Atomistic molecular dynamics insights on water local structure and dynamics on different surfaces of zeolitic-imidazolate frameworks

Mohammad R. Momeni*, Dil K. Limbu, Sara Abdelhamid, Shaina Pearson, and
Farnaz A. Shakib*

*Department of Chemistry and Environmental Science, New Jersey Institute of Technology,
Newark 07102, NJ United States*

E-mail: momeni@njit.edu, shakib@njit.edu

Abstract

Most of chemistry in nanoporous materials with small pore sizes and windows is known to occur on the surface which is in immediate contact with substrate/solvent, rather than inside pores and channels. Here, we report the results of our comprehensive atomistic molecular dynamics simulations on deciphering the intermolecular hydrogen bond network of water on outer surface of a nanoparticle model of ZIF-8 vs. inner surfaces of its pristine crystalline bulk model. Using a finite ≈ 5.1 nm nanoparticle model with edges containing under-coordinated Zn^{2+} metal sites we show that water exposed to the surface of the nanoparticle exhibits both interfacial and bulk-like characters. Furthermore, we illustrate that as water content increases larger droplets are formed with water molecules starting to diffuse into the nanopores. While the confined water in the crystalline bulk simulations is pushed to the vacant pores due to hydrophobic inner surfaces, the outer surface water molecules form chemical bonds with under-coordinated Zn^{2+} metal sites which act as nucleation sites for the water

droplets to form and hence making the surface hydrophilic. By adapting a similar mechanism to the *dangling linker defect formation* mechanism, we probe the tendency of the outer surface of ZIF-8 nanoparticles to water attack and hydrolysis. Results presented in this work are useful in designing more robust materials for applications in humid environments.

Introduction

Zeolitic-imidazolate frameworks (ZIFs),^{1,2} a subclass of metal-organic frameworks (MOFs),^{3,4} are chemically tunable and permanently porous materials built by forming coordinative bonds between tetrahedral Zn^{2+} and/or Co^{2+} ions and imidazole linkers (Figure 1). In recent years, ZIFs have found numerous applications in gas storage,⁵ chemical sensing,⁶ separation,^{7,8} encapsulation and controlled delivery,⁹ as well as water harvesting^{10,11} and catalysis.^{12,13} These diverse applications stem from the differences in topologies, aperture sizes and steric environments of ZIFs as well as a large variety of imidazolate linker functional groups leading to hydrophobic or hydrophilic surfaces. It is expected that water, by

Figure 1: (a) Molecular building blocks of ZIF-8 and ZIF-90 with sodalite topologies and similar ≈ 0.34 nm window and ≈ 1.2 nm pore sizes. (b) A ≈ 5.1 nm nanoparticle model of ZIF-8 (3865 atoms) containing coordinatively unsaturated Zn^{2+} sites on its outer surface.

Figure 2: Calculated 2D density maps of the oxygen of water in the NP (a-c) vs. the CB (d-f) models of ZIF-8 with different 1n (left), 2n (middle) and 3n (right) water loadings.

being present in both atmosphere and aqueous solutions, has a determining factor on the structural stability of these porous materials and the durability of composite devices made from them. In particular, hydrophobic ZIF-8, with 2-methylimidazolate linkers (Figure 1), shows good stability in aqueous solutions,² humid air and dry acidic gases such as SO_2 .^{14,15} However, it is shown that it degrades in humid acidic gases, approaching a complete loss of pore volume within 10 days of humid SO_2 exposure.^{14,15} Interestingly, hydrophilic ZIF-90, with 2-imidazolecarboxaldehyde linkers (Figure 1), shows the same stability behaviour of hydrophobic ZIF-8 in different environments. Indeed, they show similar pore volume retentions in different environments in spite of much higher pK_a of ZIF-8. Even more interesting observation is that after 10 days exposure to humid SO_2 14% of Zn–N bonds in hydrophobic ZIF-8 are cleaved while this number is only 2% in hydrophilic ZIF-90.¹⁴ Despite several recent studies,^{14,16–21} an unambiguous and full atomistic level understanding of the competing interatomic water-water and water-framework interactions, with possible explanation of the dissolution of the ZIF nanoparticles in humid environments, is still missing. The reason can

be partially traced back to the fact that most studies on ZIFs, and other porous materials in general, have focused on pristine crystalline bulk models and ignored the effects of particle’s size/shape and external surfaces which normally contain defects and under-coordinated metal centers. This is counter intuitive as most of reactivity is known to stem from the surface of these materials, which are in immediate contact with water than inside nano confined channels and pores. For example, in a seminal work of Pang et al. on hydrolytic stability of ZIF-8 nanoparticles, humid SO_2 was found to lead to the hydrolysis of only the surface of the particles, by forming $\text{Zn}(\text{OH})_2$ -like species and protonated imidazolate linkers, while the core of nanoparticles was shown to stay intact.¹⁵

Here, we report the results of our atomistic molecular dynamics simulations on the local structure and dynamical properties of water on inner vs. outer surfaces of ZIF-8 as a representative of the ZIF family. Both pristine crystalline bulk (CB) and a realistic nanoparticle (NP) model were considered where the latter features edges containing under-coordinated Zn^{2+} metal centers (Figure 1). Our simulations provides microscopic molecular level insights on how water nucleates and grows droplets inside the nanopores and channels of the hydrophobic ZIF-8 vs. on the outer surfaces/edges of the realistic ≈ 5.1 nm NP model. Comparisons are made, whenever informative, with confined water thermodynamics and dynamics in hydrophilic ZIF-90 framework. Our findings in this work are helpful in deciphering water adsorption properties in ZIFs and other similar nanoporous materials with small particle sizes, pores and apertures where surface-to-volume ratio is high.

