The Structure of Water in Silica Mesopores – Influence of the Pore Wall Polarity

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In the spatial confinement of cylindrical mesopores with diameters of a few nanometers, water molecules experience restrictions in hydrogen bonding. This leads to a different behavior regarding the molecular orientational freedom (‘structure of water’) compared to the bulk liquid state. In addition to the pore size, the behavior is also strongly affected by the strength of the pore wall-to-water interactions, that is, the pore wall polarity. In this work, this is studied both experimentally and theoretically. The surface polarity of mesoporous silica (SiO₂) is modified by functionalization with trimethylsilyl moieties, resulting in a change from a hydrophilic (pristine) to a hydrophobic pore wall. The mesopore surface is characterized by N₂ and H₂O sorption experiments. Those results are combined with IR spectroscopy to investigate pore wall-to-water interactions leading to different structures of water in the mesopore. Furthermore, the water’s structure is studied theoretically to gain deeper insight into the interfacial interactions. For this purpose, the structure of water is analyzed by pairing densities, coordination, and angular distributions with a novel adaptation of surface-specific sum-frequency generation calculation for pore environments.

1. Introduction

In water molecules, the difference in electronegativity between hydrogen and oxygen, as well as the free electron pairs in the latter, lead to electrostatic attraction between adjacent molecules. Such hydrogen bonds in water exhibit dissociation energies of 12.5–20.9 kJ mol⁻¹ which lies between the weaker van der Waals forces and the stronger covalent/ionic bonds. Nevertheless, the sheer amount of hydrogen bonds creates a dominant influence on the behavior of water. In the liquid state, water exhibits a coordination number of 4.4, while in the most common ice phase (I₃; hexagonal space group P₆₃/cmc) it is reduced to precisely 4.² The dynamics can explain the differences in liquid water compared to the ordered hexagonal structure in I₃ ice. We speak of an ice structure if a high degree of order, that is, crystal structure, can be achieved. When water molecules assemble in a structure more ordered than liquid water but not entirely crystalline, the term ‘ice-like’ water is frequently used. It refers to strongly hydrogen-bonded tetrahedrally coordinated water molecules as can be characterized by infrared (IR) spectroscopy. Ice-like water is marked by a characteristic vibration mode at ca. 3230 cm⁻¹, overlapping with the band of ‘liquid’ water (ca. 3400 cm⁻¹). In this context, the term ‘liquid’ refers to water molecules that are closely related to bulk water.² As mentioned above, the bulk properties of water are dominated by the intermolecular hydrogen bonds between adjacent molecules; deviations from bulk behavior occur when these interactions are disturbed, for example, by restriction in confined space. In a mesopore environment, such confinement can lead to significant changes in the coordination number; in the distance between nearest-neighbor water molecules, and in the angles of H←O←H (106.8°, I₃) and H←O⋯H (109.7°) because the water molecule is not surrounded by a sufficient number of neighbors, as compared to bulk liquid water or ice.²⁹ Some theoretical studies regarding the existence of supercooled bulk water in confined geometries have been carried out,²⁹ and the fragile-to-strong transition of supercooled water has been studied in confined systems.²⁹,³⁰ While the impact of confinement on the coordination number has been studied for some cases, not always is surface-bonded water quantitatively included in the considerations, nor has
there been extensive research of the coordination number for varying hydrophobicity and pore sizes.\cite{11-13}

Obviously, the degree of confinement-related effects in mesopores is expected to depend on the pore size.\cite{14-17} However, varying the pore size within the low nanometer range turns out to have only little impact on the IR/Raman spectra, compared to bulk water. Ilgen and coworkers investigated the effect of confinement on the melting/freezing point, density, and surface tension of water in various silica samples (SBA-15 and disordered silica); they found that a change in pore size from 8 nm to 2 nm did not have a strong effect on the vibration spectra.\cite{18} Similar results were obtained by Le Caër et al.\cite{19} for porous glasses (pore size 8–320 nm) and by Lendl et al. for porous films (3–8 nm).\cite{20} All these studies conclude that the pore size has a rather low impact on the O=H stretching vibration bands at 2800–4000 cm\(^{-1}\). It must be pointed out, however, that the influence of the pore size on the phase behavior of water at low temperature can be much more significant.\cite{17,20–22} Another spectroscopic method to study water in mesopore confinement is \(^{1}H\) NMR spectroscopy.\cite{23,24,25}

For example, Buntkowsky et al. studied the NMR response of water in MCM-41 and SBA-15 silica, slowly filling the pore volume in the process. They found that water in MCM-41 is first wetting the surface, while some free water groups exist. In filled pores, they observed only hydrogen first-principles bonded water bonding either with the surface or itself.\cite{26}

