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Cellulose microfibril interactions with water: A density functional theory study of H₂O incorporation into the cellulose microfibril structure

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Abstract

Periodic density functional theory calculations were performed on the 234432 model of primary plant cell wall cellulose microfibrils. Energy minimization calculations of dry, water external, water internal and water internal+external were carried out to explore the structure of cellulose hydration and energetics of H-bonding. Results indicate that the cellulose structure can accommodate a significant amount of H₂O without disrupting the XRD-determined structure. H₂O-cellulose H-bonds form in the interior that strengthen the cellulose microfibril. The external H-bonding was also analyzed to assess potential pathways for C-O-C linkage hydrolysis. The potential for D₂O to diffuse into the structure and lead to H-D exchange between water and cellulose was also tested.

Introduction

The work of R. Malcolm Brown Jr. extensively impacted the field of cellulose research. His approach to understanding cellulose biosynthesis led him to utilize numerous methodologies to gain insight into this critical biochemical process. Most relevant to this study was the pioneering work he published with Susan K. Cousins (Cousins and Brown, 1995, 1997) that combined X-ray diffraction and classical molecular dynamics simulations of cellulose-water interactions. These papers provided significant advances to our understanding of cellulose microfibril (CMF) assembly. A key to CMF assembly is the preferential interaction of water with (110) surfaces over (200) surfaces. The results contained in this study are focused on these cellulose-water interactions and could be used as the basis for further study of CMF assembly.

The applications of cellulose products are myriad as discussed in a recent review by Etale et al. (2023). Cellulose-water interactions are critical in many of these applications especially water treatment. This study focuses on a model cellulose developed for primary plant cell walls (Kubicki and Yang, 2018; Yang and Kubicki, 2020) rather than processed products such as nanocellulose, but the techniques employed herein and insights derived from this model should provide guidance to modeling cellulosic materials in general.

Agarwal and coworkers have shed significant light on cellulose-water interaction using a number of techniques with FT-Raman spectroscopy leading the way. For example, Agarwal (2014) showed exterior to interior variations in cellulose structure that were mediated by H-bonding

between cellulose microfibrils (CMFs) and CMFs and water. Following on that study, Agarwal et al. (2016) used 1064-nm FT-Raman spectroscopy to probe never-dried cellulose crystallinity. They found that never-dried cellulose is less crystalline, hydroxymethyl groups are in both the tg and gt conformations, and that there is a lack of crystallinity as suggested by the absence of a Raman bands at 93, 140, 154, and 170 cm^{-1} . Furthermore, immersion in D_2O led to intensity changes of the 1380 cm^{-1} indicating H-D exchange at CH_2OH sites. They interpreted their results as CMFs having both water-accessible and water-inaccessible regions with heat treatment leading to more water-inaccessible domains. Following up, Agarwal et al. (2018) studied heat treatment effects on cellulose structure and concluded that the decrease in water-accessible regions were due to CMF aggregation. We note that our present study does not examine CMF aggregation, but further work is recommended on this topic as the single CMF system used here could be replicated to model aggregation.

Paajanen et al. (2019) used weight measurements to determine the non-freezing bound water (NFW) and freezing bound water (FBW) contents of commercial pulp cellulose. They found an NFW of 0.21 g H_2O /g cellulose which was about one-half of the FBW at 0.42 g H_2O /g cellulose. The system was modeled with classical molecular dynamics simulations as a function of CMF aggregation. However, H_2O s were not included inside the CMF, the CMFs were 24-chain models, and the rate of twisting (4.2°/nm unbundled and 0.9°/nm bundled) was significantly higher than that modeled with DFT and constrained by observed ^{13}C NMR chemical shifts (Shklyayev et al., 2014).

Vibrational spectroscopy has been highly useful to probe H-bonding in cellulose. Infrared and Raman spectroscopy have been applied for decades (Old references). Kubicki et al. (2013) found that DFT was capable of accurately reproducing both IR and Raman frequencies. More recently, techniques such as Total Internal Reflection Sum Frequency Generation Vibrational Spectroscopy (TIR-SFG-VS) and SFG-VS (non-TIR) have been applied. Zhang et al. (2017) found both the surface and interior layers of I β cellulose to be crystalline although they exhibit different spectra because of differences in the H-bonding between surface and core. Lee et al. (2015) used polarized IR and SFG spectra to obtain frequencies associated with H-bonding in cellulose, and DFT was able to reproduce observed frequencies and provide information on the vibrational modes associated with each peak. Lee et al. (2017) then applied time-dependent DFT (TD-DFT) to the cellulose model and demonstrated the dependence of the C-H/O-H intensity ratio is a function of the polarity of the CMF packing.

