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# Translational and Rotational Motion of C8 Aromatics Adsorbed in Isotropic Porous Media (MOF-5): NMR Studies and MD Simulations

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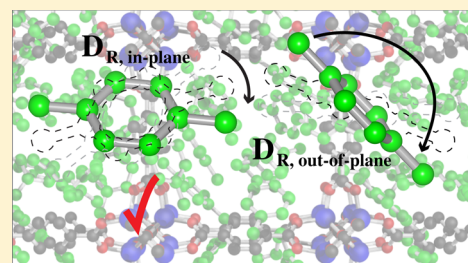
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## Supporting Information

**ABSTRACT:** We combined nuclear magnetic resonance (NMR) and molecular dynamics (MD) simulation to study xylene behavior in MOF-5, probing the effects of adsorbate geometry in a weakly interacting model isotropic metal organic framework (MOF) system. We employed NMR diffusometry and relaxometry techniques at low field (13 MHz) to quantify the self-diffusion coefficients ( $D_s$ ) and the longitudinal relaxation times ( $T_1$ ) of xylenes in MOF-5 as a function of temperature at the saturated loading for each xylene. These experiments reveal the translational motion activation energies to be 15.3, 19.7, and 21.2  $\text{kJ mol}^{-1}$  and the rotational activation energies to be 47.26, 12.88, and 11.55 for the (*p*-, *m*-, *o*-) xylene isomers, respectively. Paraxylene exhibits faster translational motion, yet shows four times the activation energy barrier for rotational motion vis-à-vis the other isomers. MD simulations performed on these model systems corroborate the findings for paraxylene and suggest that paraxylene has the lower free energy barrier for hopping away from its binding sites, yet has the slowest rotational motion in the plane of the xylene molecule.



## INTRODUCTION

MOFs are a type of porous media under investigation for applications that require molecular specificity.<sup>1</sup> Since the initial discovery of MOF-5 (also known as IRMOF-1),<sup>2</sup> this novel class of materials has been explored for potential use in gas separation and storage, selective catalysis, and numerous other industrial applications. Targeted design and synthesis<sup>3</sup> enable modularity in MOFs achieving highly desired adsorbent characteristics.<sup>4,5</sup> More recently, MOFs have been investigated for many liquid separation processes that require a distinctive difference in the transport behavior of small molecules.<sup>6</sup>

To determine the suitability of these adsorbents for particular applications, transport phenomena are commonly investigated by performing macroscopic measurements (e.g., breakthrough measurements) that characterize effective mass transport values containing contributions from both the intercrystalline and the intracrystalline regimes.<sup>7</sup> To gain insight into the mechanisms that determine these macroscopic measurements, molecular-scale interactions need to be measured. In particular, MOFs offer the nanoporous media community a unique opportunity to improve our understanding of how adsorbed molecules move in a confined spaces since both the topology and the chemical affinity are well-defined.<sup>8</sup> Although MD simulations have been instrumental in developing a physical description of adsorbate motion in porous media, there are very few

experimental studies on motional dynamics of the adsorbed molecules that can be used to validate these findings.

Many researchers employ NMR-based techniques to quantify the self-diffusion coefficients in an effort to understand translational motion. The NMR longitudinal relaxation times are analogous to the self-diffusion coefficients,<sup>9</sup> in quantifying rotational motion of adsorbates in MOF systems.<sup>10–13</sup> Most of these studies have focused on determining differences between strongly and weakly adsorbed molecules, where stark differences in the observed self-diffusion coefficient and longitudinal relaxation time are used to understand motion and selectivity.<sup>12,13</sup>

The separation of xylene isomers poses a lucrative scientific challenge, as a distillation of these isomers accounts for a significant amount of global energy consumption.<sup>14</sup> Composed of a conjugated ring perturbed by two methyl groups, xylene isomers have similar kinetic diameters (less than 1 Å difference) and similar chemical interaction energies which make the design of a selective adsorbent difficult. The selectivity of MOFs such as MIL-47<sup>15–17</sup> and MIL-53<sup>18–21</sup> for xylene isomers has been studied and attributed to framework

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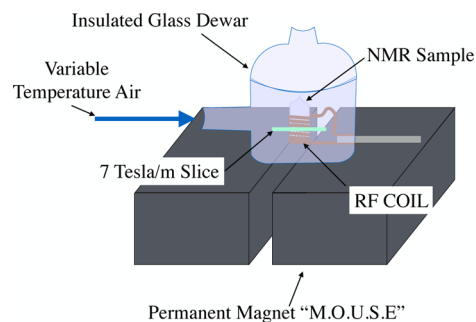
anisotropy that affects  $\pi$ - $\pi$  stacking, which was identified as the dominant type of host-guest interaction. Macroscopic breakthrough measurements at high temperature (553 K) and pressure (1.2 bar) were used to determine transport intracrystalline diffusivities of xylenes in MOF-5 and showed that the vapor phase paraxylene diffused two times more slowly than the other isomers.<sup>22</sup> Previous descriptions of how C8 aromatics diffuse in a porous environment postulate that entropy may play a greater role in determining the molecular mobility,<sup>23–26</sup> yet present very little systematic experimental evidence.

We have chosen to employ magnetic resonance methods to quantify  $D_s$  as a characterization of translational motion and NMR relaxometry to probe the local rotational motion of adsorbed xylene isomers in the MOF-5 framework. We explore how subtle geometric differences in the xylene isomers are manifested in translational and rotational motion. To further analyze the interplay between rotational and translational motion, we conduct MD simulations to calculate  $D_s$ , spatial probability distributions, rotational diffusion coefficients, and relative orientations of the xylene isomers in MOF-5.

## METHODS

**MOF-5 Synthesis and Characterization.** MOF-5 was synthesized by preparing a 3:1 mixture of zinc nitrate hexahydrate and 1,4-benzenedicarboxylic acid (Sigma-Aldrich chemicals, 99.95% purity) in 100 mL of diethylformamide (DEF) and heating for 72 h at 90 °C, resulting in a typical crystal size of 425  $\mu\text{m}$ . Solvent exchanges from DEF to dry dimethylformamide (DMF) were followed by solvent exchanges from DMF to dry dichloromethane (DCM) in preparation for activation. After solvent exchange, powder X-ray diffraction spectra were measured at room temperature using a D8 Discover GADDS Powder XRD (see Supporting Information) and nitrogen (Praxair, 99.999%) adsorption isotherms were collected using a Micromeritics TriStar 3000 BET instrument determined the BET surface area of the crystals to be 3565  $\text{m}^2 \text{g}^{-1}$ . A flow of argon gas at a temperature of 150 °C degassed the samples overnight. Afterward, a 425  $\mu\text{m}$  sieve separated approximately 100 mg of the larger crystals, which were activated overnight at 150 °C and 0.001 mbar of vacuum in a flame-dried 5 mm glass NMR tube.