The strength of interactions between the pore wall and the confined water molecules can dominate the behavior as such. The effect is related to the surface polarity, as a hydrophilic surface interacts more strongly with water molecules than a hydrophobic one.\cite{26–29} For example, Fröba and coworkers studied water adsorption and mobility in periodic mesoporous organo-silica materials and found that water adsorbing to bare (hydrophilic) silica and to organic (hydrophobic) moieties within the same mesopore can be discriminated, for example, by NMR and Raman spectroscopy. In general, the strength of interaction between water molecules and (organo-) silica pore wall can be studied by H\(_2\)O sorption experiments.\cite{31–37} Interestingly, water molecules attach to silica surfaced not only by physisorption but also by chemisorption, through hydrolysis of siloxane bonds and creation of silanol groups. This reaction changes the surface polarity. In this work, two consecutive cycles of water adsorption/desorption are therefore measured. At theoretical level, many studies focused on the crystalline quartz hydroxylated surface, but less work has been done studying amorphous surfaces. Cimas et al. found a relatively high amount of disorder in the water interface layers.\cite{38} Gallo et al.\cite{39} and Rieth et al.\cite{40} investigated the hydration level of a silica pore and how the surface polarity impacts the structure and dynamics at different stages of the filling process (i.e., at different levels of humidity). Gallo et al. also studied pores based on varying hydration levels to estimate different density environments.\cite{39} Studying realistic density levels is an issue rarely discussed in pore or confined set-ups. One used idea is evaporating oversupply of water by molecular simulation. Several computational studies have been dedicated to the structure and dynamics of water in confined spaces, including carbon nanotubes and amorphous silica systems such as MCM-41, respectively. However, most of those studies are based on conventional force-field-based methods that are empirically parameterized. Only recently, studies using a parameter-free first-principles level of theory have emerged.\cite{42} Those studies are still limited to relatively small systems and short time scales because of the high computational costs. This limits the statistical uncertainties of properties generated with those methods. Semiempirical methods,\cite{43} however, provide an interesting bridging point by combining first-principles electronic structure methods with a parameterized Hamiltonian that have been validated. The PM6 model\cite{44} and its predecessors have been parameterized and used extensively to calculate static and dynamic properties over a wide range of elements. Thus, PM6 is versatile and provides a good theory level to calculate the structure and dynamics at the interface of our varying pore systems.

IR spectroscopy has been used in theoretical studies to analyze the structure of water in hydrophilic confinement. Allolio et al.\cite{12} found a blueshift of the IR response at the interface compared to bulk, which they explained by a decrease in the coordination number they observed. Another study by Sulpizi et al. reported a redshift on an alpha quartz interface attributed to a higher coordination number.\cite{45} In this work, we will differentiate between coordination with the surface or water molecules and compare the studied systems of different hydrophobicity to gain information about the pore wall–water interactions. When analyzing the IR spectra, the density of silanol groups at the pore walls and the hydrogen bond definition must be considered. In this work, we are calculating all those aspects in combination with using sum-frequency generation (SFG) spectra, which are not only surface specific, but also induct information about the orientation of the stretching modes. Together a more complete picture of H-bonding and competition at the confined pore interface can be gained.\cite{46} There have been several studies using SFG to investigate the properties of interfaces at quartz interfaces,\cite{43} but the interpretation of peaks is still widely discussed. One view is that the prominent peaks arise from the hydrogen bonds with an ‘ice-like’ ordering and more disordered networks. Ohto et al. developed a method to calculate the SFG response from the velocity–autocorrelation function, which in our work was adapted for pore systems. They also did some studies regarding the SFG response of water at the water–vapor interface.\cite{47}

Here we present a study of water sorption in the cylindrical mesopores of MCM-41 silica. The impact of hydrophobization of the pore walls is studied by functionalization with trimethyl-

![Figure 1. MCM-41 silica with cylindrical mesopores exhibits silanol groups that can be (partially) exchanged against trimethylsilyl (TMS) groups leading to a hydrophobization of the surface.](image-url)
silyl (TMS) groups to reduce the surface polarity (see Figure 1). The interaction between pore wall and water is investigated by 1R spectroscopy and water vapor sorption analysis. Theoretical calculations provide deeper insight into the coordination (i.e., water–water, water–pore wall), stretching vibrations, and angular distribution of water relative to the pore wall.

2. Results and Discussion
2.1. N\textsubscript{2} and H\textsubscript{2}O Sorption

We have studied two distinct types of mesoporous MCM-41 silica materials, namely as-prepared (‘hydrophilic’) and surface-functionalyzed (‘hydrophobic’) samples. In the latter case, the pore walls are decorated with methyl groups, as described in the Experimental section, and confirmed by \textsuperscript{29}Si MAS NMR spectroscopy (see Figure S2, Supporting Information). \textsuperscript{29}Si NMR analysis (Figure 2a) reveals type-IV isotherms with weak H1-type hysteresis for both materials, as frequently observed for small, cylindrical mesopores that are not interconnected (which would be the case for more complex SBA-15 silica structures).\[48] The pore size distribution (evaluated by the NLDFT data-based method, Figure 2b) has its maximum at 4.1 nm in case of the hydrophilic sample; it is slightly shifted to 3.8 nm for the hydrophobic material, due to the space requirement of the trimethylsilyl (TMS) groups. The BET surface areas are 950 (hydrophilic sample) and 840 m\textsuperscript{2} g\textsuperscript{-1} (hydrophobic sample); the lower value in the latter case is mostly attributable to the higher sample mass (due to post-synthetic functionalization). Likewise, the specific pore volume is reduced from 0.83 (hydrophilic) to 0.67 mL g\textsuperscript{-1} (hydrophobic). The periodically ordered structure of the pore system is not affected by the functionalization, as confirmed by low-angle powder X-ray diffraction (see Figure S3, Supporting Information).

