientational order parameter (defined originally by Steinhardt *et al.*<sup>52</sup>) to distinguish between ordered and disordered structures. To compute  $Q_6$ , we define the various bonds connecting each water molecule  $i$  with its next nearest neighbors in the second shell and compute for each bond its azimuthal and polar angles ( $\theta$ ,  $\phi$ ). Next, we compute the average of the spherical harmonic function ( $\bar{Y}_{lm}(\theta, \phi)$ ) over these bonds of atom  $i$ . Finally, we compute the order parameter as follows:

$$Q_{li} = \left[ \frac{4\pi}{2l+1} \sum_{m=-l}^{m=l} |\bar{Y}_{lm}|^2 \right]^{1/2} \quad (3.3)$$

For  $l = 6$ , the average value  $Q_6$  is then given by:

$$Q_6 = \frac{1}{N} \sum_{i=1}^N Q_{6i} \quad (3.4)$$

The value of the global bond orientational order parameter  $Q_l$  has a higher value for ordered systems such as crystal structures [0.574 for fcc, 0.511 for bcc and 0.485 for hcp]. For uncorrelated systems, the order parameter  $Q_6 = 1/\sqrt{12} = 0.289$ .

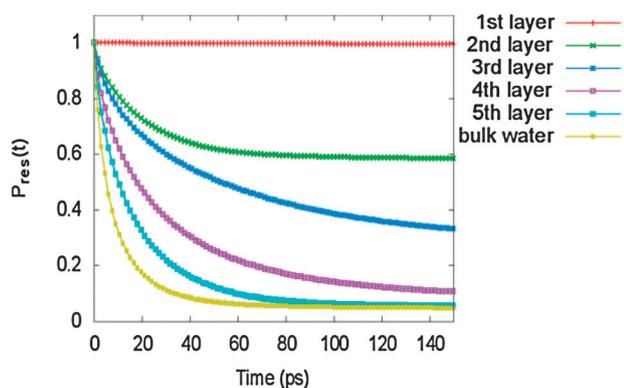
Fig. 6(b) shows the order parameter  $Q_6$  calculated for the various water layers away from the oxide interface. As seen in Fig. 6(b), the ordered layers of water close to the oxide surface have higher values of order parameter ( $\sim 0.344$ ). The change in the order parameters is more pronounced with increasing distance from the oxide surface, which suggests a rapid decrease in the extent of ordering of water molecules. Bulk water shows an order parameter  $Q_6 \sim 0.289$ . Thus, the water layers near the oxide surface (first-second) are strongly ordered whereas the layers (beyond 3rd) farther away are being much less affected by the oxide surface. It is worth noting that this analysis suggests that the  $Q_6$  parameter is not as sensitive to the

extent of ordering (varies from 0.34 for the first layer to 0.29 for bulk) as the translational order parameter (varies from 3.2 for the first layer to 1.2 for bulk).

### 3.3 Residence probability of water molecules near the oxide surface

The residence probability ( $P_{\text{res}}(t)$ ) of water molecules confined between oxide surfaces and bulk water was calculated. Water molecules were divided into different layers based on their distance from the surface of the MgO(100) slab. Five layers of water molecules were defined as follows: (1st layer) water molecules within 3.0 Å, (2nd layer) water molecules between 3.0 Å and 5.0 Å, (3rd layer) water molecules between 5.0 Å and 7.0 Å, (4th layer) water molecules within 7.0 Å and 9.0 Å, and (5th layer) water molecules within 9.0 Å and 11.0 Å.  $P_{\text{res}}(t)$  was defined, by continuous definition, as the probability of finding a water molecule in one of the above defined regions without departing from that region at any time between time  $t_0$  and  $t + t_0$ .  $P_{\text{res}}(t)$  was averaged over several different simulation frames that were collected over a time frame of 1 nanosecond in intervals of 1 ps.