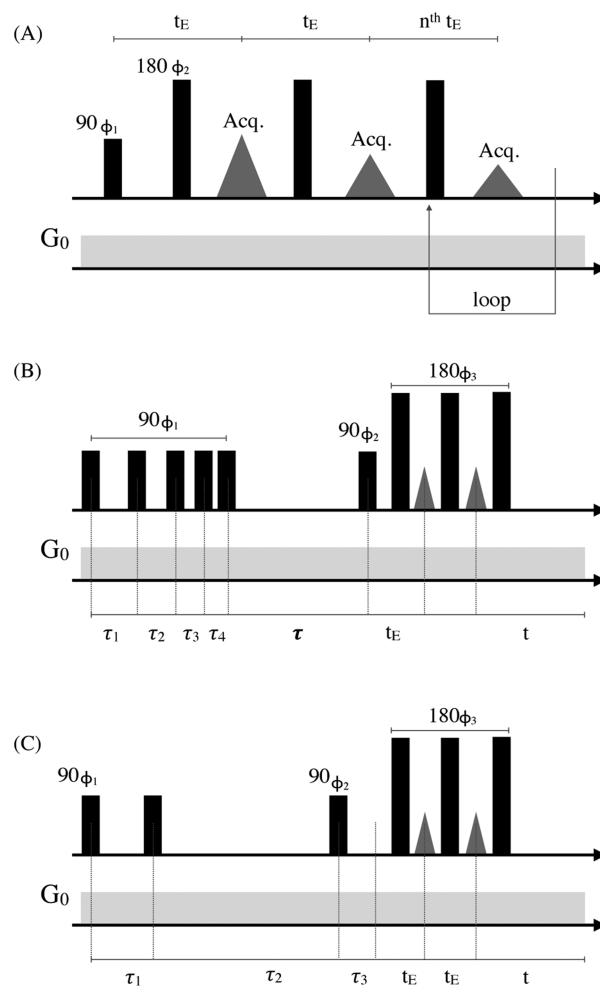
**Ex Situ NMR Preparation and Measurements.** After activation, the sample was dosed with a predetermined microliter amount of high purity degassed anhydrous xylenes purchased from Sigma-Aldrich. NMR spin counting methods (7.4 T magnet using a Tecmag Discovery Magnet with a 5 mm Solid State NMR MAS Doty probe), as well as gravimetric methods, yielded loadings of (49 to 56 molecules/unit cell) for each xylene isomer. These loadings ensure that all adsorbed xylene molecules were in the high-density liquid-like phase based on theoretically determined vapor-liquid phase diagrams provided previously.<sup>27</sup> The samples were flame-sealed using a cold bath and liquid nitrogen, giving a minimal headspace of approximately 0.018  $\text{cm}^3$ . The linear strayfield of a 0.3 T single sided magnet<sup>28</sup> equipped with a temperature controlling dewar was used for all NMR experiments (Figure 1). The magnetic field gradient strength was confirmed to be 7  $\text{T m}^{-1}$  through liquid diffusion calibrations. In order to increase sensitivity we constructed a home-built probe using a solenoid copper coil oriented perpendicular to the magnetic field direction, combined with a remote tuning box (Figure 1). A Magritek Kea II Spectrometer was used with Prospa operating software



**Figure 1.** Schematic representing the custom home-built probe and temperature control setup used to make measurements. A volumetric coil is centered in the 1 mm selective slice inherent to xylene. A glass dewar was placed on top of the permanent magnet and was used to insulate the sample and electronics from the environment.

for the data acquisition. Power modulation was used to control the pulsed angle during all experiments.

The CPMG sequence<sup>29</sup> was used to measure the transverse relaxation time ( $T_2$ ), as shown in Figure 2A. Further basic pulse sequences employed a CPMG acquisition train. The saturation



**Figure 2.** Standard NMR schematic for (A) the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence, (B) the saturation recovery pulse sequence with CPMG acquisition for inhomogeneous fields and (C) the stimulated echo sequences with CPMG acquisition for inhomogeneous fields.

recovery pulse sequence (Figure 2B) was used to measure the longitudinal relaxation time constant,  $T_1$ . A constant gradient stimulated echo (STE) pulse sequence with a CPMG acquisition and phase tables<sup>30</sup> (Figure 2C) were used to determine the apparent  $D_s$ . These were interpreted as the intracrystalline diffusivities due to the large crystal size (450  $\mu\text{m}$ ) and small diffusion time,  $\tau_2$ , (10 to 100 ms) chosen. This sequence has been shown to minimize decoherence of the signal due to transverse relaxation by storing the signal along the  $z$ -axis during the experimental diffusion time. During this storage interval, the signal experiences negligible longitudinal relaxation. The resulting signal was  $T_2$ -corrected during post-processing for the transverse relaxation experienced during the intervals of  $\tau_1$  and  $\tau_3$ . The signal intensity as a function of  $\tau_1$  was analyzed using numerical non-negative linear “inverse” Laplace transformation (NNL) with Tikhonov regularization to yield a spectrum of self-diffusion coefficients.<sup>30,31</sup> This algorithm was provided with the Prospa software from Magritek.

**Molecular Dynamics Simulation Details.** Molecular dynamics simulations were conducted with LAMMPS<sup>32</sup> in the NVT ensemble using a time step of 0.5 fs, the Nosé–Hoover chain thermostat,<sup>33,34</sup> and a rigid-body time integrator.<sup>35</sup> The Lennard-Jones potential, shifted and truncated at 12.0 Å, was used to describe dispersive interactions. Framework atoms were modeled with a previously published force field,<sup>36</sup> adsorbate molecules were modeled with the TraPPE force field,<sup>37</sup> and Lorentz–Berthelot mixing rules were used to calculate cross-interactions; this force field has been shown to provide good agreement with experimental diffusion coefficients of small aromatic molecules in MOF-5.<sup>36</sup> As the TraPPE models do not have partial charges, Coulombic interactions were not calculated. The framework was assumed to be rigid since it has been shown<sup>38</sup> that framework flexibility does not have an effect on adsorbate diffusion in MOF-5 and the experimental crystal structure<sup>39</sup> was used.

The frameworks were loaded with guest molecules at densities corresponding to the saturated liquid densities found by simulations in a previous study.<sup>27</sup> These densities are shown in Table 1, below. The periodic simulation box comprised 1 unit cell of MOF-5 (cubic with a 25.832 Å side length).