Water vapor sorption studies of both materials are shown in Figure 3. Isotherms were measured in two consecutive cycles of adsorption and desorption, without degassing between the cycles. This procedure accounts for the fact that, in addition to (reversible) physisorption, water may cause irreversible cleavage of surface-near siloxane (Si–O–Si) bonds, leading to formation of silanol groups (Si–OH), as will be elucidated below. All measurements show type-V isotherms. The hydrophilic sample displays a steeper and much stronger step in water uptake than the hydrophobic sample; the step occurs at lower relative pressure. This clearly confirms that the hydrophobic material has a significantly reduced pore-wall surface polarity. It shows a much lower overall amount of water uptake per sample mass of only 0.21 mL g\textsuperscript{-1} (in the first adsorption branch), as compared to 0.72 mL g\textsuperscript{-1} in case of the hydrophilic sample (Table 1).

Obviously, these water uptake values are clearly lower than the pore volumes that were determined by \textsuperscript{29}Si NMR analysis, which indicates that fewer water molecules are accommodated in the pores than would be geometrically possible for bulk liquid water. This finding can be described as a reduced average density of water in the pores, as suggested by Thommes and Fröba et al.\[13] They have determined the density as the ratio of water uptake (per mass) and pore volume (per mass) for mesoporous carbon and periodic mesoporous organosilica materials, respectively, and obtained values <1. It is quite likely that the density of water varies within the pores, especially in hydrophobic materials.\[49–54] The lower average water density in the pores may be attributable to the formation of water domains around adsorption sites (most likely silanol groups or defects\[55,56]) and nanovoids (with low water density or no water at all) in the more hydrophobic pore regions.\[57,58] In our case, the water density varies between 0.84 and 0.87 for the hydrophilic materials and 0.84 and 0.87 for the hydrophobic materials.\[31–040] which corresponds well to previous literature results.\[15]

The quantification of surface polarity in porous materials is subject to ongoing debate. The strength of adsorbate–adsorbent interaction is accessible through the BET approach. The dimensionless C constant in the BET equation is exponentially related to the adsorption energy of the first monolayer.\[48,59] According to N\textsubscript{2} physiosorption (77 K), the hydrophilic silica sample exhibits a value of C = 103, significantly larger than the functionalized material (C = 41). Due to the N\textsubscript{2} molecule’s quadrupole

| MCM-41 sample | Pore size [nm] | \(A_{\text{BET}}[\text{m}^2 \text{g}^{-1}]\) | \(C[\text{mL g}^{-1}]\) | \(V_{\text{p}}[\text{mL g}^{-1}]\) |
|---------------|---------------|-------------------------------|-----------------|------------------|
| Hydrophilic   | 4.1           | 950                           | 103             | 0.83             |
| Hydrophobic   | 3.8           | 840                           | 41              | 0.67             |

\(A_{\text{BET}}\): BET surface area; \(C\): material-specific constant in BET equation; \(V_{\text{p}}\): total pore volume.
moment, the surface-chemical properties can influence the sorption measurement, leading to uncertainties of up to 20% in surface area. When the BET approach is applied to H$_2$O (293 K), overall lower C values between 6 and 9 are observed for the two materials, indicating weaker interaction strength for H$_2$O–silica than for N$_2$–silica at the respective temperature. This is also reflected by the fact that a type-IV behavior is observed only in the N$_2$ sorption isotherm, while the H$_2$O isotherm shows type-V behavior, typical of weaker adsorbate–adsorbent interaction. With large C constants ($\geq 80$), an inflection point occurs in the isotherm, indicating the pressure at which a statistical monolayer has formed. It needs to be stressed that the BET approach is IUPAC-recommended only for data with C constants $> 2.0$. Otherwise, mono- and multilayer adsorption overlap, and the statistical monolayer point cannot be determined; thus, neither can the BET surface area. Since the C values based on our water sorption data are well above the lower limit, we used the first five adsorption points to determine a ‘virtual’ BET surface area, assuming that one water molecule adsors on one silanol group. This leads to a silanol group density of 1.9 for the hydrophilic silica sample and 0.3 nm$^{-2}$ for the hydrophobic one (from the first H$_2$O adsorption branch after degassing at 120 °C for 12 h in vacuum). The calculated amount fits well to the results reported by Rother et al. (1.2–3.4 nm$^{-2}$, at similar degassing temperatures of 383–423 K) as well as by other groups (see Table S1, Supporting Information).

