Dynamics and vibrational spectroscopy of water at hydroxylated silica surfaces†

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In the present study, the structural and dynamical properties of water at hydroxylated silica surfaces are investigated with classical molecular dynamics simulations. Depending on the nature of the interface, water molecules are observed to have well defined ordering and slower dynamics compared to bulk water. These properties include the orientation of water near the surface, reorientational relaxation times, translational diffusion coefficients, planar density distribution and vibrational spectroscopic features. The dynamical and structural features are affected up to ≈ 6–10 Å away from the surface, depending on the properties considered (lateral diffusion coefficient, charge density profile, rotational orientational time). Water molecules at the silica surface show a marked decrease in the diffusion coefficient and an increase in rotational correlation times. The presence of the polar –OH group on the hydroxylated silica surface provides adsorption sites for water with preferred orientations. In addition to the known broadening of the water spectrum in the bonded OH-stretch region for first-layer water molecules, the present simulations find a characteristic band at 1150 cm⁻¹, which is assigned to the HO(water)–H(SiOH) bending vibration. Because this signal only occurs for water molecules in the first layer, it should be experimentally accessible through surface sensitive techniques such as vibrational sum frequency generation spectroscopy (VSFG).

1. Introduction

Water molecules at the solid–liquid interface play important roles in surface science (adsorption/desorption), geology, material science, diffusion of ions in nanopores, biological membranes and in interfacial chemistry.1–6 A number of experimental7–12 and theoretical studies13–20 have provided deeper insight into the molecular level behavior of water itself and at interfaces. It has been found that properties of water at surfaces can be strongly affected by the existence and the nature of the solid substrate and is due to the heterogeneous environment

† Electronic supplementary information (ESI) available: planar density distribution, vibrational spectra of water with the simple charge model (TIP3P). Vibrational spectra for isotopically substituted water molecules (HOD and D₂O) with MTP water model. See DOI: 10.1039/c3fd00096f
generated by the surface itself. The resulting effects on water are observed through changes in the spectroscopic response, pronounced density layers, the change in the local dielectric constant and in different structural and dynamical properties of water at these interfaces.21,22 Such phenomena are also important technologically in the context of electrolytes near a charged surface23 and in chromatographic processes.24,25 As to the latter, various theoretical studies involving classical molecular dynamics, ab initio molecular dynamics and experimental techniques like non-linear optical spectroscopy have been used to characterize silica–water interfaces.26,27 Computer simulations considered interfacial water at quartz,27–34 metal35,36 and other mineral surfaces.37,38 These investigations clearly show how the solid substrate perturbs the local structure and hydrogen bond dynamics of water up to 10–15 Å away from the surface.

Water has been investigated particularly well at the water–air interface.26,27,39–47 These studies found spectroscopic features that extend from around 3200 to 3700 cm\(^{-1}\). The analysis of the spectroscopic signatures in terms of their origin and the local orientation of the water molecules has lead to a number of, sometimes conflicting, interpretations.39,47–49 Also, water at mineral surfaces has been investigated by spectroscopic means. For water at silica surfaces the pH-dependent VSFG spectra were recorded at a quartz(0001) surface. A prominent two-peak structure with spectroscopic signals around 3200 cm\(^{-1}\) and 3400 cm\(^{-1}\) was found at high pH (SiO\(^-\)) whereas at low pH (SiOH) the double-peak was less prominent.50

The hydrogen bond and orientational dynamics of water in contact with nanoscopic environments has also attracted considerable attention. Of particular relevance are experimental and simulation studies of water in reverse micelles, which provide a well defined chemical environment to study water dynamics in contact with a surface.51–54 The reorientational dynamics were found to contain multiple time scales, extending from the sub-picosecond librational dynamics to several ten picoseconds involving the reorganization of the water-hydrogen-bonded network. Comparing experimental and simulation results it was found that the nonexponential decay of the orientational diffusion is comparable although they do not agree quantitatively.54

In the context of chromatography, the role of water molecules has been recognized for quite some time. The existence of more or less ordered water networks has been postulated or found in chromatographic columns. Already 30 years ago, Scott and co-workers have suggested that individual water molecules can bind to the –OH groups of a silica surface and form a thermodynamically stable (fractional) monolayer.55 These water molecules, thought to be present up to temperatures of several hundred Kelvin, can serve as H-bond donors to additional water molecules, which eventually form filaments between the stationary (silica surface) and the mobile (solvent mixture) phase. The existence, morphology, and stability of such water filaments has been recently investigated by using atomistic simulations.25 These studies also corroborated the notion of water layers with differing stability depending on their separation from the stationary phase in chromatographic systems. The existence of surface-bound water molecules in chromatographic systems has been also established from atomistic simulations using a range of force fields and simulation strategies.25,56,57