**Table 1. Loadings Used in the MD Simulations in Units of Molecules Per Unit Cell**

temperature (K)	<i>o</i> -xylene	<i>m</i> -xylene	<i>p</i> -xylene
270	54	53	53
280	53	53	53
290	53	51	51
300	52	50	50

All MD simulations were equilibrated for 5 ns, followed by a production period of at least 100 ns, which was found to be sufficiently long for the mean-squared displacement (MSD) to become a linear function of time, as verified by measuring the slope of the MSD plot on a log–log scale. Self-diffusion coefficients were obtained by fitting the Einstein relation,  $D_s = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle [r(t) - r(0)]^2 \rangle$ , to the linear portion of the MSD versus time plot, using the order- $n$  algorithm<sup>40,41</sup> to collect MSD data.

**Rotational Calculation of Spatial and Orientational Probability Distributions.** Spatial density distributions of

xylenes were generated from MD simulations (Figure 3), where the center-of-mass of each xylene molecule was recorded every 5 fs and binned into a  $100 \times 100 \times 100$  grid overlaid on the MOF-5 structure. As MOF-5 is cubic, the three-dimensional grid was reduced to a two-dimensional grid by averaging together all slices in one of the dimensions. In Figure 3 these data are presented in the form of a probability map. The angle between methyl groups on xylene molecules and the nearest neighboring carboxylate group was recorded every 0.5 ps. The methyl bond vector was defined as pointing from the aromatic carbon atom on the xylene to its bonded united atom methyl group. The carboxylate bond vector was defined as having either the carboxylate oxygen or carboxylate carbon as its vertex such that the vector always pointed in the positive  $x$ ,  $y$ , or  $z$  direction. These definitions yield symmetric distributions of the calculated angle. In Figure 4, these data are presented in the form of probability density functions.

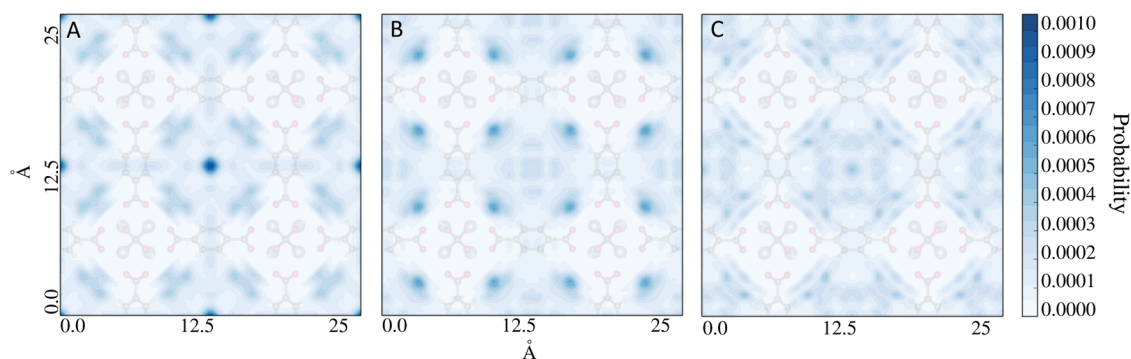
**Rotational Diffusion Coefficient Calculations.** We define rotational displacement as  $\hat{\psi}(t) = \int_0^t \Delta\hat{\psi}(t') dt'$  where both the magnitude and direction of vector  $\Delta\hat{\psi}(t')$  are given by the normalized vector of interest  $u(t)$  at times  $t = t'$ ,  $t' + dt'$ . The magnitude of  $\Delta\hat{\psi}(t')$  is given by  $|\Delta\hat{\psi}(t')| = \cos^{-1}(u(t' + dt') \cdot u(t'))$  and direction is given by  $u(t' + dt') \times u(t')$ .<sup>42</sup> In this work, the vector of interest  $u(t)$  is either the bond vector pointing from an aromatic xylene ring carbon to the its bonded methyl group (in-plane,  $\parallel$ ) or the vector normal to the aromatic xylene ring (out-of-plane,  $\perp$ ).

Analogously to translational motion, rotational self-diffusion coefficients were obtained by fitting the relation  $D_r = \frac{1}{4} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle [\hat{\psi}(t) - \hat{\psi}(0)]^2 \rangle$  to the linear portion of the rotational MSD versus time plot, defined as  $\langle \psi^2(\Delta t) \rangle = \langle [\hat{\psi}(t + \Delta t) - \hat{\psi}(t)]^2 \rangle$ .

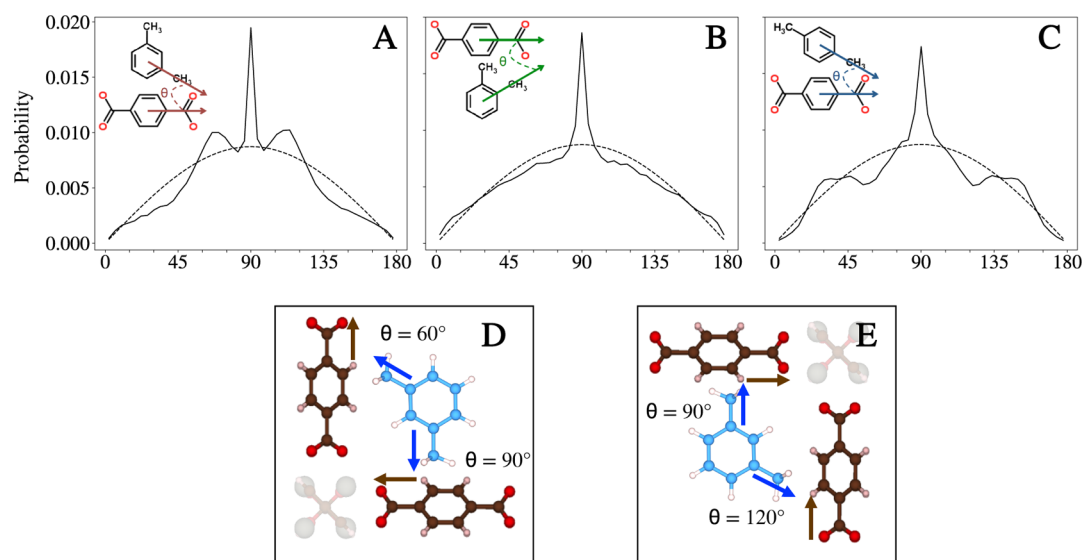
## RESULTS AND DISCUSSION

**Translational Motion.** The self-diffusion coefficients of (*p,m,o*)-xylene were measured as a function of diffusion time ( $\tau_2$ ) ranging from 10 to 100 ms, and temperatures ranging from 253 to 293 K. These diffusion times were chosen to ensure that the xylene molecules would spend most of their time sampling the intracrystalline environment belonging to MOF-5 and very little time experiencing the intercrystalline environment. The characteristic length ( $l_D$ ) traveled by the adsorbed molecule was estimated using  $l_D = \sqrt{D_{\text{app}}\tau_2}$ ; varying diffusion times from 10 to 0.001 ms yielded a range of characteristic lengths from 100 to 0.1  $\mu$ , much smaller than the MOF-5 crystal size. None of the self-diffusion coefficients of the xylene isomers demonstrated a strong dependence on the diffusion time,  $\tau_2$  (see Supporting Information). All self-diffusion coefficients of the xylene isomers were dependent on the temperature and were analyzed with an Arrhenius fit of the self-diffusion coefficients at the shortest  $\tau_2$  value (10 ms). In this way the values of translational activation energy ( $E_{a,\text{trans}}$ ) and the entropic pre-exponential coefficient ( $D_{a,\text{trans}}$ ) of the xylene isomers were determined (Figure 5 and Table 2).