Nuclear magnetic resonance (NMR) spectroscopy has also been used for decades to probe cellulose structure (old references). DFT was found to be capable of predicting ^{13}C chemical shifts that correlated well with observation. The resolution of peaks was enhanced significantly, however, by Hong and coworkers who ^{13}C -labeled cellulose in plant cell walls. For example, Wang et al. (2016) found seven sets of ^{13}C chemical shifts ($\delta^{13}\text{C}$) in cellulose with five assigned to interior chains and two to surface chains. Again, DFT was able to reproduce the chemical

shifts associated with the observed peaks and confirm their assignments as surface chains adopt the *gt* conformation of the hydroxymethyl group whereas interior chains are in *tg* conformation.

Numerous classical MD simulations have been performed on CMFs in water (e.g., old references). Of these, the paper by Matthews et al. (2011) is highly relevant as it includes discussion of H-D exchange in the interior of the CMF. These authors hypothesized that H-D exchange occurs from the exterior to interior via H-bonded O-H groups within the CMF without penetration by D₂O even at high temperatures. Kubicki et al. (2014) modeled H₂O-cellulose surface interactions to estimate H-bond energies, types and impacts on structure ascertained by calculated vibrational frequencies and $\delta^{13}\text{C}$ values with DFT.

The models used in this study are the same as those found in Del Mundo et al. (2023). In that study, the CMF structure was probed with grazing-incidence wide-angle X-ray scattering (GI-WAXS) as a function of dehydration. Del Mundo et al. (2023) found that “the removal of water may weaken cellulose-water and cellulose-cellulose hydrogen bonds in a manner that decreases the (110/1-10) lattice spacing.” The DFT results were qualitatively in agreement with the GI-WAXS data. Dehydration disrupted the H-bonding network and caused the glucan chains to contract towards the CMF core and decrease the average (110/1-10) spacing by 0.05 Å. These authors also suggested that H₂O in the interior of the CMF may limit collapse of the (200) spacing upon dehydration as the interior water remains after exterior H₂O has evaporated. Thus, the NFW may include interior H₂O as well as H₂O strongly H-bonded to the CMF surface.

Methods

We based our CMF model on a 6-layer CMF in an arrangement of 234432 glucan chains where each integer represents the number of chains in a given layer (Kubicki et al., 2018). The unit cell of cellulose was doubled to include 4 glucan units along the c-dimension, and 18 polymer CMFs were constructed in Materials Studio 2016. Four 234432 models with different water contents were obtained via energy minimization conducted with Vienna Ab-initio Simulation Package (VASP – Kresse and Hafner, 1993; Kresse and Hafner, 1994; Kresse and Furthmüller, 1996a,b; Kresse and Joubert, 1999). Model 1 is comprised of a CMF without any H₂O molecules (72 C₆O₅H₁₀), Model 2 of a CMF with a monolayer of H₂O molecules [72 C₆O₅H₁₀ + 102H₂O (external)], Model 3 of a CMF with H₂O molecules internal to the CMF [72 C₆O₅H₁₀ + 36H₂O (internal)], and Model 4 of a CMF with H₂O molecules inside the cellulose microfibril plus a monolayer of H₂O molecules [72 C₆O₅H₁₀ + 36H₂O (internal) + 108H₂O (external)]. Initial atomic structures of CMF with a monolayer of H₂O molecules in Model 2 were based upon classical molecular dynamics (MD) simulations (Kubicki et al., 2018; Oehme et al., 2018). From the last step of the classical MD simulation, the 18-chain fibril plus all H₂O molecules within 3 Å of the fibril (i.e., a “monolayer” of hydration) were extracted for DFT energy minimizations. Initial atomic structures of Model 3 and 4 were generated by manually placing H₂O molecules, the number of which was arbitrarily selected that could fit within the CMF in Model 1 using the Visualizer module of Materials Studio.