In the present study, classical molecular dynamics simulations are used to provide insight into atomistic details of water at the silica–water interface relevant to chromatographic studies. We report on the structural and dynamical properties
of the solvent including the effect of multipolar interactions in the electrostatics on vibrational properties of water and provide an atomistic interpretation of the observed data. To this end, two different water models are used in the simulations—the widely used TIP3P parametrization\textsuperscript{58} and a flexible, multipolar water model. First, the computational realization of the system and the analysis of the data is described. Then, static and dynamical properties of water at a silica (101) face at low pH are reported and finally, the infrared spectroscopy is discussed.

2. Computational methods

2.1. Description of the system

The model silica layer was constructed by slicing two 8.75 Å thick segments of the (101) face of a quartz crystalline lattice with dimensions of 36 × 41 Å. This resulted in two surfaces with 64 silica hydroxy groups. The distance between the two silica layers was 30 Å, which resulted in a unit cell with dimensions 36 × 41 × 47.5 Å\textsuperscript{3}. A 30 Å wide water box was superimposed and all water molecules overlapping with the silica layers were removed. Fig. 1 shows a schematic representation of the system, which has also been used previously in the study of chromatographic interfaces.\textsuperscript{25,56,59,60}

In the present work, two water models were employed. One is the TIP3P water model\textsuperscript{58} and the second one is a flexible model based on the parametrization by Kumagai, Kawamura and Yokokawa (KKY),\textsuperscript{61} which was used with a quadrupolar charge model (see below). The functional form of the KKY potential for the stretching and bending energies is

\begin{equation}
E_{\text{str}} = D \left(1 - \exp\left[-\beta(r - r_0)\right]\right)^2 \\
E_{\text{bend}} = 2f_k k_1 k_2 \sin^2(\theta - \theta_0)
\end{equation}

Fig. 1  The solid silica layer with water. Water molecules are in CPK representation, the silica layer is in licorice representation. Color code: oxygen atoms of water and the silica layer are shown in red, silica atoms are shown in yellow and hydrogen atoms are shown in white. The z-axis is normal to silica surface.
where

\[ k_i = \frac{1}{\exp \left[ g_r (r_i - r_m) \right] + 1} \]

in which \( r_i \) is the equilibrium distance of the O–H bond of the water molecule and \( g_r \) and \( r_m \) are reported in Table 1. For the electrostatics, a monopolar (i.e. TIP3P) and a multipolar charge model with a geometry independent quadrupole on the oxygen atom and up to monopoles on the hydrogens was used. The electrostatic parameters for the multipolar model were obtained from \textit{ab initio} calculations at the MP2/aug-cc-pVQZ level of theory and are described in Table 2. The Lennard-Jones (LJ) parameter for this flexible water model was the same as for the TIP3P water model. The parameters for the silica surface were taken from our previous work.  

With the original parametrization of the KKY potential for water the stretching frequencies obtained were \( \nu_1 = 3720 \text{ cm}^{-1} \), \( \nu_2 = 1525 \times 10^4 \text{ cm}^{-1} \) and \( \nu_3 = 3763 \text{ cm}^{-1} \), which do not yield correct frequencies for the water bending mode. In the present study a reparametrization was used, which gives fundamentals at \( \nu_1 = 3689 \text{ cm}^{-1} \), \( \nu_2 = 1595 \text{ cm}^{-1} \) and \( \nu_3 = 3724 \text{ cm}^{-1} \).

### 2.2. Molecular dynamics simulations

All MD simulations were carried out with the CHARMM program with provisions for multipolar interactions. The number of water molecules in the system was 1310. Simulations for H2O, HOD and D2O followed identical protocols as described below. All simulations were carried out with periodic boundary conditions (PBC) and nonbonded interactions (electrostatic and Lennard-Jones) were truncated at a distance of 12 Å and switched between 10 and 12 Å. The atomic position of the bulk quartz surfaces with the exception of the exposed hydrogen atoms of the silanol groups (1664 atoms) were held fixed during the simulations. Initially the system was heated and equilibrated for 20 ps followed by 100 ps of production at 300 K in the NVT ensemble. The time step used was \( \Delta t = 0.4 \text{ fs} \) for all the simulations with the flexible KKY model. For these simulations, a Nose–Hoover thermostat with a thermal piston mass of \( Q = 50 \text{ kcal mol}^{-1} \text{ ps}^{-2} \) was used. For each of these systems with H2O, D2O and HOD, multiple independent simulations, each of 100 ps, were carried out and the results were averaged. For the TIP3P water model two simulations were run, one single trajectory of 5 ns length with \( \Delta t = 1 \text{ fs} \) using SHAKE and one trajectory for 100 ps with \( \Delta t = 0.4 \text{ fs} \), to calculate the vibrational spectra of water. However for some specific analysis (exchange dynamics), simulations with