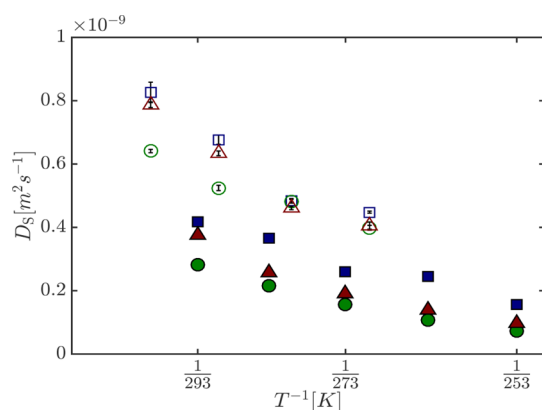
Paraxylene displays the fastest experimentally determined self-diffusion coefficients at all temperatures (Figure 5) and the lowest experimentally calculated activation energy for translational motion (Table 2). Paraxylene translational motion in MOF-5 deviates from bulk isomer behavioral trends<sup>43</sup> by exhibiting the smallest pre-exponential factor; this is surprising because when measured in bulk it has the largest.<sup>44</sup> The



**Figure 3.** Results of the MD simulations at 280 K and loadings as shown in Table 1 displaying the spatial probability distribution of liquid phase xylene molecules in the MOF-5 structure: (A) metaxylene, (B) orthoxylene, (C) paraxylene.



**Figure 4.** Probability density functions describing the likelihood of finding a methyl bond on a xylene molecule oriented at a range of angles relative to the nearest neighboring carboxylate group on a framework linker, demonstrated by (D) and (E), and the resulting distributions (A) metaxylene, (B) orthoxylene, and (C) paraxylene. In (A), (B), and (C), the dashed black lines reflect a random distribution of methyl orientations. In (D) and (E), oxygen atoms are red, hydrogen atoms are light pink, and carbon atoms on the xylene and linker are blue and brown, respectively.



**Figure 5.** Plot of the experimental inverse temperature dependence of the self-diffusion coefficient for each xylene (para ■, ortho ●, meta ▲) isomer at constant loading of 6 to 7 molecules/cage, and the simulated self-diffusion coefficients, (para □, ortho ○, meta △). All errors are calculated as the standard deviation of the measurement and are contained within the demarcation.

simulated  $D_s$  are in the same order of magnitude as the experiment and display the same ordering between isomers.

**Table 2.** Translational Activation Energy ( $E_{a,trans}$ ) Calculated from an Arrhenius fit to the Experimental Data and Simulated Data from Figure 5<sup>a</sup>

	<i>p</i> -xylene	<i>m</i> -xylene	<i>o</i> -xylene
Experimental			
$E_{a,trans}$ (kJ mol <sup>-1</sup> )	15.3	19.7	21.2
$D_{0,trans}$ (m <sup>2</sup> s <sup>-1</sup> )	$1.8 \times 10^{-7}$	$1.68 \times 10^{-6}$	$2.45 \times 10^{-6}$
Simulated			
$E_{a,trans}$ (kJ mol <sup>-1</sup> )	15.3	16.1	10.3
$D_{0,trans}$ (m <sup>2</sup> s <sup>-1</sup> )	$3.79 \times 10^{-7}$	$3.93 \times 10^{-8}$	$5.06 \times 10^{-7}$

<sup>a</sup>The actual  $D_{0,trans}$  were taken from the intercept of the linear fit with inverse temperature.

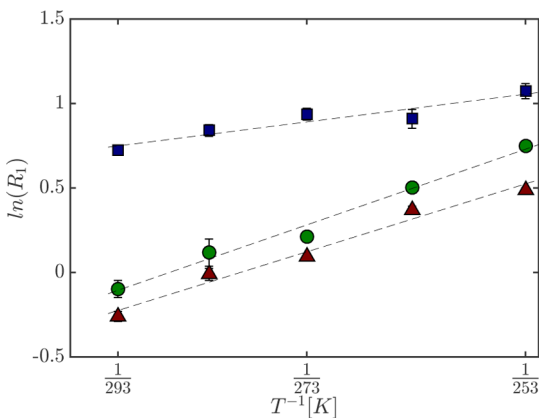
However, the temperature dependence of the simulated  $D_s$  do not compare well with experiment, which is likely due to the  $D_s$  being very sensitive to adsorbate loadings, the temperature dependence of which could only be estimated based on past simulation work (Table 1).

We further explored the guest molecule configurations by considering the spatial probability distributions from the MD simulations (Figure 3). These figures reveal the preferential adsorption sites of each xylene isomer. Metaxylene prefers to

adsorb in the center of the pore, while orthoxylene prefers adsorption closer to those metal clusters that are located at the corners of the pore (Figure 3A and B, darker shaded areas). Paraxylene, by contrast, shows a more uniform distribution (Figure 3C). The presence of multiple and proximal preferential adsorption sites for orthoxylene and metaxylene suggests that their translational diffusion mechanism involves the hopping of molecules between these sites and that these adsorbates must overcome a larger free energy barrier to translate compared to paraxylene. These observations are consistent with the trend in the experimentally determined translational activation energies.

**Rotational Motion.** The standard expression of the spin–lattice relaxation rate as a result of homonuclear dipolar coupling is  $R_1 \propto J(\omega) + 4J(2\omega)$ ,<sup>45,46</sup> where  $R_1$  is the inverse of  $T_1$ ,  $J$  is the spectral density function, and  $\omega$  is the Larmor frequency. We employ the simplified Lipari-Szabo model<sup>47,48</sup> as the descriptor for the spectral density function to separate the contributions of molecular rotational motion and internal methyl motions to  $R_1$ . In this model-free formalism the spectral density is related to the correlation times by the expression  $J(\omega) = \frac{2}{5} \frac{\tau_m S^2}{1 + \omega^2 \tau_m^2} + \frac{(1 - S^2)\tau}{1 + [\tau^2 \omega^2]}$ , where  $\tau_m$  is the isotropic rotational correlation time of the molecule  $\tau = \frac{\tau_m \tau_e}{\tau_m + \tau_e}$ , and  $\tau_e$  is an effective correlation time for internal motions (associated with methyl groups for xylene isomers);  $S^2$  is a generalized order parameter ranging from 0 to 1 representing the degree of spatial restriction of the molecule in a medium.<sup>46</sup>