Model and Simulation Details

Using the experimentally reported crystal structures of $2 \times 2 \times 2$ crystalline bulk (CB) models of ZIF-90 and ZIF-8 and a ≈ 5.1 nm nanoparticle (NP) model of ZIF-8 built based on the experimentally available SEM/TEM images and measured surface areas,²² atomistic molecular dynamics simulations were performed at 300 K and 1 atm. The flexible ZIF-FF²³ force field was used for all bonded and non-bonded parameters in ZIF-8 while for ZIF-90, a combination of ZIF-FF and the generalized amber force field (GAFF),²⁴ as reported in Ref.

25, was used without modification. To model water, we employed the flexible and anharmonic four-site q-TIP4P/F²⁶ water potential model as implemented in our in-house developed general purpose software package DL_POLY Quantum v1.0²⁷ derived from DL_POLY Classic v1.10.²⁸ DL_POLY Quantum provides an efficient platform for large scale dynamics simulation of condensed phase chemical systems. The framework-water interactions were modeled using the non-bonded electrostatic and Lennard-Jones terms with parameters for ZIFs taken from Refs. 23,25 while parameters for water were taken from the q-TIP4P/F water model which are the same as the original rigid TIP4P/2005²⁹ water model. Lorentz–Berthelot mixing rules were used to drive cross interaction terms. Atom-atom cutoff distance of 15.0 Å was employed for truncating the short-range interactions in the CB models whereas the long-range electrostatics were calculated using the Ewald summation method.³⁰ Water molecules explicitly included in our simulations were added using PACKMOL.³¹ The equations of motion were propagated according to the velocity–Verlet algorithm. The temperature was kept constant using a Nosé–Hoover chain comprised of four thermostats with a time–step of 0.2 fs as implemented in DL_POLY Quantum v1.0. For classical simulations in DL_POLY Quantum v1.0, the Nosé–Hoover chain thermostat is implemented based on the Suzuki–Yoshida scheme^{32–34} whereas the Nosé–Hoover chain thermostat/barostat for isothermal-isobaric ensemble (NPT) is implemented through the Martyna–Tobias–Klein (MTK) algorithm.^{35,36} For modeling the nanoparticle model of ZIF-8, the particle was positioned at the center of a cubic box of length 75.0 Å with the atom-atom cutoff distance set to 35.0 Å. Water dynamical properties including reorientation relaxation time and total self diffusion were calculated using procedures outlined in our previous work.³⁷ For simulations of bulk water, 216 water molecules were packed inside a cubic box of length 35.233 a.u. which corresponds to a density of 0.997 g/cm^{−3} for bulk liquid water at 298 K with the atom-atom cutoff distance set to 9.0 Å. For ice, 324 water molecules were equilibrated at 100 K in a hexagonal cell with a cutoff distance of 9.0 Å.

Results and Discussion

Figure 3: Calculated N-H_W (hydrogen of water) RDFs of the MD equilibrated CB models of (a) ZIF-8 and (b) ZIF-90 with different water loadings at 300 K and 1 atm.

It is now well established that a material’s particle size/shape and the presence and density of the open-metal sites are crucial factors that need to be included in simulations especially when pores and windows are too small to allow guest molecules to freely diffuse into the pores. In this work, we address this via employing a realistic ≈ 5.1 nm nanoparticle model of ZIF-8, built based on the experimentally available SEM/TEM images and measured surface areas,²² and comparing its properties to $2 \times 2 \times 2$ pristine crystalline bulk (CB) models with no defects and/or coordinatively unsaturated open-metal sites (Figure 1). The importance of structural flexibility and presence of deformations and defects with open-metal sites on different properties of MOFs has been highlighted before.^{37–46} To reflect this in our simulations, here, we employ a flexible force field developed exclusively for ZIF structures, i.e. ZIF-FF combined with the flexible and anharmonic q-TIP4P/F water model. To probe the flexible and dynamic hydrogen bond (HB) network of confined vs. surface water, 1–6 H₂O per Zn²⁺ metal centers (hereafter 1n–6n) were equilibrated in the CB models of ZIF-90 and ZIF-8 (corresponding to 96, 192, 288, 384, 480, and 576 water molecules, respectively). In the case of the NP model of ZIF-8, considering the cost of the simulations, 1–3 H₂O per Zn²⁺ centers (hereafter 1n–3n corresponding to respectively, 192, 384 and 576 water molecules) were uniformly packed on the exterior of the nanoparticle. Figure 2 illustrates the calculated