### Table 1

Parameters for water potential reported in the work of Kumagai et al. and used in this work, together with the harmonic frequencies computed from them

<table>
<thead>
<tr>
<th></th>
<th>( D ) (( E_h ))</th>
<th>( \beta ) (( a_0^{-1} ))</th>
<th>( r_0 ) (( a_0 ))</th>
<th>( f_k ) (( E_h ))</th>
<th>( \theta_0 ) (deg)</th>
<th>( r_m ) (( a_0 ))</th>
<th>( g_r ) (( a_0^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>KKYb</td>
<td>0.120</td>
<td>1.45</td>
<td>1.55</td>
<td>2.5 \times 10^6</td>
<td>99.5</td>
<td>2.65</td>
<td>3.7</td>
</tr>
<tr>
<td>This work</td>
<td>0.120</td>
<td>1.44</td>
<td>1.81</td>
<td>0.0388</td>
<td>99.5</td>
<td>2.65</td>
<td>3.7</td>
</tr>
</tbody>
</table>

\(^a\) Atomic units are used for \( D \), \( \beta \), \( r_0 \), \( f_k \), \( r_m \) and \( g_r \). \( \theta_0 \) is given in degrees. \(^b\) The literature data were converted to atomic units from the following parameters: \( D = 75.0 \text{ kcal mol}^{-1} \), \( \beta = 2.74 \text{ Å}^{-1} \), \( r_0 = \text{Å} \), \( f_k = 1.1 \times 10^{-1} \text{ J} \), \( r_m = 1.40 \text{ Å} \) and \( g_r = 7.0 \text{ Å}^{-1} \).
the MTP water model are run for several nanoseconds. The MTP water model with inclusion of quadrupole is a computationally expensive water model and this is the reason for carrying out multiple short simulations (100 ps). It had been observed from other simulations performed on silica surfaces\textsuperscript{66,67} that the water dynamics (translational diffusion, orientational relaxation time) converges well within 10–30 ps. Furthermore, convergence tests for calculated IR spectra of single spectroscopic probes suggest that 500 ps simulations are appropriate for this property.\textsuperscript{68}

**Exchange dynamics.** For the analysis of the water dynamics, the system was divided into layers of thickness 3 Å each, parallel to the Si-surface and commensurate with the typical size of a water molecule. The first layer (layer I) includes water molecules which are within 3 Å of the oxygen atoms of the silica layer, which serve as the reference \( z = 0 \). The second layer (layer II) extends from 3 to 6 Å, and the third layer (layer III) from 6 to 9 Å. The exchange of water molecules is quantified by considering water molecules which are in layer I at \( t = 0 \) and move to layer II during the simulation and vice versa.

**Infrared spectra.** The infrared (IR) spectrum is calculated from the Fourier transform of the dipole moment autocorrelation function \( C(t) = \langle \vec{\mu}(0)\vec{\mu}(t) \rangle \), which is accumulated over \( 2^n \) time origins, where \( n \) is an integer such that \( 2^n \) corresponds to between 1/3 and 1/2 of the trajectory, with the time origins separated by 0.8 fs. \( \hat{C}(\omega) \), which is the Fourier transform of \( C(t) \), is computed using a fast Fourier transform (FFT) with a Blackman filter to reduce noise. The final infrared absorption spectrum \( A(\omega) \) is then calculated from

\[
A(\omega) = \omega \{ 1 - \exp[-\omega/(k_B T)] \} \hat{C}(\omega)
\]

where \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature in Kelvin.

### 3. Results and discussion

With a fully hydroxylated surface (SiOH), the simulations in the present work correspond to low-pH conditions in actual experiments. First, static properties are discussed, after which the translational, rotational and exchange dynamics are considered and the infrared spectra are presented.

#### 3.1. Static properties

**Charge density profile.** The charge density profile of water and deuterated water as a function of the distance away from the silica surface is shown in Fig. 2.