Under the conditions in which the internal motion of methyl groups is extremely fast,<sup>49</sup>  $\tau_e \ll \tau_m$ , and the order parameter is large, the truncated form of the Lipari-Szabo spectral density function is suitable and internal motions (second additive terms) are neglected. The extreme motional narrowing regime applies, making it appropriate to associate  $R_1 \propto S^2 \tau_m$ , assume the correlation time is exponential, and then employ an Arrhenius analysis to determine the activation energies for restricted rotational motion of the xylenes adsorbed in MOF-5 (see Figure 6 and Table 3). Paraxylene is found to have almost four times the rotational activation energy of the other isomers and thus experiences some combination of increased spatial restriction (higher  $S^2$  value) and/or a longer isotropic rotational correlation time. This is different from bulk behavior where the



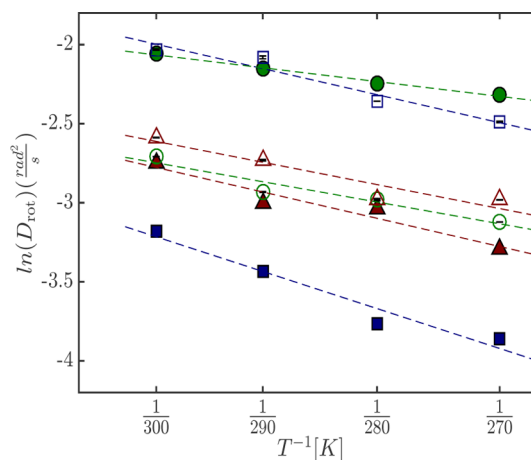
**Figure 6.** Plot of the experimental inverse temperature dependence of  $R_1$  for each xylene (para ■, ortho ●, meta ▲) isomer at constant loading of 6 to 7 molecules/cage.

**Table 3.** Experimental Rotational Activation Energy ( $E_{a,rot}$ ) of Xylene Molecules Calculated from Fitting the Experimental Longitudinal Relaxation Rate to an Arrhenius Relation Given in Figure 6

	<i>p</i> -xylene	<i>m</i> -xylene	<i>o</i> -xylene
$E_{a,rot}$ (kJ mol <sup>-1</sup> )	47.26	12.88	11.55

rotational activation energy ( $E_{a,rot}$ ) were all in the same order of magnitude.<sup>50</sup>

MD simulations were performed at the aforementioned loadings and affirm the notion of paraxylene restricted rotational motion. For all three xylenes, two types of rotational motion were distinguished and tracked during the course of MD simulations. In-plane xylene rotation was tracked with the methyl bond vectors as a reference, and out-of-plane xylene rotation was tracked with the vector normal to the aromatic ring as a reference. Paraxylene displays a large difference between the in-plane and out-of-plane diffusion coefficients, with the out-of-plane coefficients being a factor of 3 larger (Figure 7). The trend in the in-plane activation energies



**Figure 7.** Inverse temperature dependence of the simulated rotational self-diffusion coefficients for each xylene isomer at constant loading, where the filled symbols represent the in-plane rotation results (para ■, ortho ●, meta ▲) and the empty symbols represent the out-of-plane results (para □, ortho ○, meta △). The dashed lines represent the linear fit for an Arrhenius relationship.

derived from these simulations show that paraxylene's activation energy is greater than that of both metaxylene and orthoxylene (Table 4).

To further explore the effect of confinement on the orientations sampled during rotational motion, the angle between the methyl bond and the bond connecting the nearest-neighbor carboxylate group to the aromatic part of organic linker was tracked. The probability of finding a

**Table 4.** Simulated In-Plane and Out-of-Plane Rotational Activation Energies and the Pre-Exponential Factors Fitted from an Arrhenius Relation in Figure 7

	para	meta	ortho
$E_{a,rot,  }$ (kJ mol <sup>-1</sup> )	17.03	11.37	6.0
$D_{0,rot,  }$ (rad <sup>2</sup> ps <sup>-1</sup> )	37.83	5.95	1.4
$E_{a,rot,\perp}$ (kJ mol <sup>-1</sup> )	10.84	10.06	9.05
$D_{0,rot,\perp}$ (rad <sup>2</sup> ps <sup>-1</sup> )	10.43	4.2	2.44

molecule oriented at a particular angle was then calculated for each xylene and the results are displayed in Figure 4. The observed probability distributions shown in solid black lines can be compared to the dashed black lines, which shows a random distribution of methyl group orientations with the functional form  $P(\theta) = \frac{1}{2}\sin(\theta)$ . All xylenes display a dominating peak larger than that of the random distribution around  $90^\circ$ . This suggests the most favored orientation for a methyl group relative to the framework phenyl ring may be a *t*-configuration near the  $\pi$ -pocket of the ligand. This is not the case for orthoxylene, as Figure 3 shows that the molecular center-of-mass is predominantly found in the corners of the pore rather than the center.

Additional features in the metaxylene and paraxylene angle probability distributions can be intuited by considering the positions of the two methyl groups relative to each other. Figure 4D,E demonstrates the proposed metaxylene configurations. The peaks at  $60^\circ$  and  $120^\circ$  in the metaxylene plot are observed because when one methyl group is in the favored orientation (perpendicular to one set of linkers) and the aromatic xylene ring is parallel to the other set of organic linkers, the second methyl group forms a  $60^\circ$  or  $120^\circ$  angle with the nearest neighboring carboxylate group. The paraxylene distribution is unique because when the aromatic xylene ring is similarly aligned parallel to one set of organic linkers, both methyl groups would be perpendicular to the other set, and there would be only a single peak at  $90^\circ$ . The additional features at  $140^\circ$  and  $40^\circ$  indicate that paraxylene cannot fit into configurations where it is oriented exactly parallel to a set of organic linkers and must be tilted with respect to the pore. Paraxylene therefore samples a more restrictive environment due to its rigid rod-like shape.