2D density maps for the oxygen of water equilibrated on the NP model (a–c) and inside the pores of the CB model of ZIF-8 (d–f) which shed light on the local intermolecular HB network of water on the outer vs. the inner surfaces. The calculated 2D density maps show formation of nano droplets of water on the surface of the NP model as water content is increased from 1n to 3n. This underscores the hydrophobic nature of ZIF-8 which forces all the water molecules to create an intramolecular water-water HB network (Figure 2). On the other hand, confinement effects in the CB model separate water molecules and force them to relocate to nearby pores and form smaller droplets (Figures 2e and 2f). In hydrophobic CB ZIF-8, with no under-coordinated open metal sites, the steric hindrance of the methyl substituents on imidazolate linkers protects metal centers from the nucleophilic water attack and Zn–N bonds from cleavage. As expected, no Zn–O_W radial distribution function (RDF) peaks were observed in equilibrated CB systems. Almost all confined water molecules were found to be free with hydrogen bonding to the imidazolate nitrogen being the main mode of interaction with the framework (Figure 3). As can be seen from the N–H_W (hydrogen of water) RDFs for the CB model of ZIF-8 shown in Figure 3a, at low water content, the water molecules remain far from the inner surfaces of the pores. However, as water content increases two N–H_W RDF peaks start forming at 2.75 Å and 5.5 Å. This can be contrasted to the RDFs for the CB model of ZIF-90, with 2-imidazolecarboxaldehyde linkers, which does not show the 2.75 Å peak at higher water contents. This is due to the fact that most prominent form of water–framework interaction in ZIF-90 involves the carbonyl functional group of the linker not the N atoms. Based on the current framework of MD simulations of confined water in ZIF-8 and ZIF-90, it will be interesting to explore the impact of including nuclear quantum effects on the differential water–water vs. water–framework interactions which is possible for instance through path integral⁴⁷ methodology. Opposite to the inner surfaces, outer surfaces of the NP model of ZIF-8 features under-coordinated Zn²⁺ metal centers. Hence, water molecules were found to be coordinated to these Zn²⁺ open metal sites for all studied 1n–3n water loadings. As can be seen in Figure 4a the Zn–O_W RDF

Figure 4: (a) Calculated Zn-O_W (oxygen of water) RDFs of the MD equilibrated NP model of ZIF-8 with different water loadings at 300 K. (b) Calculated normalized tetrahedral order parameters (q_{tetra}) of the CB models of ZIF-8 and ZIF-90 with the highest 6n water loadings as well as (c) the NP model of ZIF-8 with different 1n-3n water loadings at 300 K. Corresponding data for bulk water at 298 K and ice at 100 K are given for comparison.

peaks in all three cases are centered at ≈ 2.05 Å. As mentioned before, water tends to form rather large droplets on the surface of the nanoparticle (Figure 2). These droplets remain on the surface of the NP by forming HBs with the coordinated water molecules in the form of Zn-OH₂ moieties which act as nucleation sites. To shed more light on the local HB network of water on inner and outer surfaces vs. bulk water and ice we calculated normalized orientational tetrahedral order parameters (q_{tetra}),⁴⁸⁻⁵⁰ which identifies the presence of four nearest neighbor water oxygen atoms according to

$$q_{\text{tetra}} = 1 - \frac{3}{8} \sum_{j=1}^3 \sum_{k=j+1}^4 \left(\cos \psi_{jk} + \frac{1}{3} \right)^2. \quad (1)$$

Here, ψ_{jk} is the angle formed between the oxygen of water of interest and its nearest neighbor oxygen atoms (j) and (k) (located at distances less than 3.5 Å). The q_{tetra} values range from 0 for an ideal gas to 1 which indicates an ice-like structure with a close to perfect tetrahedral arrangement. Figure 4b illustrates our MD calculated q_{tetra} for the highest 6n water loading in the CB models of ZIF-8 and ZIF-90 compared to those of bulk water and ice. Interestingly, the calculated q_{tetra} values show that confined water in both hydrophobic ZIF-8 and hydrophilic ZIF-90 exhibits very similar structures with maxima centered at ≈ 0.45 compared to ≈ 0.8 and ≈ 1.0 for bulk water and ice, respectively. The similarity in calculated

q_{tetra} values is most likely related to the fact that ZIF-8 and ZIF-90, which have similar sodalite topologies, share almost the same pore and window sizes. Our calculated q_{tetra} for the NP model of ZIF-8 is shown in Figure 4c for three different water loadings. At the lowest water loading, it features a distinct sharp peak centered at $q_{tetra} \approx 0.3$ which is absent in the case of the CB model of ZIF-8 shown in Figure 4b. We attribute this distinct peak to the water molecules that are coordinated to the open metal centers (W_{coord}) on the surface which demonstrates a lower tetrahedrality compared to the confined water interacting with the inner surface, see the peak at ≈ 0.45 for the CB models in Figure 4b. This clearly signals that the local HB network of the coordinated water on the exterior surface of the nanoparticle with open Zn^{2+} sites is more frustrated than inside the nanopores of the CB model. As water content increases from 1n to 3n (i.e., from 192 H_2O to 576 H_2O), a second peak starts to emerge with maximum centered at $q_{tetra} \approx 0.8$. This peak almost overlaps with the corresponding peak for the bulk water (Figure 4c) and hence we call these water molecules with higher tetrahedrality, bulk-like water (W_{bulk}). Interestingly, a third peak also appears at the $q_{tetra} \approx 0.45$ as the water loading increases. This peak resembles the q_{tetra} peak of the confined water in the bulk model of ZIF-8, see Figure 4b. The appearance of this peak signals diffusion of some water molecules inside the NP under the studied conditions which is confirmed by inspecting our MD trajectories. Figure 5a displays three different dynamical behaviour of water molecules on the surface of the NP model of ZIF-8 with a focus on the change of the position of O_W from the center of mass (CoM) of the NP. W_{coord} represent water molecules which are coordinated to the open metal sites on the surface as mentioned above. As can be seen coordination happens in the very early stages of the dynamics simulation and remains stable till the end of simulation. Such water molecules have limited movements. We note that since our NP is not a perfect sphere the position of these water molecules depends on the distance of the open metal site from the CoM. W_{conf} represent water molecules which have a very vivid range of motion and finally diffuse inside the NP as opposed to W_{bulk} which in spite of their vivid motions do not diffuse inside the