As indicated above, the presence of water in the mesopores may lead to hydrolyzation of surface-near siloxane (Si–O–Si) bonds, thereby increasing the density of silanol groups (Si–OH). This is often observed to some degree at room temperature, although without structural collapse of the pore system. Since this reaction is an irreversible process, it has some impact on the water sorption data. On the one hand, it is a possible explanation for the observed hysteresis between the adsorption and desorption branches within each measurement cycle. On the other hand, it is a likely reason for the differences between the isotherms belonging to the two distinct adsorption/desorption cycles that were carried out consecutively, without degassing between cycles. The siloxane bond hydrolysis causes an increase in pore wall polarity, which is why the steep uptake of water is shifted to lower relative pressure. The silanol group density increases by 31% (to 2.5 nm$^{-2}$) in the hydrophilic material, and by 75% (to 0.7 nm$^{-2}$) in the hydrophobic sample (Table 2). The change in surface polarity also explains the lower degree of hysteresis within the second cycle as compared to the first cycle, for both materials.

### Table 2. Parameters of hydrophilic (pristine) and hydrophobic (functionalized) MCM-41 silica, derived from H$_2$O vapor sorption analysis in two consecutive cycles of adsorption and desorption.

| Sample       | First cycle | Second cycle |
|--------------|-------------|--------------|
| V$_\text{BET}^{\text{a}}$ (m$^3$ g$^{-1}$) | V$_\text{C}$ (m$^3$ g$^{-1}$) | Si–OH$_\text{d}$ (nm$^{-2}$) | V$_\text{BET}^{\text{a}}$ (m$^3$ g$^{-1}$) | V$_\text{C}$ (m$^3$ g$^{-1}$) | Si–OH$_\text{d}$ (nm$^{-2}$) |
| Hydrophilic  | 220         | 0.72         | 1.9         | 290         | 0.69         | 2.3         |
| Hydrophobic  | 50          | 0.21         | 0.4         | 70          | 0.27         | 0.7         |

$^{a}$‘Virtual’ BET surface area (see text); $^{b}$Material-specific constant in BET equation; $^{c}$Total pore volume; $^{d}$Silanol group density.

### 2.2. FT-IR Spectroscopic Investigation of Intra-Pore Water

To elucidate the structure of water in the pores in more detail, we carried out IR spectroscopic investigations in the energy range that spans the O–H stretching vibration. For this purpose, we prepared samples of both the hydrophilic and the hydrophobic material with variable amounts of water within the pores. Figure 4 shows the FT-IR spectra (measured in attenuated total reflection mode, ATR) in the wavenumber region of 4000–2700 cm$^{-1}$; the pores of the materials are filled with a maximum amount of water in this case, that is, the amount of water corresponds to the above-described total water uptake volume of the respective material. Since the hydrophilic MCM-41 sample takes up a larger water volume (0.69 mL g$^{-1}$) than the hydrophobic one (0.27 mL g$^{-1}$), the intensity of the vibration bands in the hydrophilic sample is larger than in the hydrophobic sample. Water, either in the bulk state or in confinement, exhibits a continuum of configurations with O–H vibration modes in the IR region of 3700–2900 cm$^{-1}$. In addition, dangling silanol groups also need to be considered here. Therefore, we performed a deconvolution of the observed absorbance by a least-square fit of three Gaussian profiles. These three distinct vibration modes can be assigned as follows: (i) a weak band at ca. 3600 cm$^{-1}$ corresponds to ‘dangling’ OH groups of the first monolayer of surface-adsorbed water molecules and/or surface silanol groups. Its relative intensity (with respect to the other two peaks) is 6% in the hydrophilic material and 1% in the hydrophobic sample, which is consistent with the notion that the latter sample contains fewer silanol groups and will have less water molecules directly adsorbed to the pore walls due to the methyl groups; (ii) a band at 3400 cm$^{-1}$ is assigned to bulk-like liquid water, that is, to water molecules that are not situated near the pore walls and therefore not affected by confinement. This peak has a relative intensity of 38% for the hydrophilic sample, while it is by far the most dominant peak (86%) in the hydrophobic sample; and (iii) the third band at ca. 3230 cm$^{-1}$ belongs to water molecules that exist in a more ordered state than bulk liquid water. They are less strongly oriented than surface-bound water molecules, but their orientation is still influenced by the first monolayer to some degree; they form the first few layers beyond

![Figure 4. FT-IR spectra of a) hydrophilic and b) hydrophobic MCM-41 silica, each with the maximum amount of water inside the mesopores.](image-url)
the surface-next monolayer. These molecules are frequently referred to as ‘ice-like’ water, although the implication of this term is misleading since the translational degree of freedom of these molecules is clearly higher than in the solid state. The band has a relative intensity of 56% in the hydrophilic material, but only 12% in case of the hydrophobic sample, consistent with the observation of fewer silanol groups and surface-bound water molecules. Additionally, a small C–H stretching vibration peak of the methyl groups is observed in the hydrophobic sample at ca. 2960 cm⁻¹. These findings confirm that the hydrophobic sample exhibits fewer surface silanol groups to which water molecules can attach by hydrogen bonding. Consequently, no continuous monolayer can form at the surface, and fewer water molecules can exist in a semi-constrained (‘ice-like’) state. Most of the water molecules are unaffected by the pore walls (bulk-like liquid).