<table>
<thead>
<tr>
<th>( Q_{00}^O ) (e)</th>
<th>( Q_{10}^O ) (e( a_0 ))</th>
<th>( Q_{20}^O ) (e( a_0^2 ))</th>
<th>( Q_{22}^O ) (e( a_0^2 ))</th>
<th>( Q_{10}^H ) (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>-0.595922</td>
<td>-0.065831</td>
<td>-0.041591</td>
<td>-1.125991</td>
</tr>
</tbody>
</table>

\( a \) In the multipole component \( Q_{xu}^x \), \( u \) represents angular momentum labels (00, 10, 11c, 11s, 20, 21c, 21s, 22c, and 22s) and \( x \) represents the atom type (O or H). The units of \( Q_{xu}^x \) are given in parentheses in the table. Only nonzero components are shown.
with the silanol oxygen atom defining $z = 0$. Fig. 2 shows that the presence of the surface perturbs the interfacial water structure up to $\approx 5$ Å away from the silica surface. A similar behavior is observed for HOD and D$_2$O. The data in Fig. 2 is consistent with an orientation of the interfacial water where the water-H atom points towards the surface. The positive charge excess at $z = 0$ is due to the water oxygen H-bonded to the hydrogen of silanol group and the water-H atom pointing downwards between two adjacent silanol groups and was also found in previous studies.\textsuperscript{29,69,70} The excess of negative charge at $z = 4$ is due to the second layer of water molecules interacting through hydrogen bonding with the first layer, as shown in the inset. These charge density profiles are expected to affect the distribution of charged species at solid–water interfaces, possibly contributing to the adsorption of lactates\textsuperscript{71} and amino acid\textsuperscript{72} analogues on the hydrated silica surface.

**Orientalional behavior of water.** The presence of the surface is expected to perturb the local structure of water.\textsuperscript{32,33,38} The orientation of water molecules near the surface can be quantified by considering the water-OH vector relative to the space fixed $z$-axis. For this, the scalar product $\cos \alpha = \frac{\vec{r}_{OH} \cdot \vec{e}_z}{|\vec{r}_{OH}| |\vec{e}_z|}$ is computed for water in different layers. Fig. 3 reports the orientational probability $p(\alpha)$ for the OH-vectors involving both hydrogen atoms, H1 and H2, of the water molecules. For bulk water the water-OH vectors are expected to exhibit quite a uniform distribution as shown in Fig. 3A, whereas water molecules near the surface should have clearly preferred orientations. This is indeed observed for the three orientations I to III in Fig. 3B. For orientation I (H$_w$–O$_w$ points towards the surface-O atom, i.e. “H$_w$-down” configuration) the scalar product is $\approx 0$, whereas for orientation II (H$_w$–O$_w$ points towards the water above) it is $-1.0 \leq \cos \alpha \leq -0.8$ or $140^\circ \leq \theta \leq 180^\circ$, see Fig. 3B. For orientation III both water-H$_w$–O$_w$ vectors form an equal angle with the SiOH-hydrogen atom and yield $0.4 \leq \cos \alpha \leq 0.6$ as shown in Fig. 3B. Comparing this result with the orientation of the water TIP3P model (see Fig. 3C), we note that orientation III is considerably less populated.

![Fig. 2](image_url) Charge density profile of water as a function of the vertical distance $z$ from the silica layer where $z = 0$ corresponds to the oxygen atom of the silanol group. This data is plotted for H$_2$O, HOD, D$_2$O with the quadrupole moment on oxygen atoms. Color code: black for H$_2$O, blue for HOD, magenta for D$_2$O.
when using a TIP3P water model. This can be understood in terms of a favourable and stabilizing multipole-charge interaction between the water molecules and the surface-silanol hydrogen atoms compared to charge–charge interaction in the TIP3P water model. The increased population of state III should also affect other properties of the system, including the diffusional behaviour and the spectroscopy of surface-near water molecules.

**Planar density distribution.** The simulations allow to characterize the distribution and ordering of surface-bound water molecules. The planar density
distribution of the first layer water molecules is shown in Fig. 4. Due to the presence of the SiOH-groups, surface-bound water molecules can strongly interact with the surface, which leads to pronounced density maxima between these attachment points. The distribution of water oxygen atoms was calculated separately in layers parallel to the surface (x-y-plane) and of thickness 3 Å each. The silica oxygen atoms on the surface provide hydrogen bonding sites for interfacial water molecules and are shown as white dots in Fig. 4A. We observe the formation of closed ring structures (yellow trace) of water molecules occupying the space around a single Si-OH group, see Fig. 4A, which can be easily understood in terms of water molecules around –OH groups of the silica surface as shown in Fig. 4B (black dotted ring). Consequently, water molecules optimize their orientation relative to the surface SiOH groups. A similar analysis for simulations with the TIP3P water model is shown in Fig. S1, ESI,† which displays a less ordered structuring for surface bound water. This corroborates the finding that including multipoles in intermolecular interactions affects the structuring of the interfacial layer.