Fig. 7 shows the  $P_{\text{res}}(t)$  for water molecules in the various layers away from the oxide surface as well as bulk water. The residence probability is calculated using the continuous definition that allowed us to quantify how long on average, one water molecule continuously resides in a given region, namely, confined water and bulk water. We find that  $P_{\text{res}}(t)$  of water molecules decreases with increase in their distance from the oxide surface. The slow dynamical behavior for the interfacial water layer, supported by the structural properties of interfacial water molecules discussed in the earlier sections, indicates energetically stable configurations arising from the proximity to the oxide surface. The slow dynamical behavior is consistent with the findings of Pal *et al.*, who observed that the residence times and the lifetimes of hydrogen bonds among water molecules bound to the hydrophilic surface was found to be much higher than that of free water molecules.<sup>53</sup> In another work, they show that the slowness in the orientational time correlation function originates partly from the formation of bridge hydrogen bonds between the polar head groups in an aqueous micelle of cesium perfluorooctanoate (CsPFO). The oxide surfaces also fall under the category of hydrophilic surfaces. The observed variation in the residence



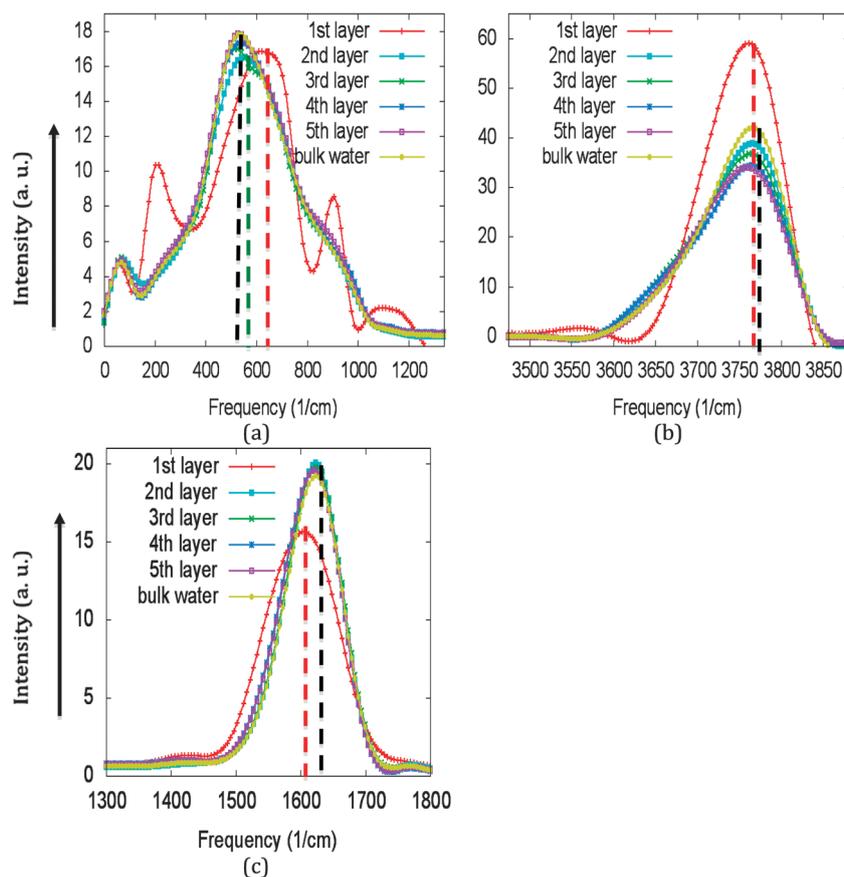
**Fig. 7** Residence probability ( $P_{\text{res}}(t)$ ) of water molecules, by continuous definition, for various layers near the oxide surface. Comparison to the residence probability in pure bulk water is also shown.

probabilities can be explained by the fact that water molecules in the interfacial layer are strongly hydrogen bonded to the oxide surface and hence have much higher residence probabilities than that of pure bulk water. Similarly, Fenn *et al.*<sup>54</sup> find that the orientational relaxation times for interfacial water molecules in reverse micelles measured with ultrafast infrared spectroscopy are much smaller than that of bulk water, which is consistent with that observed for interfacial water molecules in our work. The residence time for  $P_{\text{res}}(t)$  to decay to  $1/e$  is  $\gg 150$  ps for interfacial water molecules in the first and second layers whereas  $P_{\text{res}}(t)$  is approximately  $\sim 150$  ps for the 3rd layer,  $\sim 40$  ps for the 4th and  $\sim 20$  ps for the 5th layer. The significantly increased residence time for the interfacial water molecules is in good agreement with that reported by Kerisit, who found residence times  $\gg 1000$  ps for interfacial water near calcite surfaces.<sup>55</sup>  $P_{\text{res}}(t)$  is  $\sim 8$  ps for bulk water that is similar to that obtained by Argyris *et al.*<sup>16</sup> Thus, as the distance from the oxide surface increases, the dynamical properties of the water molecules begin to approach that of bulk water.