NP. These three classes of water molecules are in perfect agreement with the three q_{tetra} peaks as discussed in Figure 4c. Figure 5b illustrates the dynamical motions of all 192 water molecules with respect to their distances from the CoM of the NP. One can see the long range of motions of W_{conf} induced by the hydrophobicity of the inner surfaces of the NP model of ZIF-8. More interestingly, some water molecules diffuse towards the CoM but then are pushed back toward the outer surface. Figure 5c illustrates the dynamical motions of all 576 water molecules with respect to their distances from the CoM of the NP. For the highest studied water loading, clearly more water molecules are able to diffuse toward the CoM of the NP model with a few that are even able to reach the CoM of the NP at some point of their journey.

Figure 5: (a) A representative scheme of the dynamics of different classes of water molecules on the surface of the NP model of ZIF-8; the distance of oxygen of a representative water molecule from the center of mass (CoM) of the NP is displayed. Similar figures for all 192 (b) and 576 (c) water molecules are also given.

Water dynamical properties including reorientation relaxation time (τ_2) and total self-diffusion coefficient (D_{tot}) were calculated for different water loadings in both the CB models of ZIF-90 and ZIF-8 as well as for the NP model of ZIF-8 as tabulated in Table 1. Calculated dynamical properties point toward higher freedom of movements in the confined water within the ZIF-8 framework than ZIF-90. For instance, calculated τ_2 values for ZIF-90 is 8.9 ps for the 6n water loading while the corresponding value for the CB model of ZIF-8 is 5.5 ps (Table 1). A trend can be observed for the calculated diffusion coefficients that are $\approx 30\%$ higher in ZIF-8 than ZIF-90 for all studied water loadings. Considering the experimentally measured τ_2 (1.7–2.6 ps^{51–53}) for bulk water as well as our MD simulated value (3.0 ps), these data

Table 1: Computed water reorientation relaxation time (τ_2 in ps) and total self diffusivity (D_{tot} in ps/ $\text{\AA}^2$) for the CB models of ZIF-90 and ZIF-8 as well as the NP model of ZIF-8 with different water loadings at 300 K. The corresponding experimental (Exp.) and MD simulated (Simul.) values for the bulk water at 298 K are given for comparison.

$\text{H}_2\text{O}/\text{Zn}^{2+}$	ZIF-90 (CB)		ZIF-8 (CB)		ZIF-8 (NP)	
	τ_2	D_{tot}	τ_2	D_{tot}	τ_2	D_{tot}
1n	4.1	0.146	2.0	0.191	5.0	0.251
2n	4.6	0.119	2.8	0.154	5.9	0.151
3n	4.9	0.115	3.3	0.133	4.8	0.206
4n	5.8	0.096	3.9	0.119	—	—
5n	7.0	0.081	4.5	0.097	—	—
6n	8.9	0.057	5.5	0.076	—	—
Exp.	1.7–2.6 ^{51–53}	0.229 ⁵⁴				
Simul.	3.0	0.167				

clearly signal that water has more freedom in ZIF-8 than ZIF-90. An interesting observation from Table 1 is related to the lowest water loading, 1n, in the CB model of ZIF-8, which corresponds to a relative humidity of ≈ 8 wt %. This low water content confined in the pores of hydrophobic ZIF-8 is calculated to be even more free/mobile than the bulk water (Table 1). It is however worthwhile mentioning that stemming from the hydrophobic nature of ZIF-8, different meta-stable configurations exist that interconvert inside its nanochannels and pores. The rather higher mobility observed for the smallest water content in hydrophobic ZIF-8 agrees qualitatively with a recent study⁵⁵ on water transport through hydrophobic hBN nano-capillaries where mono-layer water clusters were shown to have diffusion coefficients up to four times higher than that of bulk water. Our findings in this work are also in general in accordance with previous studies on anomalous behavior of water at extreme mechanical nano/sub-nano confinement conditions.^{56–62} It is thus expected that confinement in hydrophobic environments can open up new opportunities for example in generating ions that are more mobile. This is similar to what has already been shown for proton transport in small linear water wires⁶³ and in narrow channels of the (6,6) carbon nanotubes.⁶⁴ This could also be translated to overall lower barriers for proton/electron transfer or proton-coupled electron transfer reactions in confinement which is currently an active research area.^{59–62} In comparison, water dynamics in the NP model of ZIF-8 does not show a systematic trend,

as in the case of the CB model, upon increasing the water content. Since the movement of water molecules are not mechanically confined, the total diffusion is the results of a competition between interfacial/diffused and free water molecules. Nevertheless, considering the computed D_{tot} values, it is evident that, apart from the diffused water molecules, due to the lack of the mechanical confinement effects water in the NP model is more free/mobile than the confined water in the CB model of ZIF-8 (Table 1). Overall, the rather significant differences in calculated structural and dynamical properties of water as outlined above underscores the importance of adapting a suitable model for simulations of nanoporous materials in condensed phases.