In addition to the above-discussed samples loaded with the respective maximum amount of water, we also varied the degree of loading down to 20% of the maximum. The resulting IR spectra, including the deconvolution of the three vibration bands, are shown in Figure S4, Supporting Information. Thus derived relative peak intensities are shown in Figure 5. Values for the hydrophilic sample with 20% loading are missing because reliable deconvolution of these spectra was not possible due to low signal/noise ratio. In both samples (hydrophilic and hydrophobic), the relative intensities of the band belonging to ‘dangling’ (water and/or surface-silanol) OH groups turn out to be mostly independent of the degree of loading. Different behavior is observed for both materials regarding to the other two peaks. In the hydrophilic sample, both peaks are unaffected by the loading degree, while the hydrophilic sample shows a strong dependence: The intensity of the bulk-like liquid water peak is approximately the same for 20% and 40% loading, respectively (ca. 80% relative intensity), but then decreases with increased loading (down to the above-reported value of 38% relative intensity at 100% loading). In turn, the peak belonging to ‘ice-like’ water increases in relative intensity by the same degree as the bulk-like liquid peak decreases.

The following adsorption mechanism of water can explain these findings in the silica pores: at first, adsorption of water molecules occurs at surface silanol groups. We assume one water molecule per silanol group; this effect can be utilized for the BET-like interpretation of the water sorption experiments above. This approach was recently established by Rother et al.⁴⁵ This leads to the formation of distinct water ‘clusters’,⁷¹,⁷² that is, nuclei for the formation of a liquid phase. With further adsorption, the clusters grow; initially, they remain separated from each other. This situation has been described as a ‘bridging effect’, in which parts of the pore wall are not in contact with the water at all, while adjacent clusters may start interacting with each other.⁶⁶,⁶⁸,⁷³,⁷⁴ Finally, a certain threshold size is reached, at which point the clusters coalesce to form a continuous sorption layer. Before this threshold, no significant degree of ‘ice-like’ orientation of water molecules is possible since no long-range assembly of water exists. This mechanism also explains why the relative intensities of the IR bands are initially similar for both the hydrophilic and hydrophobic sample, as long as the amounts of water are still low. According to several studies, adsorbed water forms ‘ice-like’ regions, especially in close vicinity to the pore walls and in the center region of the pores; these two regions differ in water density and configuration.²³,²⁶–²⁸,⁷⁵–⁷⁸

2.3. Characterization of Simulated Pore Systems Based on Surface Area, Effective Diameter, and Functional Group Density

For the theoretical investigation, both systems were studied, that is, hydrophilic MCM-41 silica (having silanol groups at the pore walls) and MCM-41 functionalized with trimethylsilyl (TMS) groups. The surface area was calculated according to the pore size before functionalization. The density of functional groups was calculated by dividing the number of functional groups of hydrophilic (OH) or hydrophobic (Si(CH₃)₃) nature by the surface area of said pore. The fraction of hydrophobicity is given by the number of hydrophobic groups divided by the number of hydrophilic groups as summarized in Table 3. The surface area of the hydrophilic pore is less than that of the hydrophobic one, because it was chosen to consider the introduction of larger functional groups in the hydrophobic system. The functional groups will decrease the effective pore size, bringing the effective diameter more in line with the hydrophilic pore which will minimize the finite size effect on pore structure and dynamics. The functional group density at the pore surface, as described in Table 3, is 6.84 silanol groups per nanometer square for the hydrophilic pore; for the hydrophobic pore, the overall functional group density (i.e., silanol groups plus TMS groups) is slightly lower at ~6.56 per nanometer square. Si–OH is exchanged with TMS groups so that roughly 19% of groups are TMS, while the remaining 81% remain hydroxyl groups.

Table 3. Data to characterize the theoretical pore models based on surface area, Si–OH density, functional group density, and hydrophobicity.

| Pore                      | Surface area [nm²] | Si–OH density [nm⁻²] | TMS density [nm⁻²] | Hydrophobicity |
|---------------------------|-------------------|----------------------|--------------------|----------------|
| Hydrophilic (pristine)    | 5.85              | 6.84                 | 0                  | 0%             |
| Hydrophobic (TMS)         | 8.10              | 5.32                 | 1.24               | 19%            |
2.4. Radial Density Distribution of Water and Defining Functional Group Elements

We calculated the particle densities of water and the respective pore surfaces in different pore setups, as shown in Figure 6. The radial density of the water in the pore is shown in blue, while the density of the surface functional groups is shown in orange. In the hydrophilic pore the surface is made up of silanol groups. As such, the hydrogen density can give an estimate of the surface coordinates in the system. In the case of the hydrophilic pore in Figure 6a, the hydrogen density is shown in orange with scaled density to ensure visual comparability of the graphs. The model of the Gibbs dividing surface is used to quantify the distance between the medium and pore surface. In the hydrophilic pore, the Gibbs dividing surface is located at a distance of ca. 0.60 nm. The water is structured roughly into two layers, one close to the pore surface and one at the center of the pore.