The interior H₂O molecules then were relaxed through Geometry Optimization using the COMPASSII force field in Materials Studio while the atoms of the CMF were constrained to the positions originally derived from DFT-D3 calculations. The model structures were converted into VASP input files (POSCAR) via a Perl script written by Andrei V. Bandura (Saint Petersburg State University, Russia) within a simulation cell of 40 x 40 x 40 Å³. All atomic positions were relaxed during energy minimizations with periodic DFT-D3 calculations^{34,35} with PBE0 pseudopotentials, ENCUT = 500 eV, D3 dispersion correction of Grimme et al. (2011) using the VASP code.

Results

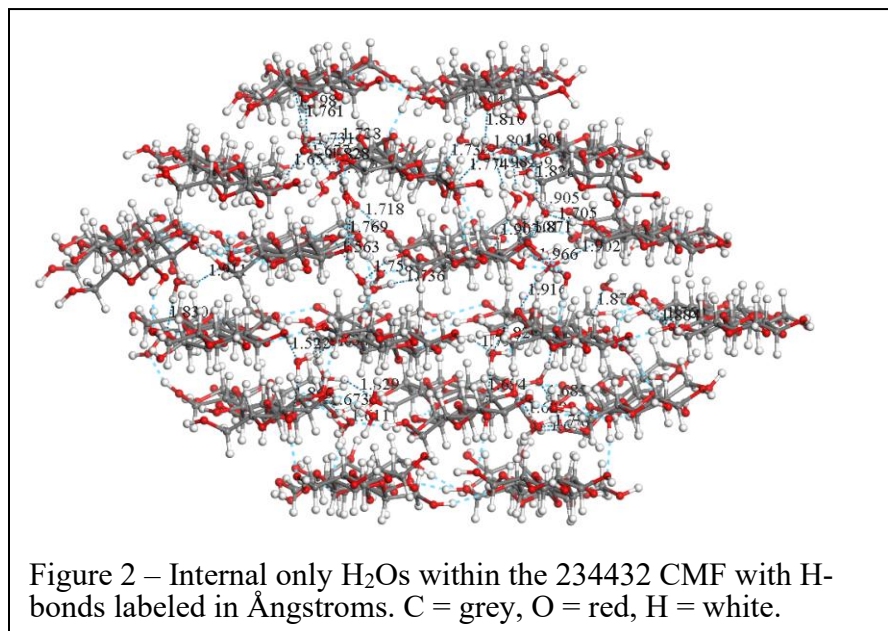
The model cellulose structure used here has been developed and tested by comparison to XRD, IR and Raman data (Kubicki et al., 2013), sum-frequency generation spectra (Lee et al., 2015) and ¹³C NMR spectra (Wang et al., 2016; Kubicki et al., 2018; Yang and Kubicki, 2020). The interior and surface structures replicate observe $\delta^{13}\text{C}$ values accurately and the 234432 habit is also justified by its lower potential energy. All CMFs results are in good agreement with observation with the 234432 model having a slightly better fit based on the root-mean-squared (RMSE) and maximum errors (MaxE). Average ¹³C NMR chemical shifts in the explicit water condition compare well with Wang et al. (2016) experimental values. In addition, the 234432 habit correlates with the hexamer of trimers structure of the cellulose synthase complex (CSC; Yang and Kubicki, 2020). Lastly, agreement with the changes in the GI-WAXS data upon dehydration demonstrates the model CMF-water interaction are reasonably well represented. Thus, use of this particular model structure is justifiable for exploring CMF-water interactions.

External CMF-H₂O

Table 1 – Average H-bond lengths and number of H-bonds formed between external H₂O_s and the CMF.

Face/H-bond type	Length (Å)/Number
(210) OH ₂ ---OH	1.89/11
(210) OH ₂ ---COC	1.95/2
(110) OH ₂ ---OH	1.85/29
(110) COH-OH ₂	1.78/17
(110) OH ₂ ---COC	1.88/1

to hydrolysis of the ether linkage, hydrolysis rates could depend on the amount of H₂O within the CMF as solvation of the reactants and products would be necessary to facilitate the H₂O dissociating to form 2 C-OH groups. Also, note that there are 2 H-bonds between H₂O molecules at this level of hydration. These bonds stretch across CMF layers and would presumably become more prevalent the greater the degree of internal hydration.