### 3.4 Vibrational spectra of water molecules

To calculate the vibrational spectra for the interfacial water molecules, we divided water molecules into different layers based on their distance from the surface of the MgO(100) slab. Five layers of water molecules were defined as follows: (1st layer) water molecules within 3.0 Å, (2nd layer) water molecules between 3.0 Å and 5.0 Å, (3rd layer) water molecules between 5.0 Å and 7.0 Å, (4th layer) water molecules within 7.0 Å and 9.0 Å, and (5th layer) water molecules within 9.0 Å and 11.0 Å. To compare the spectra of these water molecules with the pure bulk water, we independently carried out simulations of 1024 water molecules. Vibrational spectra comprising of the libration, stretching, and bending band for hydrogen atoms of water molecules found in different layers are shown in Fig. 8 (a), (b), and (c), respectively. Fig. 9 shows the spectra of oxygen atoms of water molecules found in different layers of water molecules and for pure bulk water.

**3.4.1 O–H libration band of hydrogen atoms of water.** The libration band of the O–H spectra governs the intermolecular vibrations and can be characterized from its hydrogen atom vibrational spectra. Fig. 8(a) shows the O–H libration band for the hydrogen atom of water molecules observed in different layers and for pure bulk water. The libration band in the case of pure bulk water is represented by a characteristic peaks at  $\sim 50$   $\text{cm}^{-1}$  and at  $\sim 500$   $\text{cm}^{-1}$ . The O–H libration band of water molecules that are present in the 1st layer shows characteristic peaks/shoulder at  $\sim 50$ ,  $\sim 193$ ,  $\sim 630$ ,  $\sim 920$ , and  $\sim 1100$   $\text{cm}^{-1}$ , respectively. These multiple peaks/shoulder can possibly arise due to the presence of hydrogen bonded water clusters of different sizes ( $\sim 2$  to  $\sim 14$  water molecules). For example, the peak observed at  $\sim 193$   $\text{cm}^{-1}$  can be attributed to the hydrogen-bonded dimer of water molecules.<sup>56</sup> Similarly, the peak observed in the O–H libration band at  $\sim 630$   $\text{cm}^{-1}$  has been assigned to the presence of a hydrogen bonded cluster consisting of 5 water molecules.<sup>56</sup> As seen in Fig. 8(a), the blue shift in the peak observed at  $\sim 630$   $\text{cm}^{-1}$  can be attributed to the hydrogen atoms of water molecules that are involved in the hydrogen bonds with the oxide surface.



**Fig. 8** (a) Libration band of the vibrational spectra of hydrogen atoms of water molecules found in different layers and hydrogen atoms of pure bulk water. (b) Stretching band of the vibrational spectra of hydrogen atoms of water molecules found in different layers and hydrogen atoms of pure bulk water. (c) Bending band of the vibrational spectra of hydrogen atoms of water molecules found in different layers and hydrogen atoms of pure bulk water.

Pal *et al.* also found a blue shift in the librational band of the interfacial water molecules relative to bulk water in their simulation studies of water molecules in an aqueous micelle of cesium perfluorooctanoate (CsPFO).<sup>57</sup>