The hydrogen density is showing a shallow double peak from the different silanol group arrangements. In hydrophilic silica pores, the OH groups can either be free and pointing away from the surface, which we attribute to the first peak, or form hydrogen bonds with other OH groups, orienting them parallel to the surface (second peak).[38] The hydrophilic system (Figure 6b) inhibits less structure, but a steady increase in density toward the center of the pore in a more uniform distribution. The same is true for the methyl hydrogens representing the pore surface of the hydrophobic system. The modeled TMS-functionalized pore seems to be more uneven with the free radius of the pore varying as the slope of the density is much shallower. The distance of the Gibbs dividing surfaces is ≈0.098 nm. This is more than in the hydrophilic pore that had a distance of ≈0.60 nm. Water tends to be further away from the pore surface and one at the center of the pore.

For the hydrophilic environment in Figure 7b, the decrease in total coordination number is a bit less smooth though still constant at the surface. Even though the density profile as seen in Figure 6b is less structured than that of the hydrophilic pore, the total coordination is very similar, indicating that the water is naturally rearranging its coordination, thus balancing molecular variances in density. The water–silanol coordination is present over the whole radius, but closest to the surface TMS is the main source of water coordination. At the surface, water–water coordination plays the least important role. The water molecules would act as hydrogen bond donors and move very close to the surface. We attributed those silanol groups to the hydrogen peak at 0.6 nm radius in Figure 6a.

For the hydrophobic environment in Figure 7b, the decrease in total coordination number is a bit less smooth though still constant at the surface. Even though the density profile as seen in Figure 6b is less structured than that of the hydrophilic pore, the total coordination is very similar, indicating that the water is naturally rearranging its coordination, thus balancing molecular variances in density. The water–silanol coordination is present over the whole radius, but closest to the surface TMS is the main source of water coordination. At the surface, water–water coordination plays the least important role. The main mechanism seems to be a competition between the functional groups for water coordination relative to their density. In this case, as described in Table 3, the ratio of silanol to TMS is ≈4:1. It has to be mentioned that not only the hydrogen bonding capability influences the surface polarity, but also the change in dipole moment when exchanging functional groups. The interplay between the surface polarity, the formation of hydrogen bonds and the structure of water at a flat plane is theoretically investigated by Debenedetti al.[82]

2.5. Coordination Number of Water Molecules with Itself and with the Surface-Silanol

As hydrogen bonding plays an important role in the structure of water inside the pore and in regards to the surface polarity, we attempt to gain a more profound understanding of the hydrogen bonding process. We calculated the hydrogen-bond coordination number across the pore based on r_HO < 3.55 Å and (O_H2O) < 30°, which is a common definition.[80,81] We also included the coordination numbers of the water molecules with the hydroxyl and TMS groups in our systems using r_CO < 3.65 Å and (C_OH) < 30°. For the hydrophilic pore shown in Figure 7a, the water–water hydrogen bond coordination number decreases constantly from 0.6 nm onwards (blue), while the water–silanol coordination increases steadily (orange), though providing less coordination in total (green). That leads to a lower coordination number close to the surface and a relatively deep impact onto the interface structure. Comparing the results to those in Figure 6, most water molecules in pore areas with high densities are highly coordinated, but a small amount of water at the surface is less coordinated. One possible explanation is that less coordinated molecules only interact with silanol groups that are oriented parallel to the surface and have already formed hydrogen bonds with other silanol groups. Those water molecules would act as hydrogen bond donors and move very close to the surface. We attributed those silanol groups to the hydrogen peak at 0.6 nm radius in Figure 6a.

2.6. Analysis of the Water Structure at the Surface Based on Surface-Specific SFG Calculations

We used the previously adapted SFG method to calculate the responses for the hydrophilic and hydrophobic pores (Figure 8). The characteristic response important to our discussion is happening between 2200 and 2800 cm⁻¹. The shift compared to the experimental results (Figure 4) is based on the use of the
Figure 8. Imaginary part of the second order SFG spectra of the hydrophilic pore (blue) and hydrophobic pore (orange) in the range between 2000 and 3000 cm\(^{-1}\).

The angular distribution in the hydrophilic pore is generally broader compared to the hydrophobic pore. Therefore, it is more likely to find water in configuration A (H and H\(^{\prime}\) pointing away from the pore surface, \(\alpha = 74^\circ\), \(\beta = 104^\circ\)) and B (\(\alpha = 56^\circ\), \(\beta = 160^\circ\)), and C for the hydrophilic surface compared to the hydrophobic one, even though A is a quite unlikely configuration overall. These effects were already observed in the SFG spectra in Figure 8 as the negative signal (O–H stretch modes pointing away from the surface like in configuration A and D) is more pronounced in the hydrophilic case.
pronounced for the hydrophilic pore. The water molecules generally prefer to orient both of their O–H stretch modes toward the silica surface (configuration B and D; both with a positive response in the SFG spectra in Figure 8). Thus, the ‘ice-like’ negative SFG response can likely be attributed to configuration D and A with lesser impact from B. As A and D can act as hydrogen bond donor to unbound silanol groups they play the biggest part in explaining the structure in the hydrophilic pore regarding the existence of ‘ice-like’ bonding. It is noteworthy to mention that the angular distribution of the stretching modes is not only affected by the interaction strength at the interface but also by the curvature of the surface.\cite{16} Within this study only samples with very similar curvature were studied and therefore the interplay of curvature was neglected.