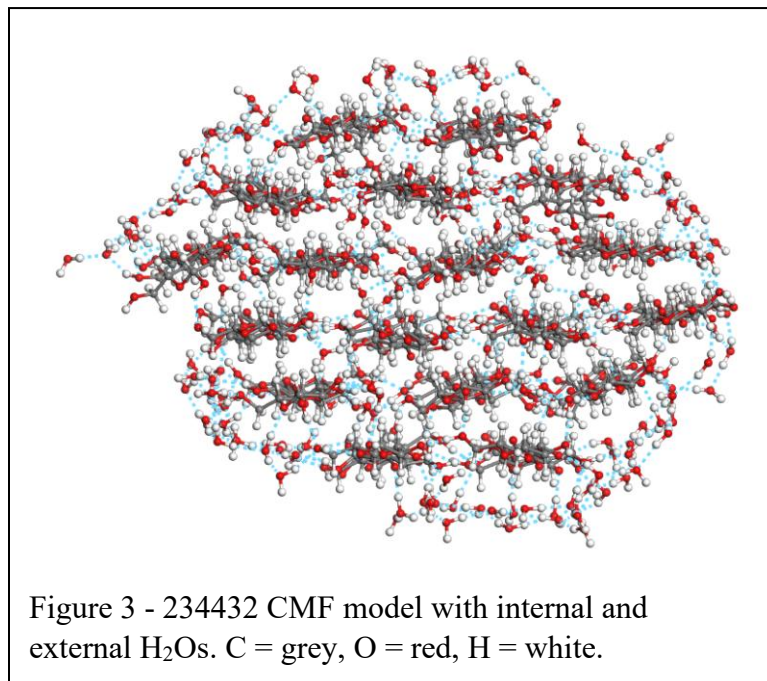
Table 2 – H-bonding for H₂O internal only.

Face/H-bond type	Length (Å)/Number
OH ₂ ---OH	1.79/25
OH ₂ ---COC	1.82/4
COH-OH ₂	1.74/15
OH ₂ ---OH ₂	1.83/2

External+Internal CMF-H₂O

Figure 3 illustrates the case where both external and internal hydration of the CMF are modeled. The H-bonding between H₂Os and the CMF in this case is a combination of internal only and external only models; hence, we do not report the average H-bond length and number of H-bonds. Although the lattice spacings as measured by GIWAXS and modeled by DFT change only slightly upon dehydration (DelMundo et al., 2023), we note that internal+external hydration does create disorder within the CMF. If these results are accurate, then room temperature

dehydration would remove the external H₂O_s and result in a change in the I(110/1-10)/I(200) intensity without much change in the d-spacings as observed in DelMundo et al. (2023).



H₂O Diffusion into CMF & H-D Isotopic exchange

The question of the presence of H₂O within the CMF is addressed indirectly by the deuteration of interior CMF hydroxyl groups or alternatively, the re-hydrogenation of deuterated CMFs. For example, Matthews et al. (2011) suggested that H-bonded chains within the CMF allowed for a concerted deuteration of interior CMF hydroxyl groups based on the modeled H-bonding pattern. They suggested that there would be preferred H-D exchange along the (100) and (110) planes. However, these authors interpreted the work of Horikawa and coworkers (Horikawa et al., 2006; Horikawa and Sugiyama, 2008) to indicate “that H/D exchange does not proceed to the interior of cellulose microfibrils at room temperature”. Subsequently, Matthews et al. (2011) proposed an H-D exchange pathway for higher temperatures that did not include H₂O or D₂O penetration through the CMF. The Horikawa papers used deuterated CMFs and re-hydrogenated them for only 60 minutes at each temperature (*i.e.*, 25, 180, 220, and 240°C). Thus, the experiments may just not have been long enough and methods sensitive enough to detect small amounts of re-hydrogenation at 25°C. Furthermore, Song et al. (2020) have observed H-D exchange at 105°C which is accelerated at higher temperatures and interpreted their results as resulting from “the higher pressure caused by higher temperature helped the D₂O molecule to penetrate into the cellulose crystalline bundles, which promotes the exchanging of hydrogen and deuterium.”

To test this interpretation, we have modeled diffusion of a single H₂O molecule through the outer chains of the CMF into the interior. To do so, we extracted 4 cellulose tetramers and 1 exterior H₂O from the periodic simulation of the interior+exterior CMF and water model (Figure 3) to create a molecular cluster. This speeds up the computational time dramatically and allows for modeling the transfer of the H₂O between the cellulose chains (Figure 4). By constraining the C atoms to their positions in the periodic model, we impose a similar atomic environment upon the model. We then constrain the position of the O atom in the H₂O to various positions between the cellulose chains and calculate the energy change to transport the H₂O into the CMF interior.

