The effects of electronic polarization on water adsorption in metal-organic frameworks: H$_2$O in MIL-53(Cr)

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The effects of electronic polarization on the adsorption of water in the MIL-53(Cr) metal-organic framework are investigated using molecular dynamics simulations. For this purpose a fully polarizable force field for MIL-53(Cr) was developed which is compatible with the ab initio-based TTM3-F water model. The analysis of the spatial distributions of the water molecules within the MIL-53(Cr) nanopores calculated as a function of loading indicates that polarization effects play an important role in the formation of hydrogen bonds between the water molecules and the hydroxyl groups of the framework. As a result, large qualitative differences are found between the radial distribution functions calculated with non-polarizable and polarizable force fields. The present analysis suggests that polarization effects can significantly impact molecular adsorption in metal-organic frameworks under hydrated conditions. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4739254]

I. INTRODUCTION

The molecular-level characterization of the structure and dynamics of water in confining environments is key to understanding many processes of relevance to chemistry,$^{1,2}$ geology,$^3$ and biology.$^4$ Furthermore, determining how the thermodynamic behavior and molecular mobility of water change upon confinement is of fundamental importance on its own for the development of a microscopic understanding of the unique properties of water under different conditions.$^5,6$ In this regard, it has been shown that the interactions with chemically different substrates significantly perturb the water hydrogen-bond network, leading to pronounced changes in the phase behavior$^7$ and orientational dynamics.$^8,9$ The impact of nuclear quantum effects on the water properties upon confinement has also been studied.$^{10,11}$

Metal-organic frameworks (MOFs) represent a relatively new class of nanoporous materials consisting of metal ions or clusters coordinated to organic molecules that act as linkers to form extended three-dimensional networks.$^{12}$ Because of their chemical diversity, high surface area, and porosity, MOFs have recently received increasing attention for potential applications in gas storage and separation, catalysis, sensing, nonlinear optics, luminescence, and magnetism.$^{13}$ In particular, it has been shown that MOFs exhibit exceptional CO$_2$ adsorption capacity under equilibrium conditions,$^{14-16}$ which makes these materials promising candidates for CO$_2$ capture and separation from flue gas emitted by fossil-fuel power plants. However, before MOFs can actually find practical applications in large-scale technologies, it is critical to assess their stability and adsorption capacity under realistic conditions.$^{17}$ Since the flue gas is not pure CO$_2$ but rather a mixture of ~12% CO$_2$, ~73% N$_2$, and ~11% H$_2$O (the balance is composed of O$_2$, SO$_2$, and NO$_x$), with H$_2$O effectively competing for the binding sites within the framework and directly impacting the stability of the overall structure, a molecular-level characterization of the MOF-water interactions is needed.$^{18}$

It has been observed experimentally that the behavior of MOFs in the presence of water displays a large degree of variability. Some frameworks degrade irreversibly under low-hydration conditions, while other structures remain highly stable even when completely immersed in water.$^{19-23}$ Framework functionalization with water-repellent groups has recently been shown to represent a viable route for improving the stability of MOFs under hydrated conditions.$^{24-26}$ In general, it has been found that the hydrothermal stability of MOFs correlates with the estimated dissociation energy of the metal-ligand bond.$^{27}$ In this context, computer modeling plays an important role in the characterization of the adsorption capacity of MOFs, providing molecular-level insights into the binding sites, adsorption energies, and distribution of guest molecules within the nanopores. With very few exceptions,$^{28-31}$ all computer simulations of MOFs have been carried out with fixed charge (i.e., non-polarizable) force fields. Although common non-polarizable force fields incorporate polarization effects in an average fashion, it is recognized that these models are not capable of correctly reproducing the variation of the electrostatic environment in inhomogeneous molecular systems.$^{32}$ Importantly, the behavior of molecules adsorbed in the MOF nanopores can vary significantly as a function of loading and can be qualitatively different from that of the bulk phase, which is generally used as the reference state in the parameterization of non-polarizable force fields.