Finally, to distinguish the inner and outer surfaces of ZIF-8 during the water attack and subsequent hydrolysis we turn to quantum mechanical calculations (see the Electronic Supplementary Information (ESI) for details). Here, we consider a similar mechanism to the previously proposed *dangling linker defect formation* mechanism.⁶⁵ Our mechanism is comprised of two steps. The first step involves water interaction with the saturated tetra-coordinated and unsaturated tri-coordinated Zn^{2+} metal centers representing the inner and outer surfaces, respectively. For the latter case with three-coordinated Zn^{2+} complexes, this would involve formation of $Zn-OH_2$ bonds. The second step corresponds to the imidazolate linker displacement with newly added water molecule. We opt to call these steps the addition step and the displacement step, respectively. The displacement step is followed by proton transfer from the coordinated water to the displaced imidazolate linker leading to the formation of the final $Zn-OH$ products. Our computed free energy changes (ΔG s) for this mechanism are given in the ESI Figure S1 for both the tetra- and the tri-coordinated complexes. We found the displacement step to be the rate-determining step of the reaction for both cases. Interestingly, the computed free energy barrier ($\Delta G^\ddagger$ s) for the tri-coordinated complex was found to be half of its tetra-coordinated analogue (i.e., 5.2 vs. 10.4 kcal/mol, respectively, ESI Figure S1) demonstrating the higher susceptibility of the outer surface of ZIF-8 to water attack in comparison to the inner surface. We attribute the higher reactivity

of the tri-coordinated complex toward water attack to the higher positive charge on Zn^{2+} metal centers than the tetra-coordinated analogue (i.e., +1.79 e vs. +1.65 e , respectively). Our proposed mechanism is consistent with the study of Bhattacharyya et al. on degradation of ZIF-8 under humid SO_2 exposure where they suggested that cleavage of Zn–N coordinative bonds are initiated by protonation of the nitrogen atoms by sulfuric-sulfurous acidic mixtures.¹⁷ Our results are also in qualitative agreement with Pang et al. who have shown that hydrolysis only occurs on the surface of ZIF-8 with the core of the nanoparticles staying intact.¹⁵ Overall, based on the results presented in this work, we anticipate that use of surface masking agents together with functionalizing the imidazolate linkers with more bulky substituents could be among feasible ways for achieving higher water stability for ZIFs and other related nanoporous materials with small pores and windows.

Conclusions

Using two different pristine crystalline bulk and nanoparticle models, we showed that theory can provide systematic qualitative and quantitative microscopic level insights on water structure and dynamics in nanoporous materials. We illustrated in details that pristine crystalline bulk models by neglecting defects and edges which contain under-coordinated metal sites picture a drastically different scenario for water–water vs. water–framework interactions in nanoporous materials than realistic nanoparticle models. The primary mode of water adsorption in the inner surfaces of the crystalline bulk ZIF-8 were found to be weak hydrogen bonds with the nitrogen atoms of the imidazolate linkers compared to the formation of rather strong Zn–OH₂ bonds with under-coordinated Zn^{2+} metal centers on the outer surface of the nanoparticle model. These bonds were found to act as nucleation sites for forming rather large water droplets on the surface of the nanoparticle. Our mechanistic studies show that the Zn–N bonds on the exterior surface of the nanoparticle are twice more susceptible to water attack and cleavage than the analogous bonds in the tetra-coordinated Zn^{2+} metal centers. Based on current results, future works should focus on including nuclear quantum effects as well as transport properties of different ions on the surface vs confined

spaces of nanoporous materials.

Acknowledgement

FAS acknowledges support from the NJIT. This work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant numbers CHE200007 and CHE200008. This research has been (partially) enabled by the use of computing resources and technical support provided by HPC center at NJIT.

References

- (1) Huang, X.-C.; Lin, Y.-Y.; Zhang, J.-P.; Chen, X.-M. Ligand-Directed Strategy for Zeolite-Type Metal–Organic Frameworks: Zinc(II) Imidazoles with Unusual Zeolitic Topologies. *Angew. Chem. Int. Ed.* **2006**, *45*, 1557–1559.
- (2) Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O’Keeffe, M.; Yaghi, O. M. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *PNAS* **2006**, *103*, 10186–10191.
- (3) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal–Organic Frameworks. *Science* **2013**, *341*, 1230444.
- (4) Yaghi, O. M.; O’Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. Reticular synthesis and the design of new materials. *Nature* **2003**, *423*, 705–714.
- (5) Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, H.; O’Keeffe, M.; Yaghi, O. M. High-Throughput Synthesis of Zeolitic Imidazolate Frameworks and Application to CO₂ Capture. *Science* **2008**, *319*, 939–943.
- (6) Lu, G.; Hupp, J. T. Metal–Organic Frameworks as Sensors: A ZIF-8 Based Fabry-Perot