3.2. Dynamical properties

**Translational dynamics.** The translational dynamics of interfacial water molecules close to the surface perturbed by the presence of the SiOH groups can be further characterized in terms of their translational diffusion coefficients. The in-plane mean-square displacement MSD∥ for each layer is obtained from following the motion of the water-oxygen atoms according to

$$\langle D \rangle = \lim_{t \to \infty} \frac{1}{4t} \left( \sum_{i \in \text{layer}} [(x_i(t) - x_i(t = 0))^2 + (y_i(t) - y_i(t = 0))^2] \right) = \lim_{t \to \infty} \frac{1}{4t} \langle \Delta r^2(t) \rangle$$

(3)

from which the 2-dimensional self-diffusion coefficient $D$ can be determined. This was done for the TIP3P, MTP and a modified MTP parametrization.

![Fig. 4](image-url) A) Surface water density distribution parallel to the surface (x-y-plane) for water molecules in the first hydration layer. The white dots in panel A correspond to the oxygen atoms of the silica surface. “0” and “1” correspond to the minimum and maximum occupation. Relative water occupations are color coded from black (0.0) to red (1.0). B) Top view for distribution of water molecules adsorbed on the silica layer due to hydrogen bonding with –OH group of silica layer. Water molecule is shown in CPK and hydroxylated silica surface in licorice representation.
(see below) for the water molecules. As expected, the translational mobility of water molecules away from the interface is more rapid compared to layers close to the interface as shown in Fig. 5. The in-plane diffusion coefficient $D_\parallel$ for different regions were determined by fitting the 4 to 20 ps portion of $\langle \Delta r^2(t) \rangle$ to eqn (3).

With the MTP water model the in-plane diffusion coefficient for layer I ($0.004 \text{ Å}^2 \text{ ps}^{-1}$) is 35 times smaller than that in the middle of the column which is $D_\parallel = 0.14 \text{ Å}^2 \text{ ps}^{-1}$. This demonstrates that motion of water molecules adsorbed at the surface is slowed down due to strong electrostatic interactions with the surface. For the TIP3P model a similar observation is made although quantitatively, the numbers differ somewhat. They are 0.007 and 0.21 $\text{Å}^2 \text{ ps}^{-1}$. For layer III the diffusion coefficients are 0.06 and 0.08 $\text{Å}^2 \text{ ps}^{-1}$, respectively, for the MTP and TIP3P model.

In order to put these results into perspective, the (3-dimensional) diffusion coefficients for the MTP and TIP3P water models were also determined from 100 ps simulations of pure water (without silica surfaces) in a $30 \times 30 \times 30 \text{ Å}^3$ box with 1000 water molecules. They were found to be 0.052 $\text{Å}^2 \text{ ps}^{-1}$ and 0.32 $\text{Å}^2 \text{ ps}^{-1}$ for the MTP and TIP3P models, respectively, which compares with 0.22 $\text{Å}^2 \text{ ps}^{-1}$ for the experimentally determined diffusion coefficient. Hence, the quadrupolar model considerably underestimates the experimental value. This is related to the fact that the TIP3P van der Waals ranges were used in the simulations with the MTP electrostatic model. Repeating the MTP simulations with slightly increased (+2%) van der Waals ranges on the oxygen atom yields diffusion coefficients in close agreement with the experimental value. Using these scaled van der Waals ranges for the MTP model in simulations of water in contact with the silica surface, the corresponding 2-dimensional diffusion coefficients for layer I ($0.008 \text{ Å}^2 \text{ ps}^{-1}$) is 28 times smaller than that in the middle ($0.28 \text{ Å}^2 \text{ ps}^{-1}$). A similar behavior was already observed for water diffusion on hydroxylated aluminum and other polar surfaces.

Reorientational relaxation. The orientational behavior of water is highly dependent upon the surrounding environment and can result in slower dynamics close to the interface compared to bulk water. To characterize this we computed the
Reorientational autocorrelation functions for the water dipole moment vector (\(\vec{\mu}\)) and the H–H vector (\(\vec{r}_{HH}\)). The autocorrelation function used for this analysis is

\[
C_{\hat{\rho}}(t) = \frac{\langle \vec{\rho}(0) \vec{\rho}(t) \rangle}{\langle \vec{\rho}(0) \vec{\rho}(0) \rangle}
\]