3. Conclusion
When the pore wall polarity in silica mesopores is altered from hydrophilic (pristine) to hydrophobic (trimethylsilyl-functionalized), the structure of water pores changes. In the case of a hydrophilic mesopore filled with water, IR spectroscopy reveals a predominant ice-like structure because of comparably strong interactions between the water molecules with the pore wall, confirmed by calculated SFG spectra. For a hydrophobic surface, water behaves more liquid-like. As there are fewer interaction sites at the pore wall, the water molecules rather interact with each other than with the silica surface. Water sorption experiments further confirm these findings where the pore filling step is shifted to higher relative pressure for a more hydrophobic environment while the overall amount of water is reduced simultaneously. These effects can be further investigated by computed silica pores, enabling to monitor the water density distribution with respect to the distance to the silica pore wall. The coordination number changes depending on the decoration of the surface with silanol or methyl groups, as these alter the polarity of the pore wall. The calculated coordination numbers reflect the influence of the pore wall-to-water interactions from the experimental results. SFG and angular distribution calculation of the pore system reveal the water orientations most likely responsible for our findings in both systems.

4. Experimental Section

Synthesis and Functionalization of MCM-41 Silica: For the synthesis of the pristine (‘hydrophilic’) MCM-41 silica, cetyltrimethylammonium bromide (9.6 g, 26.3 mmol, ≥98%, Sigma-Aldrich) was dissolved in deionized water (480 mL, 26.7 mol) and ammonia solution (41.0 mL, 25%, Stockmeyer). After adding tetraethyl orthosilicate (TEOS; 40.0 mL, 179.1 mmol) the mixture was stirred (300 rpm) for 24 h, followed by filtration and washing with deionized water. The solid product was dried at 120 °C and then calcined for 6 h at 550 °C (heating rate 1 °C min⁻¹) leading to typical particle sizes = 0.5–2.0 μm.\cite{84} For the ‘hydrophobic’ MCM-41 silica, the pristine material was modified by post-synthesis functionalization. The pristine sample (2.0 g, 33.3 mmol) was dried at 160 °C overnight and transferred into a dried Schlenk flask. Dried toluene (40 mL) was added during a constant dry N₂ flow. After dispersing for some minutes, trimethylsilyl chloride (2.0 g, 18.4 mmol) was added. The mixture was stirred overnight, the solid filtered off and washed with toluene and acetone followed by drying at 100 °C.\cite{13}

Water Infiltration in (Functionalized) MCM-41 Silica: The silica samples (about 0.16 g) were dried at 120 °C overnight prior addition of water, followed by grinding for 6 min. The amount of water depended on the respective total pore volume, as determined by H₂O sorption experiments. For a complete filling of the pores, the required water volume (mL) was calculated from the sample mass (g) multiplied by the total pore volume (mL g⁻¹). For partial filling of the pores (20–100%) the amount of water was reduced accordingly.

Characterization: For N₂ and H₂O sorption studies, samples were degassed at 120 °C for 12 h in vacuum prior to measurements. N₂ physisorption was performed with an Autosorb 6B instrument (Quantachrome Instruments) at 77 K. BET surface areas were calculated in the relative pressure region p/p₀ = 0.1–0.3. Total pore volumes were determined from the uptake at p/p₀ = 0.99. Pore size distributions were calculated from the desorption branch by using NLDFT data (data kernel for cylindrical pores, silica). H₂O sorption experiments were performed on a 3Flex instrument (Micromeritics) at 293 K with double distilled (and degassed) water. BET surface-like determination of the adsorption sites was calculated in the relative pressure region p/p₀ = 0.1–0.15.\cite{15} Powder X-ray diffraction data were collected on a Bruker D8 Advance diffractometer (0.55° ≤ 2θ ≤ 5°) with a step size of 0.02° and a counting time of 3 s per step. FTIR spectroscopy was performed with a Vertex 70 spectrometer (Bruker) ATR mode. Proton-decoupled ²⁹Si magic-angle spinning (MAS) NMR spectra were acquired with a 300 MHz Apollo spectrometer (Tecmag) equipped with a wide-bore Oxford magnet. A Bruker MAS probe for 7 mm rotors was used; the spinning frequency was set to 3 kHz. The duration of the 90° pulse was 2.5 ms. The QSi(CH₃)₃ signal of Q₄M₄ at 11.5 ppm was used as an external chemical shift reference.