In this study, the effects of electronic polarization on water adsorption in MIL-53(Cr) are investigated using molecular dynamics (MD) simulations. MIL-53(Cr) is a

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three-dimensional MOF that is built-up from infinite chains of corner-sharing CrO$_4$(OH)$_2$ clusters interconnected by terephthalate linkers which undergoes reversible structural transitions (the so-called “breathing effect”) upon hydration. The article is organized as follows: In Sec. II, a brief description of the computational details specific to our simulations is provided. The results are discussed in Sec. III, and the conclusions are given in Sec. IV.

II. COMPUTATIONAL METHODOLOGY

A periodic system consisting of 32 MIL-53(Cr) unit cells was used in all MD simulations. To explicitly take into account polarization effects, a fully polarizable Thole-type model (TTM) (Ref. 36) of MIL-53(Cr) was developed based on the flexible force field of Ref. 35. Specifically, atomic polarizabilities ($\alpha_i$) were added to the framework atoms while retaining the original atomic partial charges and parameters for the bonded and non-bonded interactions. The atomic polarizabilities for the H, C, and O atoms were taken from Ref. 37 and the corresponding values for the Cr(III) atoms were taken from Ref. 38. The water molecules were represented by the $ab$ initio-based and polarizable TTM3-F force field. According to Thole’s approach, an effective density, $\rho(r)$, replaces the interactions between point charges/dipoles,

$$\rho \left( r \right) = \frac{1}{A} \frac{3 \alpha_i}{4\pi} \exp \left[ -\alpha_i \left( \frac{r}{A} \right)^3 \right]. \quad (1)$$

The dimensionless parameter $\alpha_i$, which determines the width of the density, was kept at the TTM3-F value ($\alpha_i = 0.175$), while $A = (\alpha_i \alpha_j)^{1/6}$ with $\alpha_i$ and $\alpha_j$ being the atomic polarizabilities of atoms $i$ and $j$, respectively. For comparison, MD simulations with the rigid TIP4P/2005 (Ref. 40) and flexible sSPC/Fw (Ref. 41) water models were also carried out in combination with the original non-polarizable MIL-53(Cr) force field. In all cases, the parameters associated with the non-bonded framework-water interactions were obtained using the Lorentz-Berthelot mixing rule. A series of MD simulations were carried out for different water loadings ($N_{\text{H}_2\text{O}}$), ranging from 1 to 20 H$_2$O molecules per unit cell. The water molecules were initially distributed uniformly in the nanopores and each system was allowed to relax during a 1 ns simulation carried out at $T = 300$ K and $P = 1$ atm in the constant stress and constant temperature ($N\sigma T$) ensemble. The temperature and pressure were maintained using the Nosé-Hoover thermostat and barostat with relaxation times of 1 ps and 5 ps, respectively. The structural and thermodynamic properties of water inside the MIL-53(Cr) nanopores were then calculated from $N\sigma T$ simulations of 500 ps. In all cases, the equations of motion were propagated according to the velocity-Verlet algorithm with timesteps $\Delta t = 0.5$ fs and 0.2 fs for the non-polarizable and polarizable force fields, respectively. The short-range interactions were truncated at an atom-atom distance of 10.0 Å while the electrostatic interactions were treated using the particle mesh Ewald method and the standard Ewald sum in simulations with the non-polarizable and polarizable force fields, respectively. The simulations with the non-polarizable force fields were carried out with DL_POLY4 (Ref. 44) while those with the TTM force field were performed using a modified version of DL_POLY2.