Table 3 lists the energies corresponding to the configurations shown in Figure 4. The maximum calculated energy difference from the initial step is +670 kJ/mol. This value, if reasonably accurate, indicates a prohibitive barrier to H₂O diffusion into the CMF; but, by the same token, H₂O trapped in the CMF during the CMF formation process would face a kinetic barrier to leaving the CMF. Further work needs to be done to test the diffusion mechanism and subsequent rates such as DFT-MD simulations at elevated temperatures to see if relaxation of the CMF would allow for H₂O diffusion.

Table 3 – Energies and changes in energy from the H₂O external starting point.

Step	Energy (Hartrees)	ΔE (kJ/mol)
1	-2486.73160	0
2	-2486.69897	+86
3	-2486.71100	+54
4	-2486.58313	+389
5	-2486.47663*	+670
6	-2486.48030	+660
7	-2486.50340	+599
8	-2486.65710	+196

* - Highest energy along modeled diffusion trajectory.

(1 Hartree/molecule = 2625.5 kJ/mol)

Although a high H₂O diffusion barrier precludes H/D exchange on internal CMF sites, H/D exchange is possible on external CMF OH groups. Figure 4 illustrates a hypothesized exchange mechanism based on these DFT calculations of CMF-H₂O interactions. Because the external CMF OH groups can simultaneously form both strong H-bond donor and acceptor groups, coordinated HOD---(C)OH---OH₂ H/D exchange would occur similar to the H/D exchange in water. Since these H-bonds can be stronger than those in water (Table 1) the water-CMF H/D exchange rate would likely be even faster than in bulk water.

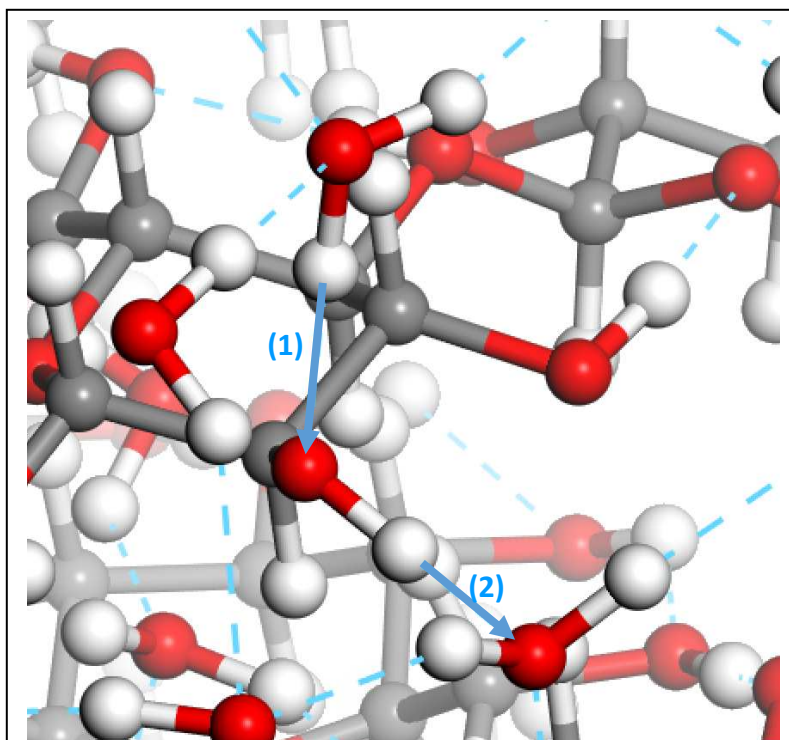


Figure 4 – H/D exchange may occur at a C-OH when a strong H-acceptor (1) forms simultaneously with a strong H-donor (2) such that coordinated exchange occurs. With abundant water at the surface, this will be relatively common. Dashed blue lines are H-bonds $< 2.25 \text{ \AA}$. Arrows indicate possible coordinated H/D-exchange.

Non-freezable “water”

Studies of “water” dynamics within cellulose samples have commonly observed three states of H_2O molecules (e.g., Zhao et al., 2019; Kramer et al., 2021; Chen et al., 2022): tightly bound water commonly assigned as directly H-bonded to hydroxyl groups on CMF surfaces, non-freezable loosely bound water, and freezable water that is often assigned to H_2O s farther from the CMF surface. This is well-stated in Zhao et al. (2019) who used dielectric measurements and low-field nuclear magnetic resonance (LF-NMR) spectroscopy to observed cellulose and water dynamics in a variety of samples –

“It is suggested that three states of bound water could

exist in moist cellulose, namely, tightly bound water that should be directly bound with the hydroxyl groups on the cellulose chain via hydrogen bond, non-freezable loosely bound water that could locate not far away from cellulose chain (in the first couple of hydration layers), and freezable loosely bound water that should be further away from cellulose molecules.”