Computational Details: An amorphous bulk silica melt structure was created by heating a beta-cristobalite crystalline silica structure containing 768 atoms (256 Si + 512 O) to 4000 K at zero pressure via an NPT-ensemble based Metropolis Monte Carlo (MC) simulation using periodic boundary conditions (PBC). The simulation uses the potential developed by D. M. Tether, and modified and tested by Cormack, Du et al. (TCD)\cite{86} for all atomic interactions. Long-range interactions were calculated using the standard Ewald summation. The simulation reaches equilibrium after 2 million MC-steps. The system’s density was 2.31 g mL⁻¹ at this stage, being very close to P. Gallo’s MCM-41 model,\cite{87} but higher than fused silica (2.2 g mL⁻¹) and lower than quartz (2.56 g mL⁻¹). Experimental data from previous studies reveal an apparent density of 2.37 g mL⁻¹ for MCM-41 silica.\cite{88} The silica pore was created by removing a cylindrical volume of a specific diameter from the melt structure of size 28.64 Å × 28.64 Å × 14.32 Å. Free valences on the inner surfaces were saturated via additional hydroxyl groups according to a defined process during which trisilanol groups and isolated oxygens were removed from the surfaces.\cite{88}

For the functionalized system, several of the hydroxyl groups were exchanged with the trimethylsilyl group, mimicking a more hydrophobic environment using the pore modulation and visualization tool Avogadro.\cite{89} This was done in a way to achieve a decently even distribution of the groups on the surface. The systems were equilibrated using the PM6 semiempirical method,\cite{90} as implemented with periodic boundary conditions (PBC) in the CP2K simulation package\cite{91} for 10 ps. Bulk water was generated via CMD simulations using the second-generation Car-Parrinello-based quantum ring polymer contraction method of Kühe et al.\cite{92} Then the water was transferred into the pore system. After inserting the water, the systems were again equilibrated for 10 ps via periodic PM6 semiempirical MD\cite{93} calculations.\cite{10} The temperature of the system was controlled via a massive CSVR thermostat at 300 K with a time constant of 300 fs.\cite{92} Using a discretized time step of 0.5 fs the total trajectory length of the production run was 40 ps for all systems.

Velocity–Velocity Surface-Specific SFG Calculation in Pore Systems: A surface-specific velocity–velocity correlation function-based SFG algorithm pioneered by Ohto et al.\cite{13} was used. SFG is a second-order nonlinear process able to characterize systems through their vibrational response. In centosymmetric systems, the SFG response vanishes, making it perfect for probing surfaces.\cite{10} To adapt the formula from a
planar to a pore interface, the location vector $\vec{r}^i(t)$ for each oxygen at time $t$ and $\varepsilon_i$ is used to calculate the transition matrix at time $t$ via:

$$R_{ij,t}(t) = \begin{pmatrix} \cos(\tan^{-1}\left(\frac{\vec{r}^i(t) \cdot \varepsilon_i}{r^i(t)}\right)) & \sin(\tan^{-1}\left(\frac{\vec{r}^i(t) \cdot \varepsilon_i}{r^i(t)}\right)) & \cos(\tan^{-1}\left(\frac{\vec{r}^j(t) \cdot \varepsilon_j}{r^j(t)}\right)) \\
-\sin(\tan^{-1}\left(\frac{\vec{r}^i(t) \cdot \varepsilon_i}{r^i(t)}\right)) & \cos(\tan^{-1}\left(\frac{\vec{r}^i(t) \cdot \varepsilon_i}{r^i(t)}\right)) & \cos(\tan^{-1}\left(\frac{\vec{r}^j(t) \cdot \varepsilon_j}{r^j(t)}\right)) \end{pmatrix} $$

(1)

Calculating the new vectors $r_j(t) = R_{ij}(t)\vec{r}_i(t)$ according to our basis transformation. A visualization of this application can be found in Figure S1, Supporting Information. With this the original response term is calculated utilizing:

$$X_{ab}^{(2)}(0) = \int_0^\infty \left\{ \int \frac{Q(a)}{i\omega^3} d\omega \right\} \sum_{i,j} g_{ij}(\vec{r}_i(0); \vec{r}_j(0)) r^i_{\text{OH}}(t) \cdot r^i_{\text{OH}}(t) \cdot r^j_{\text{OH}}(t) \right\} $$

$$ = \begin{cases} \frac{Q(a)}{i\omega^3} \sum_{i,j} g_{ij}(\vec{r}_i(0); \vec{r}_j(0)) r^i_{\text{OH}}(t) \cdot r^i_{\text{OH}}(t) \cdot r^j_{\text{OH}}(t), & \text{if } a = b \\
0, & \text{otherwise} \end{cases} $$

(2)

Where $r_i(t)$ is the distance between the center of masses of OH groups $i$ and $j$ at time $t$, $g_{ij}(\vec{r}_i(t); \vec{r}_j(t))$ is the function to control the cross-correlation terms with the cross-correlation cutoff radius of $r_i$. The intramolecular distances and velocities of OH group $j$ at time $t$ is denoted as $r^j_{\text{OH}}(t)$ and $v^j_{\text{OH}}(t)$, respectively. The quantum correction factor $Q(a)$ was taken from Ref. [47] and the Hann window function was applied for the Fourier transformation of the time-correlation function. Even though non-Condon effects are neglected generally all intramolecular coupling effects are included.[13] In our study, the cutoff $r_i$ is set to 2 Å, thus only including autocorrelation effects.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

IR spectroscopy, mesoporous silica, molecular simulation, sum-frequency generation, water adsorption

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