For pure bulk water, the O–H libration band displays a characteristic peak at  $\sim 50$  and  $500\text{ cm}^{-1}$ . Similarly, in the case of the 2nd, 3rd, 4th and 5th layer of water molecules, two prominent peaks for the O–H libration band were observed at  $\sim 50$  and  $\sim 510\text{ cm}^{-1}$ , which is very similar to that of pure bulk water. The second peak at  $\sim 500\text{ cm}^{-1}$  in the O–H libration band of the pure bulk water was slightly red-shifted by  $40\text{ cm}^{-1}$  compared to that for water molecules in the 2nd and higher layers; the extent of shift being higher for the layers closer to the oxide surface. Furthermore, we also observe a slight shoulder at  $\sim 860\text{ cm}^{-1}$  for the O–H libration band of the water molecules in the 2nd layer. A shoulder at this position and with somewhat lower intensity is observed for proximal water molecules in the subsequent layers (beyond 2nd) as well as pure bulk water. Non-existence of any significant shift in the libration band positions (2nd and beyond) suggests that the librational motions of proximal water in the 2nd layer and beyond are mostly unaffected.

### 3.4.2 O–H stretching band of hydrogen atoms of water.

Fig. 8(b) shows the spectra for the stretching band of hydrogen

atoms of water molecules found in different water layers interacting with MgO(100) and for pure bulk water. It is well known that the O–H stretching band is affected by the hydrogen bond formation.<sup>9,11,13</sup> Shen *et al.* have shown that interfacial water spectra near hydrophilic oxide surfaces exhibit additional signatures compared to those characterizing the pure bulk water.<sup>58</sup> In the case of (0001)  $\alpha$ -silica/water interfaces, the vibrational spectra determined experimentally by Shen *et al.* showed two peaks, interpreted as ‘liquid-like’ at  $\sim 3400\text{ cm}^{-1}$  and more-ordered interfacial water regions with ‘ice-like’ features at  $\sim 3200\text{ cm}^{-1}$ .<sup>59</sup> In the case of the (0001)  $\alpha$ -alumina/water interface, Shen *et al.* find similar ‘liquid-like’ and ‘ice-like’ peaks in the  $\sim 3400\text{--}3700\text{ cm}^{-1}$  range, corresponding to bulk and interfacial water. Our simulations also suggest that surface water molecules (1st layer of water molecules) can form two types of hydrogen bonds: (1) water–oxide hydrogen bonds and (2) water–water hydrogen bonds. The O–H stretching band of the vibrational spectra of the 1st layer of water molecules shows two prominent peaks at  $\sim 3560\text{ cm}^{-1}$  and at  $\sim 3750\text{ cm}^{-1}$ , respectively, which correspond to these two hydrogen bonding states. We thus assign the peak observed at  $\sim 3750\text{ cm}^{-1}$  to the hydrogen atoms of water molecules that are hydrogen bonded to other water molecules and the peak observed at  $\sim 3560\text{ cm}^{-1}$  to the hydrogen atoms of water molecules that are hydrogen bonded to the oxide surface.<sup>13</sup> On the other hand, the 2nd and

3rd layer of water molecules show a single peak for the O–H stretching band at  $\sim 3760\text{ cm}^{-1}$  which is representative of water molecules hydrogen bonded to other neighboring water molecules.<sup>9</sup> Similarly, the 4th and 5th layer of water molecules as well as pure bulk water shows an O–H stretching peak at  $\sim 3770\text{ cm}^{-1}$ .

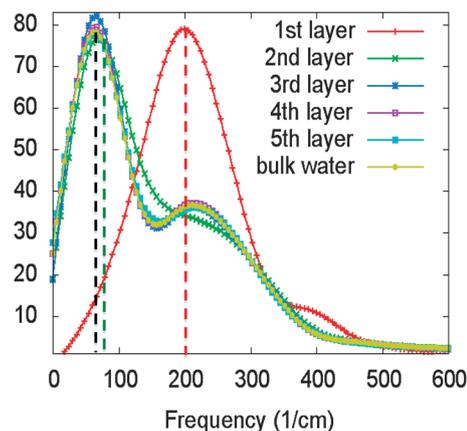
It can be seen from Fig. 8(b) that the stretching band observed at  $\sim 3750\text{ cm}^{-1}$  for hydrogen atoms of water molecules in the 1st layer shows a red shift and also has a higher peak intensity compared to the other layers of water molecules formed between MgO(100) slabs. A red shift in the stretching band of water molecules present in the 1st layer suggests that the near surface water molecules are strongly hydrogen bonded compared to those present in the other layers and in pure bulk water. We also observe that water molecules present in the 1st layer are in direct contact with the MgO surface and are almost parallel to the MgO surface. The geometrical constraints imposed by the MgO slabs lead to hindered motion of the water molecules and leads to the observed layering effect. This ordered arrangement of water molecules might facilitate the formation of strong hydrogen bonds between water and water and between water and the MgO surface. A blue shift in the high frequency stretching band of the water molecules is observed as their distance increases from the MgO(100) surface. This suggests that the hydrogen bonds formed in subsequent layers of water molecules are weaker than those formed in the 1st layer of water molecules; the strength of hydrogen bonding decreases with increasing distance from the oxide surfaces (2nd > 3rd > 4th > 5th). It is also worth noting that the O–H stretching band of water molecules in layers away from the MgO(100) surface (> 3rd) approaches that of pure bulk water.