(4)

where \(\vec{\rho}\) represents either the unit dipole moment vector \(\vec{\mu}\) or the H–H vector \(\vec{r}_{HH}\), respectively. The data for H\(_2\)O in different layers is reported in Fig. 6A. The reorientational relaxation times can be obtained from \(C(\tau)\). For water molecules in different layers we find that in the time regime from 0–30 ps the curves can be reasonably well described by triple exponentials

\[
A_1 \exp \left(-t/\tau_1\right) + A_2 \exp \left(-t/\tau_2\right) + (1 - A_1 - A_2) \exp \left(-t/\tau_3\right)
\]

with decay constants \(\tau_1\), \(\tau_2\) and \(\tau_3\). Furthermore, a

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Fig. 6  The dipole moment auto-correlation function for H\(_2\)O in different layers. A) Correlation function for \(\vec{\mu}\) for 4 different layers with the fitted data. Color code: layer I (black), layer II (green) and layer III (blue), middle (orange) and fitted data (red). Only the fit to layer I is shown. All other fits are of similar quality. The inset shows the correlation function on short times. B) Correlation function for the 9 water molecules which remain adsorbed to the surface for the entire 2.5 ns trajectory (blue) and for all water molecules in layer I (black).
stretched exponential \( \exp(-t/\tau^\beta) \) was considered and was found to equally well describe the data. The reorientational relaxation within the hydration layer (from \( z = 0 \) to 3 Å, layer I) is significantly slower than away from the surface (from \( z = 6 \) to 9 Å, layer III) and in the bulk (from \( z = 12 \) to 15 Å, middle). For all water molecules, irrespective of the layer they are in, the fastest decay occurs on a sub-picosecond time scale with \( \tau_1 = 0.5-0.8 \) ps. The second decay constant ranges from 2-5 ps with faster time scales for water in the middle of the system (i.e. “bulk”) and longer time constants for water molecules in layer I. The third decay constant has values between 11 ps and 52 ps, for water molecules in the bulk and in layer I, respectively. When fitting \( C(\tau) \) with a stretched exponential, \( \beta \) assumes values between 0.38 and 0.53.

For the dynamics on the nanosecond time scale, water molecules adsorbed for the entire simulation were analyzed separately. There were 9 molecules, i.e. 10% of the total number of water molecules in layer I (see Fig. 6B), which never exchange with neighboring layers. The corresponding rotational correlation function can be fit with time scales \( \tau_1 = 1.6 \) ps, \( \tau_2 = 42 \) ps and \( \tau_3 = 6.0 \) ns. When all water molecules in layer I are analyzed together, \( \tau_1 = 0.6 \) ps, \( \tau_2 = 19 \) ps and \( \tau_3 = 307 \) ps are obtained. Hence, the dynamics of the permanently adsorbed water molecules are distinctly different from those of the layer I molecules on average, which also contains molecules that exchange with subsequent layers. It is also interesting to note that a stretched exponential fit yields \( \beta = 0.33 \) for the 9 permanently adsorbed water molecules, which is indicative of collective and frustrated behaviour as also found in glassy systems. This observation is consistent with rotational relaxations of water on silica or other surfaces, where molecules at the surface generally reorient more slowly than in the bulk.\(^{37,38,74}\) Such long time decays have also been observed for water molecules at the surface of reverse micelles and hydrocarbons\(^{54,75}\) and also measured by NMR experiments for water molecules at silica surfaces.\(^{74}\) We further note that for \( \bar{\mu} \), the relaxation in layer II (from \( z = 9 \) to 12 Å) (Fig. 6) is very similar to bulk water, demonstrating that at a distance of 6 Å from the surface the rotational dynamics of water approaches that in the bulk. Another quantity, related to proton-NMR investigations, is the time scale of the rotational dynamics of the H–H vector (\( \vec{r}_{\text{HH}} \)). Fitting the \( \vec{r}_{\text{HH}} \) correlation function to a stretched exponential gives \( \beta = 0.34 \) and \( \tau = 238 \) ps for layer I water molecules and \( \beta = 0.49 \) and \( \tau = 172 \) ps for water molecules in the middle. This is consistent with the heterogeneous dynamics found from the dipole moment correlation functions.

**Exchange dynamics.** In chromatographic systems facile water exchange between neighboring water layers within the alkyl chains was observed.\(^{60}\) The water dynamics within the hydrophobic chains\(^{25}\) can lead to formation of water filaments, which allows intercalation of analyte molecules within hydrophobic regions.\(^{60}\) It is therefore also of interest to consider the water exchange dynamics in the present system. As was mentioned in the previous section, on a time scale of 2.5 ns about 10 of the water molecules do not desorb from the surface. The absolute number of water molecules exchanged between the first and the second layer from the silica layer for the MTP water model, together with average number of water molecules in layer I and layer II are reported in Fig. 7. Data from Fig. 7 for individual layers suggest that layer I contains around 104 water molecules, which is more than the number of silanol groups present at the surface. This is due to water molecules occupying interstitial sites between the silanol groups on the
Simulations with the MTP model find that the water flux equilibrates on the ns time scale and at equilibrium about 30 water molecules exchange between the two layers closest to the silica surface. However, it is interesting to note that even without the alkyl chains present, “avalanches” of water molecules can desorb or adsorb onto the silica surface, see e.g. the rapid change in the blue trace in Fig. 7 around 1.5 ns, which also suggests collective behaviour.