III. RESULTS AND DISCUSSION

Density functional theory (DFT) calculations were initially performed to characterize the MIL-53(Cr)-water interactions and, consequently, assess the accuracy of the non-polarizable and polarizable force fields. For this purpose, a reduced model of MIL-53(Cr) was built containing six Cr(OH)[O$_2$C–C$_6$H$_4$–CO$_2$] units (Figure 1). Six Li$^+$ ions were also included in the model system to coordinate the free $-\text{CO}_2^-$ groups of the terephthalate linkers. The hexacoordination of the Cr(III) atoms was preserved by adding two HCO$_2^-$ and three H$_2$O molecules. All calculations were performed with GAUSSIAN 09 (Ref. 46) using the M062X density functional. The cc-pVDZ basis set was used for C, H, O, and Li, while the LANL2DZ basis set was used for the Cr atoms. The M062X functional was chosen because it was shown to provide an accurate description of the electronic properties of DMOF-1, another breathing MOF, as well as of hydrogen-bonded systems. An appropriate initial guess was used to reproduce the correct spin configuration of the Cr(III) atoms and, consequently, the experimentally measured antiferromagnetism of MIL-53(Cr). To model the water-framework interactions a single H$_2$O molecule was placed in the central nanopore of the reduced MIL-53(Cr) model with the oxygen atom pointing towards the hydrogen atom of the hydroxyl (–OH$^-$) group of the framework (Figure 1).

![FIG. 1. (a) Schematic representation of the reduced MIL-53(Cr) model used in the DFT calculations. Also indicated as dashed lines are the $x$ and $y$ directions along which the potential energy scans were performed. Color scheme: Blue = Cr, red = O, gray = C, white = H, pink = Li. (b) Atom labels used in the definition of the RDFs.](image-url)
This specific orientation was chosen because it was found that the water molecules adsorbed in MIL-53(Cr) interact with the framework preferentially via hydrogen bonds to the $\text{–OH}^{-}$ groups. Potential energy scans were then performed by moving the water molecule within the nanopore along the $x$ and $y$ directions indicated in Figure 1. The comparison between the M062X potential energy profiles and the corresponding curves obtained using the non-polarizable and polarizable models is shown in Figure 2. In both cases, the three force fields provide effectively identical potential energy curves, reproducing with reasonable accuracy the DFT results. Similar agreement with the $\text{ab initio}$ data was also obtained for the same vertical and lateral scans performed for different water orientations which are reported in the supplementary material.

Direct insights into the effects of electronic polarization on the adsorption of water in the MIL-53(Cr) nanopores were obtained from MD simulations. As discussed in detail in Ref. 35, MIL-53(Cr) undergoes two distinct structural transitions from a large to a narrow pore configuration and then from a narrow to a large pore configuration as a function of water loading. The variation of the unit cell volume as a function of the number of H$_2$O molecules adsorbed per unit cell is shown in Figure 3(a). Similar results are obtained with all three force fields indicating that the breathing behavior of MIL-53(Cr) is not specifically dependent on the description of the underlying interactions but rather is related to the effective volume occupied by the H$_2$O molecules. It is important to mention that some differences exist between the present results and those reported in Ref. 35, which are due to slight different distributions of the water molecules within the nanopores.

To characterize the variation of the molecular properties as a function of loading, the distributions of the water dipole moments, $P(\mu)$, for $N_{H_2O} = 3, 5, 7, 10, 14,$ and $20$ calculated with the TTM force field are shown in Figure 3(b). It can be seen that the average value of the molecular dipole moment increases as $N_{H_2O}$ increases, with the distributions becoming significantly broader. This directly correlates with the more polarizing environment and larger number of possible hydrogen-bond configurations that exist when the H$_2$O
molecules fill the MIL-53(Cr) nanopores. Interestingly, the average H$_2$O dipole moment decreases between $N_{H_2O} = 10$ and $N_{H_2O} = 14$ as a result of the transition from the narrow to the large pore structure. It is also important to note that even at the highest loading ($N_{H_2O} = 20$), the dipole distribution is appreciably different from that of the liquid, which provides clear evidence for the different behavior of water adsorbed in the MIL-53(Cr) nanopores relative to the bulk phase.