### 3.4.3 O–H bending band of hydrogen atoms of water.

Fig. 8(c) shows the O–H bending band of the water molecules present in the various layers as well as for pure bulk water. In the case of the 1st layer of water molecules, the peak for the O–H bending band was observed at  $\sim 1610\text{ cm}^{-1}$ . A peak for the O–H bending band for the 2nd, 3rd, 4th, and 5th layer of water molecules as well as for pure bulk water was observed at  $\sim 1630\text{ cm}^{-1}$ . The peak observed at  $\sim 1610\text{ cm}^{-1}$  in the 1st layer of water molecules is red shifted compared to the peak observed at  $\sim 1630\text{ cm}^{-1}$  for the other layers of water molecules and for pure bulk water. This band position is red shifted and has a lower intensity for the proximal water molecules that are directly involved in forming hydrogen bonds with the oxide surface. The possible explanation for the observed red-shift might lie in the clustering of the water molecules in the first layer close to the oxide interface. Indeed, our analysis of simulation snapshots and trajectories suggests the presence of hydrogen bonded water clusters of different sizes ( $\sim 2$  to  $\sim 14$  water molecules). Interestingly, Asmis *et al.* found that the peak position of the bending band remains at  $\sim 1610\text{ cm}^{-1}$  until cluster size  $n = 25$ .<sup>66</sup> In the case of larger clusters ( $\sim 50$ ), they find that the bending band monotonically shifts to higher frequencies, up to  $1637\text{ cm}^{-1}$ , and approaches the value of the bending band in bulk liquid water ( $\sim 1630\text{ cm}^{-1}$ ). This might explain the shift in the bending band peak from  $1610\text{ cm}^{-1}$  in the first layer to  $\sim 1630\text{ cm}^{-1}$  for water molecules in the second layer and beyond where such clustering is not evident.

Furthermore, we also note a small decay in the peak intensity observed in the O–H bending band for as we proceed from the 2nd layer to the 5th. The peak height at  $\sim 1630\text{ cm}^{-1}$  is slightly higher for the water molecules in the 2nd layer compared to those in the 3rd, 4th, and 5th layer and to pure bulk water. In the case of water molecules in the 3rd, 4th, and 5th layer, there is not much difference in the peak heights. The peak height corresponding to the O–H bending band for the 1st layer is the lowest compared to that for water molecules present in the different layers formed between MgO slabs. The differences in the bending frequencies and intensities of water molecules, especially in the first proximal layer, that are bound to the oxide surface *via* formation of hydrogen bonds might be attributed to the clustering of water molecules. The bending motion of water molecules in the 2nd layer and beyond is largely unaffected.

**3.4.4 Vibrational spectra for oxygen atoms of water.** Fig. 9 shows the vibrational spectra for the oxygen atoms of water molecules present in the 1st to 5th layers on the MgO slab and for pure bulk water. The low-frequency vibrational spectrum of pure bulk water is characterized by two broad bands at  $\sim 50\text{ cm}^{-1}$  and  $\sim 250\text{ cm}^{-1}$ , respectively. The band around  $50\text{ cm}^{-1}$  is generally assigned to the O–O–O bending mode that involves triplets of hydrogen bonded water molecules.<sup>60</sup> On the other hand, the band at  $\sim 250\text{ cm}^{-1}$  can be attributed to the longitudinal O–O stretching mode between hydrogen bonded pairs of water molecules. The strong interactions between the oxide surface and the water molecules can modify the hydrogen bonding arrangement and in turn are likely to influence the low frequency vibrational bands of the water molecules that are proximal to the oxide–water interface. In the case of water molecules present in the 1st layer, we observe the peak corresponding to the O–O–O bending mode at  $\sim 215\text{ cm}^{-1}$ . Thus, the band corresponding to the O–O–O bending mode is shifted to higher frequency (blue shifts) for interfacial water; the extent of shift depends on the proximity to the oxide–water interface. Highly restricted transverse oscillations of interfacial water molecules due to geometrical constraints arising from stronger hydrogen bonding between oxide–water result in larger blue shifts of this band. Vibrational spectra of oxygen of water