## CONCLUSION

MOF-5, synthesized as a large crystal, was imbibed with saturated-liquid loadings of metaxylene, orthoxylene, and paraxylene. The effects of subtle geometric differences between the isomers were manifest in the guest molecule translational and rotational motions, as observed using NMR techniques. The quantification of the self-diffusion coefficient and the longitudinal relaxation time as functions of temperature at constant loading allowed for the quantification of the translational and rotational activation energies for each species. Paraxylene was experimentally observed to have the fastest self-diffusion coefficient at all temperatures ( $p > m > o$ ), the lowest activation energy for translational motion ( $p < m < o$ ), and the highest activation energy for rotational motion ( $p > m > o$ ). These results were compared with MD simulations and confirm the constriction of rotational freedom in an isotropically confined geometry and the faster translational motion of the most rod-like molecule, paraxylene. MD simulations indicate that neither metaxylene nor orthoxylene experienced comparable restrictions for in-plane rotations when adsorbed in MOF-5, supporting the experimental findings that paraxylene faces higher energy barriers for rotational motion.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b03181.

adsorption isotherms; self-diffusion coefficient; summary of experimental and simulated translational self-diffusion coefficients as a function of temperature (PDF)

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- Rowell, J. L.; Yaghi, O. M. Metal-organic frameworks: a new class of porous materials. *Microporous Mesoporous Mater.* **2004**, *73*, 3–14.
- Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. Design and synthesis of an exceptionally stable and highly porous metal-organic frameworks. *Nature* **1999**, *402*, 276–279.
- James, S. L. Metal-organic frameworks. *Chem. Soc. Rev.* **2003**, *32*, 276.
- Furukawa, H.; Müller, U.; Yaghi, O. M. Heterogeneity within order in metal-organic frameworks. *Angew. Chem., Int. Ed.* **2015**, *54*, 3417–30.
- Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. Selective gas adsorption and separation in metal-organic frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1477–1504.
- Li, J.-R.; Sculley, J.; Zhou, H.-C. *Chem. Rev.* **2012**, *112*, 869–932.
- Kärger, J.; Caro, J.; Cool, P.; Coppens, M.-O.; Jones, D.; Kapteijn, F.; Rodríguez-Reinoso, F.; Stöcker, M.; Theodorou, D.; Vansant, E. F.; et al. Benefit of Microscopic Diffusion Measurement for the Characterization of Nanoporous Materials. *Chem. Eng. Technol.* **2009**, *32*, 1494–1511.
- Davis, M. E. Ordered porous materials for emerging applications. *Nature* **2002**, *417*, 813–821.
- Stallmach, F.; Gröger, S.; Künzel, V.; Kärger, J.; Yaghi, O. M.; Hesse, M.; Müller, U. NMR studies on the diffusion of hydrocarbons on the metal-organic framework material MOF-5. *Angew. Chem., Int. Ed.* **2006**, *45*, 2123–6.
- Kolokolov, D. I.; Diestel, L.; Caro, J.; Freude, D.; Stepanov, A. G. Rotational and Translational Motion of Benzene in ZIF 8 Studied by  $^2\text{H}$  NMR: Estimation of Microscopic Self-Diffusivity and Its

Comparison with Macroscopic Measurements. *J. Phys. Chem. C* **2014**, *118*, 12873.

(11) Schlayer, S.; Pusch, A.-K.; Pielenz, F.; Beckert, S.; Peksa, M.; Horch, C.; Moschkowitz, L.; Einicke, W.-D.; Stallmach, F. X-Nuclei NMR Self-Diffusion Studies in Mesoporous Silica Foam and Microporous MOF CuBTC. *Materials* **2012**, *5*, 617–633.

(12) Pusch, A.-K.; Splith, T.; Moschkowitz, L.; Karmakar, S.; Biniwale, R.; Sant, M.; Suffritti, G. B.; Demontis, P.; Cravillon, J.; Pantosaki, E.; et al. NMR studies of carbon dioxide and methane self-diffusion in ZIF-8 at elevated gas pressures. *Adsorption* **2012**, *18*, 359–366.

(13) Chmelik, C.; Freude, D.; Bux, H.; Haase, J. Ethene/ethane mixture diffusion in the MOF sieve ZIF-8 studied by MAS PFG NMR diffusometry. *Microporous Mesoporous Mater.* **2012**, *147*, 135–141.

(14) Sholl, D. S.; Lively, R. P. Seven chemical separations to change the world. *Nature* **2016**, *532*, 435.

(15) Alaerts, L.; Maes, M.; Jacobs, P. A.; Denayer, F. M.; De Vos, D. E. Activation of the metal-organic framework MIL-47 for selective adsorption of xylenes and other difunctionalized aromatics. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2979–2985.

(16) Rives, S.; Jovic, H.; Kolokolov, D. I.; Gabrienko, A. A.; Stepanov, A. G.; Ke, Y.; Frick, B.; Devic, T.; Maurin, G. Diffusion of Xylene Isomers in the MIL-47(V) MOF Material: Synergic Combination of Computational and Experimental Tools. *J. Phys. Chem. C* **2013**, *117*, 6293–6302.

(17) Gabrienko, A.; Frick, B.; et al. Diffusion of Xylene Isomers in the MIL-47 (V) MOF Material: A Synergic Combination of Synergic Combination of Computational and Experimental Tools. *J. Phys. Chem. C* **2013**, *117*, 6293–6302.

(18) Moreira, M. A.; Santos, C.; Ferreira, A. F. P.; Loureiro, M. Influence of the Eluent in the MIL-53 (Al) Selectivity for Xylene Isomers Separation. *Ind. Eng. Chem. Res.* **2011**, *50*, 7688–7695.

(19) Duan, L.; Dong, X.; Wu, Y.; Li, H.; Wang, L.; Song, L. Adsorption and diffusion properties of xylene isomers and ethylbenzene in metal-organic framework MIL-53 (Al). *J. Porous Mater.* **2013**, *20*, 431–440.

(20) Alaerts, L.; Kirschhock, C. E. a.; Maes, M.; van der Veen, M. a.; Finsy, V.; Depla, A.; Martens, J. a.; Baron, G. V.; Jacobs, P. a.; Denayer, J. F. M.; et al. Selective adsorption and separation of xylene isomers and ethylbenzene with the microporous vanadium(IV) terephthalate MIL-47. *Angew. Chem., Int. Ed.* **2007**, *46*, 4293–7.

(21) Finsy, V.; Verelst, H.; Alaerts, L.; De Vos, D.; Jacobs, P. a.; Baron, G. V.; Denayer, J. F. M. Pore-filling-dependent selectivity effects in the vapor-phase separation of xylene isomers on the metal-organic framework MIL-47. *J. Am. Chem. Soc.* **2008**, *130*, 7110–8.

(22) Gu, Z.-y.; Jiang, D.-q.; Wang, H.-f.; Cui, X.-y.; Yan, X.-p. Adsorption and Separation of Xylene Isomers and Ethylbenzene on Two Zn-Terephthalate Metal-Organic Frameworks. *J. Phys. Chem. C* **2010**, *114*, 311–316.

(23) Gee, J. a.; Sholl, D. S. Effect of Framework Flexibility on C 8 Aromatic Adsorption at High Loadings in Metal-Organic Frameworks. *J. Phys. Chem. C* **2016**, *120*, 370–376.

(24) Germanus, a.; Kärger, J.; Pfeifer, H.; Samulevič, N.; Zdanov, S. Intracrystalline self-diffusion of benzene, toluene and xylene isomers in zeolites NaX. *Zeolites* **1985**, *5*, 91–95.