3.3. Vibrational spectroscopy

Fig. 8A gives an overview of the IR spectrum from simulations with the MTP model computed for all water molecules. Also the layer-specific spectra for layers I to IV are shown. By comparing the spectrum of layer I with those from layers II to IV it is evident that surface-bound water molecules give rise to considerably different spectroscopic signals. In particular the bonded –OH stretching region (3000 to 3750 cm$^{-1}$) differs in its width and around 1150 cm$^{-1}$ a new band, labelled $\alpha$ in Fig. 8A, arises which is absent for water molecules in layers II and beyond. Water molecules in layer I have a more heterogeneous environment compared to water molecules in layers II and beyond as they are surrounded by the silica layer and water molecules. Contrary to that, water molecules in layers away from the interface have a significantly more homogeneous environment. Experimentally, vibrational spectroscopy is a sensitive and powerful means to characterize structurally disordered condensed phase systems. In particular, surface sensitive SFG spectroscopy together with atomistic simulations$^{34,38}$ can provide detailed information about the relationship of structure and spectroscopy at interfaces.

In order to better understand the spectroscopic features of water molecules in the first layer, power spectra for different coordinates involving water molecules were also determined. In Fig. 8B, the water-IR spectrum for first layer molecules is enlarged. Fig. 8C reports power spectra for coordinates including the water-HOH bend, the water-OH and the $O_w$–$H_{SiOH}$ stretch, and the $H_Ow$–$H_{SiOH}$ bend modes.
Comparison with the IR spectrum identifies the HOw–H$_{SiOH}$ bend as being responsible for the IR peak at $\approx 1150$ cm$^{-1}$. The SiOH-hydrogen atom and water-oxygen atom give rise to strong hydrogen bonding, which leads to a libration mode as indicated in the inset of Fig. 8C. With the quadrupolar model for water, the tetrahedral geometry of the water molecules is captured more realistically. Simulations with the TIP3P water model without using SHAKE leads to a spectroscopic signal around 1150 cm$^{-1}$ but the power spectrum for the HOw–H$_{SiOH}$ bend is featureless and extends from a few hundred up to 2000 cm$^{-1}$ in stark contrast with simulations using the MTP model.

In order to study the isotope dependence, the same simulations were repeated for HOD and D$_2$O with the MTP model. The overall IR spectra are reported in
Fig. 9. The water-bending vibration shifts to the red as expected due to the larger mass in HOD and D$_2$O compared to H$_2$O. Concomitantly, the 1150 cm$^{-1}$ band shifts also to the red by $-15$ cm$^{-1}$ and $-35$ cm$^{-1}$ for HOD and D$_2$O, respectively. In the IR spectrum for D$_2$O, the DO$_{DOD}$–H$_{SiOH}$ band is hidden under the DOD bending mode. This is shown in Fig. S5, ESI† which exhibits the correspondence between the spectra for water (D$_2$O) in layer I and the power spectrum calculated for different modes. Experimentally, this band appears at 1209 cm$^{-1}$ which compares with 1180 cm$^{-1}$ from the present simulations, which emphasizes the quality of the MTP model together with the KKY parametrization for spectroscopic applications.

The orientation of water molecules with respect to the silanol group of the silica layer can be determined from angle distribution of the water-OH vector. The probability distribution is shown in Fig. 10A and 10B. Fig. 10A shows the distribution from simulations with the MTP model, whereas 10B reports that from using the TIP3P model. While the multipolar water model yields a narrow

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**Fig. 9**  Vibrational spectra of H$_2$O, HOD and D$_2$O from simulations with the KKY model with multipolar electrostatics. The isotope effect on the vibrational spectra is evident. Specifically, the band at 1150 cm$^{-1}$ for H$_2$O shifts to the red upon isotopic substitution.

**Fig. 10**  Distribution for the H(SiOH)–OH(water) angle with the KKY model and multipoles (panel A) and the TIP3P water model (panel B).
distribution peaked around 100°, indicative of a tetrahedral environment of the surface-bound water molecules, the distribution for the TIP3P model is very broad and bimodal. A similar bimodal distribution is observed for TIP3P water molecules in contact with nanoporous silica layers in which the study was focused on the orientation of water depending upon the adsorbed amount of water in the silica pore. This is due to the increased orientational freedom of water molecules described by simple point charge models – such as TIP3P – compared to parametrizations which account for higher electrostatic moments.