**Fig. 9** Vibrational spectra of oxygen atoms of water molecules found in different layers. Comparison with the spectra for oxygen atoms of pure bulk water is also shown.

molecules present in the 2nd to 5th layer show the O–O–O bending mode at  $\sim 50\text{--}70\text{ cm}^{-1}$ . The red shift in the first peak of the vibrational spectra of oxygen atoms from  $\sim 215\text{ cm}^{-1}$  to  $\sim 50\text{ cm}^{-1}$  can be attributed to the presence of stronger hydrogen bonding in the 1st layer of water molecules as compared to the water molecules present in the 2nd layer of water molecules and beyond. The red shift in the vibrational spectra of oxygen atoms of pure bulk water molecules as compared to the water molecules present in the 1st layer suggests that hydrogen bonds formed in the ordered layer of water molecules are stronger than that in pure bulk water. Compared to bulk water, the blue shifts in the peak positions of the O–O–O bending modes are higher for proximal water molecules that are closer to the oxide surface; the interfacial water molecules showing the highest blue shift. This confirms further the relatively strong effect of the oxide surface on the hydrogen bonding network in such bound water molecules.

A second prominent band around  $\sim 200\text{--}400\text{ cm}^{-1}$  appears in the case of the various water layers, which is attributed to the longitudinal O–O stretching mode between hydrogen bonded pairs of water molecules. In the case of interfacial water in the 1st layer, we find that the band corresponding to the longitudinal O–O stretching mode is blue-shifted to  $\sim 400\text{ cm}^{-1}$  compared to the layers away from the oxide surface (3rd and beyond) as well as pure bulk water. For the second layer, although the O–O stretching mode is represented by a shoulder at  $\sim 260\text{ cm}^{-1}$  and further red-shifts to  $\sim 220\text{ cm}^{-1}$  for layers away from the oxide surface (3rd and beyond). Thus, the band corresponding to the O–O longitudinal oscillations or stretching of water is found strongly affected for the interfacial water layer whereas it is found to be mostly insensitive for the water layers (3rd and beyond). As expected, this band for water layers (3rd and beyond) approaches that of pure bulk water, which indicates a much higher degree of freedom for longitudinal motion. A similar effect of nanoscale confinement of water on its low-frequency band has been previously demonstrated in the case of water confined between graphene pores, aqueous–micellar interfaces and for water confined in organic macromolecules.<sup>53,57,60–63</sup>

**3.4.5 Current and future experimental studies on vibrational spectra of interfacial water.** In the recent past, experimental techniques, such as surface-specific sum-frequency vibrational spectroscopy (SFVS),<sup>67–70</sup> and total internal reflection (TIR) sum-frequency vibrational spectroscopy (VSFS),<sup>71</sup> have been employed to gain insights into the structure of water near surfaces. These methods have helped identify ice-like, liquid-like, and dangling O–H structures in the terminated hydrogen-bonding network of the water layer located in close proximity to air–water, aqueous–organic, and water–quartz interfaces.<sup>72–74</sup> Experimental measurements that can provide a detailed atomistic view of the structure of proximal water and the nature of its hydrogen bonding have been found to be problematic due to the difficulty in selectively probing the proximal water molecules.<sup>71</sup> Furthermore, the ultrafast dynamics of proximal water layers makes it difficult to deconvolute the measured vibrational and optical spectra. In these systems, the network of hydrogen-bonded water molecules is highly dynamic and time-resolved vibrational spectroscopy studies in the picoseconds and sub-picosecond

timescales would be required to understand the ultrafast vibrational dynamics of proximal water and characterize the atomic scale structural changes.