- Device as a Selective Sensor for Chemical Vapors and Gases. *J. Ame. Chem. Soc.* **2010**, *132*, 7832–7833.
- (7) Li, K.; Olson, D. H.; Seidel, J.; Emge, T. J.; Gong, H.; Zeng, H.; Li, J. Zeolitic Imidazolate Frameworks for Kinetic Separation of Propane and Propene. *J. Am. Chem. Soc.* **2009**, *131*, 10368–10369.
- (8) Chang, N.; Gu, Z.-Y.; Yan, X.-P. Zeolitic Imidazolate Framework-8 Nanocrystal Coated Capillary for Molecular Sieving of Branched Alkanes from Linear Alkanes along with High-Resolution Chromatographic Separation of Linear Alkanes. *J. Am. Chem. Soc.* **2010**, *132*, 13645–13647.
- (9) Liédana, N.; Galve, A.; Rubio, C.; Téllez, C.; Coronas, J. CAF@ZIF-8: One-Step Encapsulation of Caffeine in MOF. *ACS Appl. Mater. Interfaces* **2012**, *4*, 5016–5021.
- (10) Kim, H.; Yang, S.; Rao, S. R.; Narayanan, S.; Kapustin, E. A.; Furukawa, H.; Umans, A. S.; Yaghi, O. M.; Wang, E. N. Water harvesting from air with metal-organic frameworks powered by natural sunlight. *Science* **2017**, *356*, 430–434.
- (11) Hanikel, N.; Prévot, M. S.; Fathieh, F.; Kapustin, E. A.; Lyu, H.; Wang, H.; Diercks, N. J.; Glover, T. G.; Yaghi, O. M. Rapid Cycling and Exceptional Yield in a Metal-Organic Framework Water Harvester. *ACS Cent. Sci.* **2019**, *5*, 1699–1706.
- (12) Chen, B.; Yang, Z.; Zhu, Y.; Xia, Y. Zeolitic imidazolate framework materials: recent progress in synthesis and applications. *J. Mater. Chem. A* **2014**, *2*, 16811–16831.
- (13) Cheng, N.; Ren, L.; Xu, X.; Du, Y.; Dou, S. X. Recent Development of Zeolitic Imidazolate Frameworks (ZIFs) Derived Porous Carbon Based Materials as Electrocatalysts. *Adv. Energy Mater.* **2018**, *8*, 1801257.
- (14) Bhattacharyya, S.; Han, R.; Kim, W.-G.; Chiang, Y.; Jayachandrababu, K. C.; Hungerford, J. T.; Dutzer, M. R.; Ma, C.; Walton, K. S.; Sholl, D. S.; Nair, S. Acid Gas Sta-

- bility of Zeolitic Imidazolate Frameworks: Generalized Kinetic and Thermodynamic Characteristics. *Chem. Mater.* **2018**, *30*, 4089–4101.
- (15) Pang, S. H.; Han, C.; Sholl, D. S.; Jones, C. W.; Lively, R. P. Facet-Specific Stability of ZIF-8 in the Presence of Acid Gases Dissolved in Aqueous Solutions. *Chem. Mater.* **2016**, *28*, 6960–6967.
- (16) Bhattacharyya, S.; Han, R.; Joshi, J. N.; Zhu, G.; Lively, R. P.; Walton, K. S.; Sholl, D. S.; Nair, S. Stability of Zeolitic Imidazolate Frameworks in NO₂. *J. Phys. Chem. C* **2019**, *123*, 2336–2346.
- (17) Bhattacharyya, S.; Pang, S. H.; Dutzer, M. R.; Lively, R. P.; Walton, K. S.; Sholl, D. S.; Nair, S. Interactions of SO₂-Containing Acid Gases with ZIF-8: Structural Changes and Mechanistic Investigations. *J. Phys. Chem. C* **2016**, *120*, 27221–27229.
- (18) Bhattacharyya, S.; Jayachandrababu, K. C.; Chiang, Y.; Sholl, D. S.; Nair, S. Butanol Separation from Humid CO₂-Containing Multicomponent Vapor Mixtures by Zeolitic Imidazolate Frameworks. *ACS Sustain. Chem. Eng.* **2017**, *5*, 9467–9476.
- (19) Leus, K.; Bogaerts, T.; De Decker, J.; Depauw, H.; Hendrickx, K.; Vrielinck, H.; Van Speybroeck, V.; Van Der Voort, P. Systematic study of the chemical and hydrothermal stability of selected 'stable' metal organic frameworks. *Micropor. Mesopor. Mat.* **2016**, *226*, 110–116.
- (20) Mottillo, C.; Friscic, T. Carbon Dioxide Sensitivity of Zeolitic Imidazolate Frameworks. *Angew. Chem. Int. Ed.* **2014**, *53*, 7471–7474.
- (21) Zhang, C.; Han, C.; Sholl, D. S.; Schmidt, J. R. Computational Characterization of Defects in Metal–Organic Frameworks: Spontaneous and Water-Induced Point Defects in ZIF-8. *J. Phys. Chem. Lett.* **2016**, *7*, 459–464.