4. Discussion and conclusion

The present work reports all-atom molecular dynamics simulations of the dynamics and spectroscopy of water at hydroxylated silica surfaces. For this, two different water models were used: a point charge-only model and one multipolar, flexible water model. Specifically, the local charge density, in-plane mobility, rotational correlation time, exchange dynamics and vibrational spectra and effect of isotopic substitution on vibrational spectra of water molecules at the interface and in the bulk were considered. Our results suggest that the presence of the solid substrate affects both structural properties of water and their dynamical behaviour. In particular, the simulations provide layer-specific information which will be of interest for future surface-sensitive experiments. The in-plane diffusion of water at the surface is considerably slowed down through H-bonding interactions and the dipole moment ($\mu$) and the HH-vector ($\vec{r}_{HH}$) correlation functions show exponents very different from 1, which suggests strongly inhomogeneous, collective behaviour. The fitting of rotational correlation functions with a sum of exponentials (3 in the present case) or with a stretched exponential is a matter of some debate. Although a 3 exponential function may describe the correlation function well, it is often difficult to associate the time scales with specific processes due to the inhomogeneous nature of the system. The orientation of water molecules at the interface is studied in terms of “OH-up” and “OH-down” configurations. The presence of the hydroxyl group on the silica surface, characteristic for silica surfaces at low pH, provides a preferential adsorption site for water molecules. Such a situation is encountered in chromatographic systems, where the functionalized and partially hydroxylated silica surface acts as a solid support for the stationary phase.

The infrared spectrum of first-layer H$_2$O at the SiOH interface features a band around 1150 cm$^{-1}$ which was assigned to the OH(SiOH)–O(W) bending vibration. This band is absent for water molecules in subsequent layers and could be an interesting marker band in future experimental studies. The bonded-OH stretch region for first-layer water molecules is considerably broadened compared to that for water molecules in layers away from the interface and extends from 3200 to 3700 cm$^{-1}$. Specifically, the first-layer spectrum has a contribution to the red side of the bonded-OH stretch compared to second- and higher-layer water molecules. This is in qualitative agreement with experimental studies. However, for a more detailed discussion of this spectral range the vibrational sum-frequency spectrum would have to be determined, which is outside the scope of the present work. One of the differences between the present work and previous experiments is the face of silica that was used in the simulations. Following our previous work on chromatographic systems, the (101) face was employed here whereas the
experiments were carried out with quartz(0001). The orientational probability functions of first-layer water molecules show three different kinds of orientations of water molecules relative to the SiOH surface. The two major populations have the water-OH bond predominantly oriented “up” and “down” relative to the SiO bond whereas a minor component has the OH(SiOH) vector pointing along the water-HOH-bisector. This last configuration is only occasionally populated when a TIP3P model is used for water whereas the quadrupolar model allows to align the water molecules along the oxygen-lone pairs. This conformation is also responsible for the predicted spectroscopic band at 1150 cm\(^{-1}\).

Commensurate with the present applications – linear spectroscopy, diffusion and rotational motion – the force constants in the KKY model realistically describe the water monomer vibrations and the multipoles correctly capture the electrostatic potential around a water monomer. The diffusion coefficient computed with the present model is in reasonable agreement with experiment but no other thermodynamic observables were determined and compared with reference data. Contrary to that, the recently parametrized E3B model contains explicit many body contributions but it is a rigid water model.\(^7\) However, we do not expect that the primary conclusions of the present work are affected by the limited comparison with thermodynamic data because all quantities of interest are of spectroscopic nature. An advantage of the “KKY plus MTP” model may be that it is a flexible model, hence no maps are required for the OH-stretch vibrations, and the electrostatics is based on a multipolar expansion, which makes it also suitable for simulations in heterogeneous environments such as the one in the present work. For such studies, water models for pure water simulations or water at the water–air interface may be less well suited.

The most notable findings of the present work concern the prediction of a spectroscopic feature around 1150 cm\(^{-1}\) involving the surface-bound water molecules and the dramatic slowdown of translational and rotational dynamics of the first- and second-layer water molecules near an SiOH surface. The spectroscopic signal is assigned to the HO\(_w\)–H\(_{\text{SiOH}}\) bending vibration. Such quantities may be observable experimentally and provide meaningful atomistic information about surfaces relevant for chromatographic systems and the behaviour of water at interfaces in general.

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References