These studies presume that there is no H_2O within the CMF. For example, see Chen et al. (2022) who modeled water-cellulose interactions between CMF bundles with non-freezable water assumed to be between CMFs rather than within CMFs. However, we note that Zhao et al. (2019) found differences in the roles of tightly-bound water and non-freezable loosely bound water. Both affect the β -relaxation (defined in Meißner et al., 2000 as “local main chain dynamic”) while the non-freezable loosely bound water acts as a “plasticizer”.

This presumption also seems to further assume that H_2O molecules directly H-bonded to the CMF surface are incapable of forming ice with the more loosely bound H_2O s farther from the surface at high relative humidities. This could be possible considering that H_2O -CMF H-bonding is generally stronger than H_2O - H_2O H-bonding and the distinctly different structural arrangement of adsorbed H_2O s on CMF surfaces (Figures 2 and 3) compared to ice and liquid water.

However, ice can form on surfaces where both of the above conditions are met (e.g.,); hence, one cannot assume that these surface-bound H₂Os will not be able to form ice with the adjacent layer of more loosely bound H₂Os. The results of this study suggest the likelihood of H₂O incorporation into the CMF, and based on this possibility, the hypothesis is proposed that isolated internal H₂Os give rise to the non-freezable tightly bound water signal (Figure 5) and their presence H-bonding directly to the main cellulose chains is why they affect the observed dynamics. One way to test this hypothesis would be dynamics experiments such as those in Zhao et al. (2019) could be repeated with D₂O pre-saturated into the cellulose, then dried and re-wet with H₂O to attempt to observe differences between water behavior within the CMF and external to it.

Conclusions

The DFT calculations indicate that there is ample space within the CMF to contain H₂O molecules. Inclusion of H₂Os into the CMF structure does not disrupt the overall order of the CMF significantly. The interior H₂Os are able to H-bond to O and H atoms of the CMF and therefore could stabilize the structure. H₂O diffusion into and out of the CMF has a prohibitive energy barrier in the one trajectory studied; however, DFT or classical MD simulations at higher T are warranted to fully study this possibility. Inclusion of isolated H₂O molecules within the CMF is consistent with the observation of unfreezable “water” in cellulose without the need to

form “bundles” where H₂Os are trapped between CMFs.

Statement and Declarations

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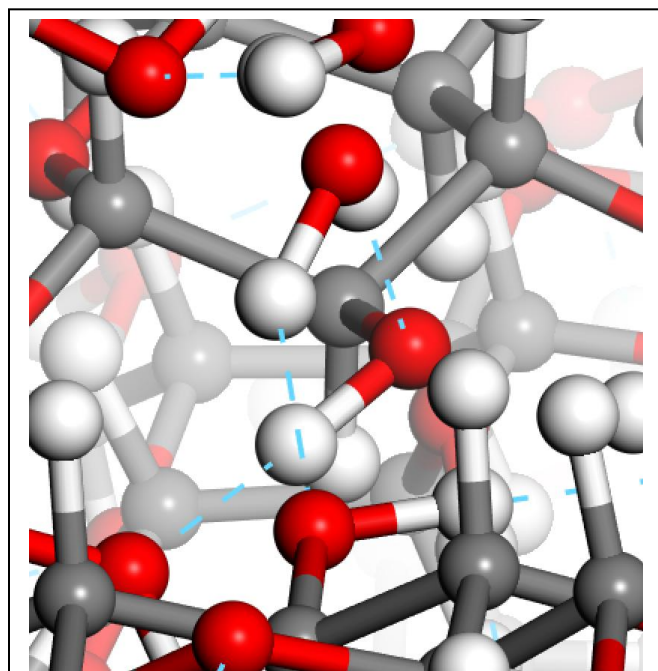


Figure 5 - Although H₂O may fit within the CMF, the H₂Os are more likely to be isolated unless the CMF swells and allows water in. H₂Os may form strong H-bonds (dashed lines), but not in geometries that allow for coordinated H⁺-exchange.

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