- (22) Proenza, Y. G.; Longo, R. L. Simulation of the Adsorption and Release of Large Drugs by ZIF-8. *J. Chem. Inf. Model.* **2020**, *60*, 644–652.
- (23) Weng, T.; Schmidt, J. R. Flexible and Transferable ab Initio Force Field for Zeolitic Imidazolate Frameworks: ZIF-FF. *J. Phys. Chem. A* **2019**, *123*, 3000–3012.
- (24) Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. Development and testing of a general amber force field. *J. Computat. Chem.* **2004**, *25*, 1157–1174.
- (25) Hunter, K. M.; Wagner, J. C.; Kalaj, M.; Cohen, S. M.; Xiong, W.; Paesani, F. Simulation Meets Experiment: Unraveling the Properties of Water in Metal–Organic Frameworks through Vibrational Spectroscopy. *J. Phys. Chem. C* **2021**, *125*, 12451–12460.
- (26) Habershon, S.; Markland, T. E.; Manolopoulos, D. E. Competing quantum effects in the dynamics of a flexible water model. *J. Chem. Phys.* **2009**, *131*, 024501.
- (27) Momeni, M. R.; Shakib, F. A. The DL_POLY Quantum molecular simulation package. Available from: https://github.com/fashakib/DL_POLY-Quantum-v1.0. The DL_POLY Quantum molecular simulation package. Available from: https://github.com/fashakib/DL_POLY-Quantum-v1.0.
- (28) Smith, W.; Forester, T. R.; Todorov, I. T. The DL_POLY Classic molecular simulation package. STFC Daresbury Laboratory. Available from: https://gitlab.com/DL_POLY_Classic. The DL_POLY Classic molecular simulation package. STFC Daresbury Laboratory. Available from: https://gitlab.com/DL_POLY_Classic.
- (29) Abascal, C., J. L. F.; Vega A general purpose model for the condensed phases of water: TIP4P/2005. *J. Chem. Phys.* **2005**, *123*, 234505.
- (30) Leach, A. R. *Molecular modeling: Principles and applications*; Pearson Prentice Hall, 2001.

- (31) Martínez, L.; Andrade, R.; Birgin, E. G.; Martínez, J. M. PACKMOL: A package for building initial configurations for molecular dynamics simulations. *J. Comput. Chem.* **2009**, *30*, 2157–2164.
- (32) Yoshida, H. Construction of higher order symplectic integrators. *Phys. Lett. A* **1990**, *150*, 262–268.
- (33) Suzuki, M. General theory of fractal path integrals with applications to many-body theories and statistical physics. *J. Math. Phys.* **1991**, *32*, 400–407.
- (34) Martyna, G. J.; Tuckerman, M. E.; Tobias, D. J.; Klein, M. L. Explicit reversible integrators for extended systems dynamics. *Mol. Phys.* **1996**, *87*, 1117–1157.
- (35) Martyna, G. J.; Tobias, D. J.; Klein, M. L. Constant pressure molecular dynamics algorithms. *J. Chem. Phys.* **1994**, *101*, 4177–4189.
- (36) Tuckerman, M. E.; Alejandre, J.; López-Rendón, R.; Jochim, A. L.; Martyna, G. J. A Liouville-operator derived measure-preserving integrator for molecular dynamics simulations in the isothermal–isobaric ensemble. *J. Phys. A: Math. Gen.* **2006**, *39*, 5629–5651.
- (37) Shi, Y.; Momeni, M. R.; Chen, Y.-J.; Zhang, Z.; Shakib, F. A. Water-Induced Structural Transformations in Flexible Two-Dimensional Layered Conductive Metal–Organic Frameworks. *Chem. Mater.* **2020**, *32*, 9664–9674.
- (38) Yang, D.; Momeni, M. R.; Demir, H.; Pahls, D. R.; Rimoldi, M.; Wang, T. C.; Farha, O. K.; Hupp, J. T.; Cramer, C. J.; Gates, B. C.; Gagliardi, L. Tuning the properties of metal–organic framework nodes as supports of single-site iridium catalysts: node modification by atomic layer deposition of aluminium. *Faraday Discuss.* **2017**, *201*, 195–206.

- (39) Momeni, M. R.; Cramer, C. J. Dual Role of Water in Heterogeneous Catalytic Hydrolysis of Sarin by Zirconium-Based Metal–Organic Frameworks. *ACS Appl. Mater. Interfaces* **2018**, *10*, 18435–18439.
- (40) Momeni, M. R.; Cramer, C. J. Structural Characterization of Pristine and Defective $[\text{Zr}_{12}(\mu_3\text{-O})_8(\mu_3\text{-OH})_8(\mu_2\text{-OH})_6]^{18+}$ Double-Node Metal–Organic Framework and Predicted Applications for Single-Site Catalytic Hydrolysis of Sarin. *Chem. Mater.* **2018**, *30*, 4432–4439.
- (41) Momeni, M. R.; Cramer, C. J. Computational Screening of Roles of Defects and Metal Substitution on Reactivity of Different Single- vs Double-Node Metal–Organic Frameworks for Sarin Decomposition. *J. Phys. Chem. C* **2019**, *123*, 15157–15165.
- (42) Kalaj, M.; Momeni, M. R.; Bentz, K. C.; Barcus, K. S.; Palomba, J. M.; Paesani, F.; Cohen, S. M. Halogen bonding in UiO-66 frameworks promotes superior chemical warfare agent simulant degradation. *Chem. Commun.* **2019**, *55*, 3481–3484.
- (43) Momeni, M. R.; Shakib, F. A. Determining role of structural flexibility on catalytic activity of conductive 2D layered metal-organic frameworks. *Chem. Commun.* **2021**, *57*, 315–318.
- (44) Zhang, Z.; Dell’Angelo, D.; Momeni, M. R.; Shi, Y.; Shakib, F. A. Metal-to-Semiconductor Transition in Two-Dimensional Metal–Organic Frameworks: An Ab Initio Dynamics Perspective. *ACS Appl. Mater. Interfaces* **2021**, *13*, 25270–25279.
- (45) Momeni, M. R.; Zhang, Z.; Dell’Angelo, D.; Shakib, F. A. Gauging van der Waals interactions in aqueous solutions of 2D MOFs: when water likes organic linkers more than open-metal sites. *Phys. Chem. Chem. Phys.* **2021**, *23*, 3135–3143.
- (46) Momeni, M. R.; Zhang, Z.; Dell’Angelo, D.; Shakib, F. A. Tuning electronic properties of conductive 2D layered metal–organic frameworks via host–guest interactions: Dioxygen as an electroactive chemical stimuli. *APL Mater.* **2021**, *9*, 051109.