Another issue with most spectroscopic measurements of water near interfaces lies in the difficulty to obtain information as a function of depth from the interface. For example, experimental studies have attempted to use VSF spectroscopy mostly to study a variety of liquid–liquid systems.<sup>75</sup> However, these studies find that the use of the spectral results from VSF to obtain dynamical information as a function of interfacial depth is very difficult. This is attributed to the fact that while VSF spectroscopy is an excellent probe of the atomic scale and molecular bonding interactions extant within the interfacial region, the observed spectral response is typically integrated over the entire interfacial region that makes depth profiling difficult. Previous studies suggest that X-ray reflectivity can be a very good technique when applied toward the measurement of interfacial depth.<sup>76</sup> Similarly, second harmonic generation (SHG) spectroscopy has been used in conjunction with tracer or probe molecules of varying lengths (termed “molecular rulers”), to explore interfacial properties as a function of depth from the interface.<sup>77</sup> But neither of these techniques can match the atomistic and molecular-level bonding information that can be measured using vibrational spectroscopic methods.

A possible solution is to combine the information obtained from molecular dynamics simulations with those obtained from vibrational spectroscopic methods. For example, molecular dynamics simulations were applied toward the generation of VSF spectral profiles of water at the carbon tetrachloride–water ( $\text{CCl}_4\text{--H}_2\text{O}$ ) and 1,2-dichloroethane–water ( $\text{DCE--H}_2\text{O}$ ) interfaces by Walker and Richmond.<sup>78</sup> They measured spectral profiles as functions of both frequency and interfacial depth, thus providing the molecular-level bonding information that are typically obtainable from VSF spectroscopic methods. An iterative scheme that combines both vibrational spectroscopic experiments and molecular dynamics can help elucidate the dynamics as a function of location with respect to the interfacial region. Walker and Richmond have shown that such a combined experimental and computational approach indeed allows for a better understanding of the interfacial region and the species of water that are present at different depths. Such information cannot be obtained by the VSF experimental measurements alone and the current computational work lays the groundwork for further experimentally probing the interfacial dynamics of various proximal water layers near oxide surfaces.

## IV. Conclusions

In summary, atomistic simulations of the  $\text{MgO}(100)$ –water system employing an SPC/EF water model were carried out to study proximity effects on the structure and dynamics of water layers near an  $\text{MgO}$  surface. Analysis of the simulation trajectories based on dynamical correlation functions such as radial distribution functions, atomic density profiles and residence time probabilities suggests that there is ordering of water molecules in the two layers close to the oxide interface. Quantitative estimates into the extent of ordering provided by the translational and orientational order parameters suggest

that the extent of ordering decreases with increasing distance from the oxide–water interface. The simulation trajectories are further used to probe the interface-proximity effects on the low, intermediate and high frequency density of states of water molecules confined between MgO slabs. Our results provide detailed insights into the differential influence on the transverse and longitudinal degrees of freedom of water interacting with a model oxide surface. We notice that the librational motion of the proximal water molecules in the MgO–water system is hindered; the degree of influence being dependent on the proximity to the oxide surface. The hindered motion also results in clustering of water molecules in the interfacial layer. The calculations also suggest that the extent of blue shifts of the O–O–O bending mode of water molecules also depends on the proximity to the oxide–water interface. In general, this particular mode is found to suffer larger blue shifts for water having increasing proximity to the interface due to their restricted transverse oscillations. The position of the O–O stretching mode due to longitudinal oscillations of water is also found to be sensitive to such proximity effects; the larger blue shifts for interfacial water indicating presence of stronger hydrogen bonding in the 1st layer of water molecules as compared to the water molecules present in the 2nd layer of water molecules and beyond. The interface proximity effects are also clearly manifested in the O–H bending and stretching bands in the vibrational density of states of water molecules. The formation of hydrogen bonds restricts the local motions of water resulting in increased red shifts in the stretching band for proximal water molecules. The results of this simulation study lay the groundwork for experimentally probing the role and structure of proximal water on an oxide surface.

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