(25) Trems, P.; Belarbi, H.; Shepherd, C.; Gonzalez, P.; Ramsahye, N. A.; Lee, U. H.; Seo, Y. K.; Chang, J. S. Adsorption and separation of xylene isomers vapors onto the chromium terephthalate-based porous material MIL-101(Cr): An experimental and computational study. *Microporous Mesoporous Mater.* **2014**, *183*, 17–22.

(26) Moreira, M. A.; Santos, C.; Ferreira, A. F. P.; Loureiro, J. M.; Ragon, F.; Horcajada, P.; Shim, K.-e.; Hwang, Y.-k.; Lee, U.; Chang, J.-s.; et al. Reverse Shape Selectivity in the Liquid-Phase Adsorption of Xylene Isomers in Zirconium Terephthalate MOF UiO-66. *Langmuir* **2012**, *28*, 5715–5723.

(27) Braun, E.; Chen, J. J.; Schnell, S. K.; Lin, L.-C.; Reimer, J. a.; Smit, B. Nanoporous Materials Can Tune the Critical Point of a Pure Substance. *Angew. Chem., Int. Ed.* **2015**, *54*, 14349–52.

(28) Chen, J. J.; Kong, X.; Sumida, K.; Manupill, M. A.; Long, J. R.; Reimer, J. a. Ex Situ NMR Relaxometry of Metal-Organic Frameworks for Rapid Surface-Area Screening. *Angew. Chem., Int. Ed.* **2013**, *52*, 12043.

(29) Carr, H.; Purcell, E. Effects of Diffusion on Free Precession in Nuclear Magnetic Resonance Experiments\*. *Phys. Rev.* **1954**, *94*, 630–638.

(30) Casanova, F.; Perlo, J. In *Single-Sided NMR*, Casanova, F.; Perlo, J.; Blümich, B., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2011.

(31) Galvosas, P.; Callaghan, P. T. Multi-dimensional inverse Laplace spectroscopy in the NMR of porous media. *C. R. Phys.* **2010**, *11*, 172–180.

(32) Plimpton, S. Fast Parallel Algorithms for Short - Range Molecular Dynamics. *J. Comput. Phys.* **1995**, *117*, 1–42.

(33) Nosé, S. A molecular dynamics method for simulations in the canonical ensemble. *Mol. Phys.* **1984**, *52*, 255–268.

(34) Hoover, W. G. Canonical dynamics: Equilibrium phase-space distributions. *Phys. Rev. A: At., Mol., Opt. Phys.* **1985**, *31*, 1695–1697.

(35) Kamberaj, H.; Low, R. J.; Neal, M. P. Time reversible and symplectic integrators for molecular dynamics simulations of rigid molecules. *J. Chem. Phys.* **2005**, *122*, 224114.

(36) Dubbeldam, D.; Walton, K. S.; Ellis, D. E.; Snurr, R. Q. Exceptional Negative Thermal Expansion in Isorectical Metal-Organic Frameworks. *Angew. Chem., Int. Ed.* **2007**, *46*, 4496–4499.

(37) Wick, C. D.; Martin, M. G.; Siepmann, J. I. Transferable Potentials for Phase Equilibria. 4. United-Atom Description of Linear and Branched Alkenes and Alkylbenzenes. *J. Phys. Chem. B* **2000**, *104*, 8008–8016.

(38) Ford, D. C.; Dubbeldam, D.; Snurr, R. Q.; Snurr, R. Q. The Effect of Framework Flexibility on Diffusion of Small Molecules in the Metal-Organic Framework IRMOF-1. *The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application* **2009**, *11*, 1–8.

(39) Lemak, A. S.; Balabaev, N. K. On The Berendsen Thermostat. *Mol. Simul.* **1994**, *13*, 177–187.

(40) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*; Elsevier Science, 2002.

(41) Dubbeldam, D.; Ford, D.; Ellis, D.; Snurr, R. A New perspective on the Order-n Algorithm for Computing Correlation Functions. *Mol. Simul.* **2009**, *35*, 1084–1097.

(42) Mazza, M. G.; Giovambattista, N.; Stanley, H. E.; Starr, F. W. Connection of translational and rotational dynamical heterogeneities with the breakdown of the Stokes-Einstein and Stokes-Einstein-Debye relations in water. *Phys. Rev. E* **2007**, *76*, 031203.

(43) Rousseau, B.; Petracic, J. Transport coefficients of xylene isomers. *J. Phys. Chem. B* **2002**, *106*, 13010–13017.

(44) Kitchlew, A.; Rao, B. D. N. Temperature dependence diffusion in liquids. *Mol. Phys.* **1971**, *21*, 1145–1147.

(45) Sudmeier, J. L.; Anderson, S. E.; Frye, J. S. Calculation of Nuclear Spin Relaxation Times. *Concepts Magn. Reson.* **1990**, *2*, 197–212.

(46) Kowalewski, J.; Maler, L. *Nuclear Spin Relaxation in Liquids: Theory, Experiments, and Applications*; 2006.

(47) Szabo, A.; Lipari, G. Model-Free Approach to the Interpretation of Nuclear Magnetic Resonance Relaxation in Macromolecules. 1. Theory and Range of Validity. *J. Am. Chem. Soc.* **1982**, *104*, 4546–4559.

(48) Andrec, M.; Montelione, G. T.; Levy, R. M. Lipari - Szabo mapping: A graphical approach to Lipari - Szabo analysis of NMR relaxation data using reduced spectral density mapping. *J. Biomol. NMR* **2000**, *18*, 83–100.

(49) Kimmich, R. Strange kinetics, porous media, and NMR. *Chem. Phys.* **2002**, *284*, 253–285.

(50) Eades, R. G.; Jones, T.; Llewellyn, J. P.; Ahmed, A. M. I. N.M.R. Investigation of Molecular Motions in Solid Xylene. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1316–1322.