- (47) Feynman, R. P. Space-Time Approach to Non-Relativistic Quantum Mechanics. *Rev. Mod. Phys.* **1948**, *20*, 367–387.
- (48) Chau, P.-L.; Hardwick, A. J. A New Order Parameter for Tetrahedral Configurations. *Mol. Phys.* **1998**, *93*, 511–518.
- (49) Errington, J.; Debenedetti, P. Relationship Between Structural Order and the Anomalies of Liquid Water. *Nature* **2001**, *409*, 318–321.
- (50) Duboué-Dijon, E.; Laage, D. Characterization of the Local Structure in Liquid Water by Various Order Parameters. *J. Phys. Chem. B* **2015**, *119*, 8406–8418.
- (51) Winkler, K.; Lindner, J.; Bürsing, H.; Vöhringer, P. Ultrafast Raman-induced Kerr-effect of water: Single molecule versus collective motions. *J. Chem. Phys.* **2000**, *113*, 4674.
- (52) Lawrence, C. P.; Skinner, J. L. Vibrational spectroscopy of HOD in liquid D₂O. D₂O . III. Spectral diffusion, and hydrogen-bonding and rotational dynamics. *J. Chem. Phys.* **2003**, *118*, 264.
- (53) Rezus, Y. L. A.; Bakker, H. J. On the orientational relaxation of HDO in liquid water. *J. Chem. Phys.* **2005**, *123*, 114502.
- (54) Krynicki, K.; Green, C. D.; Sawyer, D. W. Pressure and temperature dependence of self-diffusion in water. *Faraday Discuss.* **1978**, *66*, 199–208.
- (55) Ghorbanfekr, H.; Behler, J.; Peeters, F. M. Insights into Water Permeation through hBN Nanocapillaries by Ab Initio Machine Learning Molecular Dynamics Simulations. *J. Phys. Chem. Lett.* **2020**, *11*, 7363–7370.
- (56) Lee, C.; McCammon, J. A.; Rossky, P. J. The structure of liquid water at an extended hydrophobic surface. *J. Chem. Phys.* **1984**, *80*, 4448–4455.

- (57) Jiang, J.; Gao, Y.; Zhu, W.; Liu, Y.; Zhu, C.; Francisco, J. S.; Zeng, X. C. First-Principles Molecular Dynamics Simulations of the Spontaneous Freezing Transition of 2D Water in a Nanoslit. *J. Am. Chem. Soc.* **2021**, *143*, 8177–8183.
- (58) Hamid, I.; Jalali, H.; Peeters, F. M.; Neek-Amal, M. Abnormal in-plane permittivity and ferroelectricity of confined water: From sub-nanometer channels to bulk. *J. Chem. Phys.* **2021**, *154*, 114503.
- (59) Chakraborty, S.; Kumar, H.; Dasgupta, C.; Maiti, P. K. Confined Water: Structure, Dynamics, and Thermodynamics. *Acc. Chem. Res.* **2017**, *50*, 2139–2146.
- (60) Cervený, S.; Mallamace, F.; Swenson, J.; Vogel, M.; Xu, L. Confined Water as Model of Supercooled Water. *Chem. Rev.* **2016**, *116*, 7608–7625.
- (61) Muñoz-Santiburcio, D.; Marx, D. Confinement-Controlled Aqueous Chemistry within Nanometric Slit Pores. *Chem. Rev.* **2021**, *121*, 6293–6320.
- (62) Ceriotti, M.; Fang, W.; Kusalik, P. G.; McKenzie, R. H.; Michaelides, A.; Morales, M. A.; Markland, T. E. Nuclear Quantum Effects in Water and Aqueous Systems: Experiment, Theory, and Current Challenges. *Chem. Rev.* **2016**, *116*, 7529–7550.
- (63) Mei, H. S.; Tuckerman, M. E.; Sagnella, D. E.; Klein, M. L. Quantum Nuclear ab Initio Molecular Dynamics Study of Water Wires. *J. Phys. Chem. B* **1998**, *102*, 10446–10458.
- (64) Cao, Z.; Peng, Y.; Yan, T.; Li, S.; Li, A.; Voth, G. A. Mechanism of Fast Proton Transport along One-Dimensional Water Chains Confined in Carbon Nanotubes. *J. Am. Chem. Soc.* **2010**, *132*, 11395–11397.
- (65) Cui, K.; Bhattacharyya, S.; Nair, S.; Schmidt, J. R. Origins of Acid-Gas Stability Behavior in Zeolitic Imidazolate Frameworks: The Unique High Stability of ZIF-71. *J. Am. Chem. Soc.* **2021**, *143*, 18061–18072.