Figure 4 shows the radial distribution functions (RDFs) describing the spatial correlations between the atoms of the H$_2$O molecules and those of the framework. A specific comparison is made between the Ow-Ho, Ow-C1, and Ow-Ow RDFs obtained using the three different force fields (the atomic labels are defined in Figure 1). The comparison between all other RDFs is reported in the supplementary material. Large qualitative differences are found between the RDFs obtained from simulations with the non-polarizable and polarizable force fields. In particular, independently of the water loading, the polarizable TTM force field predicts a more localized water structure near the hydroxyl group of the framework as illustrated by the persistence of a sharp peak located at $\sim 2.0$ Å in the Ow-Ho RDFs. This first peak, which effectively represents H$_2$O molecules hydrogen-bonded to the –OH$^-$ group, is found at slightly larger Ow-Ho separations in the RDFs calculated with the TIP4P and aSPC/Fw water force fields for $N_{H_2O} \leq 7$ and then disappears at higher water loading. The different evolution of the Ow-Ho RDFs as a function of $N_{H_2O}$ implies that, at higher loading, the non-polarizable force fields predict the water molecules to interact preferentially with each other rather than with the framework. Based on the agreement with the DFT potential energy curves calculated for a single water molecule within a MIL-53(Cr) nanopore (Figure 2), this different behavior appears to be related to many-body water-framework and water-water polarization effects that cannot be effectively captured by non-polarizable force fields. Appreciable differences, which become smaller as the number of water molecules per unit cell increases, also exist in the Ow-C1 and Ow-Ow RDFs. These differences can be understood by considering that, especially at low loading, the properties of the H$_2$O molecules adsorbed in the MIL-53(Cr) nanopores are significantly different from those of bulk water, and consequently cannot be accurately described by the TIP4P/2005 and aSPC/Fw models that have been parameterized to reproduce the properties of the liquid phase. This directly correlates with the variation of the H$_2$O dipole moment as a function of loading calculated with the TTM force field (Figure 3(b)).

To characterize the specific impact of electronic polarization, $N\sigma T$ simulations were carried out with a modified TTM model in which the framework polarizability was turned off. The corresponding RDFs are compared in Fig. 5 with those obtained using the full TTM model. Evidently,
making the framework non-polarizable leads to Ow-Ho and Ow-C1 RDFs very similar to those obtained with the TIP4P/2005 and aSPC/Fw models. On the other hand, the Ow-Ow RDFs remain essentially unaltered. This analysis indicates that the explicit inclusion of polarization effects can significantly impact the binding energies and spatial distributions of the water behavior inside the MIL-53(Cr) nanopores. Studies along these lines are currently ongoing in our group using the same computational framework developed for calculating the vibrational spectra of bulk water.54,55

IV. CONCLUSIONS

In summary, this study demonstrates that electronic polarization effects play an important role in the adsorption of water in MIL-53(Cr) and, very likely, in other metal-organic frameworks containing both polar and non-polar subunits. Specifically, a fully polarizable TTM force field based on the Thole model was developed and applied to the characterization of the water behavior inside the MIL-53(Cr) nanopores as a function of loading. The comparison with DFT calculations shows that both non-polarizable and polarizable models reproduce with reasonable accuracy the interactions of a single water molecule with the framework. However, MD simulations indicate that the spatial distributions of the H2O molecules within the nanopores calculated with the polarizable TTM model are qualitatively different from those obtained using common fixed-charge water models. These differences can be related to the variation of the water dipole moments as a function of loading which gives rise to many-body water-framework and water-water effects that cannot be reproduced accurately by non-polarizable force fields. The present analysis suggests that polarization effects can significantly impact the binding energies and spatial distributions of H2O molecules in the nanopores, and, consequently, should be taken into account explicitly in simulations of molecular adsorption in MOFs under hydrated conditions.

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52 See supplementary material at http://dx.doi.org/10.1063/1.4739254 for an additional comparison between the potential energy curves calculated with the M062X functional and the force fields as well as for the analysis of all radial distribution functions between the water molecules and the atoms of the MIL-53(Cr) framework.