# Supporting information for: Translational and Rotational Motion of C8 Aromatics Adsorbed in Isotropic Porous Media (MOF-5): NMR Studies and MD Simulations

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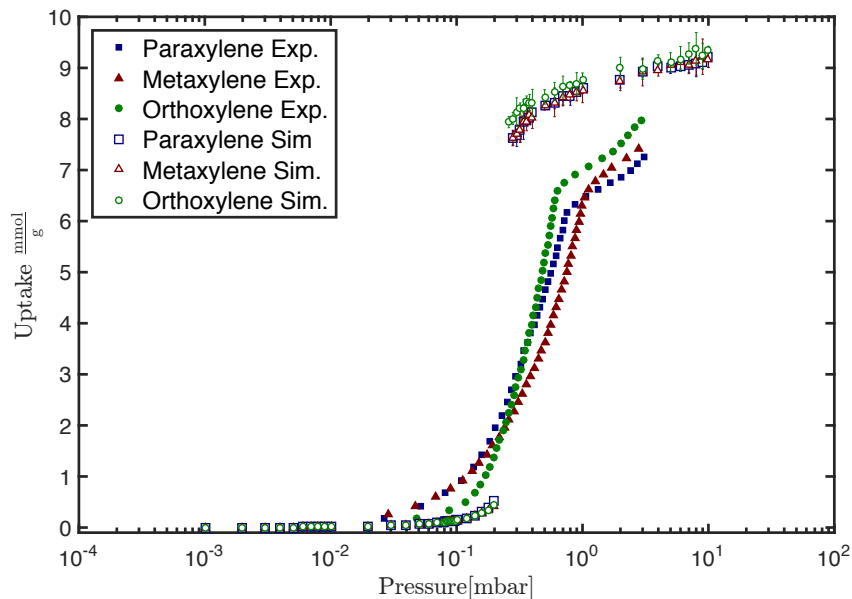


Figure S1: Experimental and simulated pure-component gas adsorption isotherms of the three xylene isomers in MOF-5, taken at 25 °C. Experimental gas phase adsorption isotherms were measured by a volumetric method using a Micromeritics 3Flex gas sorption analyzer. A typical sample of ca. 50 mg of metal-organic framework (MOF) was transferred in a nitrogen-filled glovebox to a pre-weighed analysis tube, which was capped with a Micromeritics TranSeal and evacuated by heating to 150 °C with a ramp rate of 1 °C min<sup>-1</sup> under dynamic vacuum until an outgas rate of less than 2 μbar min<sup>-1</sup> was achieved. The evacuated analysis tube containing the degassed sample was then transferred to an electronic balance and weighed again to determine the mass of sample. The tube was then transferred back to the analysis port of the gas adsorption instrument, where the outgas rate was confirmed to be less than 2 μbar min<sup>-1</sup>. For all isotherms, free space correction measurements were performed using ultrahigh purity (UHP, 99.999 %) helium gas. Pure component xylene vapor was prepared by thoroughly degassing liquid xylene by freezing the xylene, pumping on the headspace for 10 min, allowing the xylene to fully thaw, and repeating this freeze-pump-thaw cycle 3 more times. Isotherms collected were measured using an isothermal water bath. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements to prevent contamination of the. Simulated gas adsorption isotherms were obtained with grand canonical Monte Carlo simulations using the same force field as was used with the MD simulations. Data were collected over 1,000,000 cycles following 1,000,000 equilibration cycles. The simulation box consisted of 1 unit cell of MOF-5.

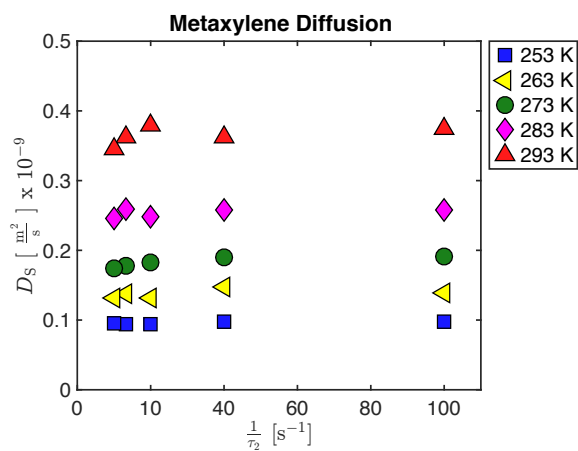


Figure S2: The self-diffusion coefficient of metaxylene versus diffusion time at various temperatures.

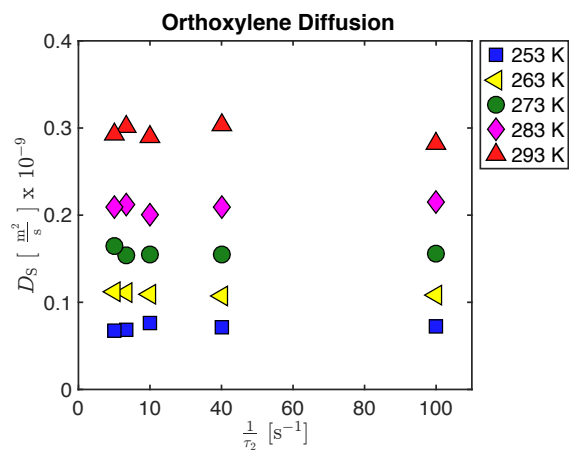


Figure S3: The self-diffusion coefficient of orthoxylene versus diffusion time at various temperatures.

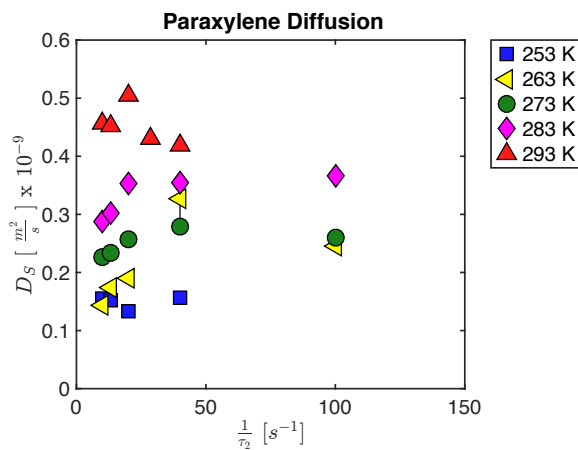


Figure S4: The self-diffusion coefficient of paraxylene versus diffusion time at various temperatures.

**Table S1: Summary of Experimental and Simulated Translational Self-Diffusion Coefficients as a function of temperature**

NMR Apparent Self-Diffusion Coefficients [ $m^2s^{-1}$ ]			
Temperature (K)	p-xylene	m-xylene	o-xylene
253	$1.558 \pm 0.0001 \times 10^{-10}$	$0.980 \pm 0.0001 \times 10^{-10}$	$0.722 \pm 0.009 \times 10^{-10}$
263	$2.457 \pm 0.061 \times 10^{-10}$	$1.390 \pm 0.018 \times 10^{-10}$	$1.079 \pm 0.005 \times 10^{-10}$
273	$2.593 \pm 0.002 \times 10^{-10}$	$1.907 \pm 0.004 \times 10^{-10}$	$1.559 \pm 0.011 \times 10^{-10}$
283	$3.657 \pm 0.005 \times 10^{-10}$	$2.579 \pm 0.018 \times 10^{-10}$	$2.152 \pm 0.022 \times 10^{-10}$
293	$4.18 \pm 0.01 \times 10^{-10}$	$3.747 \pm 0.026 \times 10^{-10}$	$2.823 \pm 0.098 \times 10^{-10}$