

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

Velencia J. Witherspoon,[†] Lucy M. Yu,[†] Sudi Jawahery,[†] Efrem Braun,[†] Sondre K. Schnell,^{†,‡} Mohamad Moosavi,[¶] Berend Smit,^{¶,†} and Jeffrey A. Reimer^{*,†,§}

[†]*Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, CA 94720, USA*

[‡]*Department of Chemistry, Norwegian University of Science and Technology, 7491, Trondheim, Norway*

[¶]*Institut des Sciences et Ingénierie Chimiques, Valais, École Polytechnique Fédérale de Lausanne (EPFL), Rue de l'Industrie 17, CH-1951 Sion, Switzerland*

[§]*Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, 94720, USA*

E-mail: reimer@berkeley.edu

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 saturated loading for each xylene. These experiments reveal the translational motion activation energies to be 15.3, 19.7, and 21.2 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 a lower free energy bar-

rier for hopping away from its binding sites. These simulations show that paraxylene has the slowest rotational motion in the plane of the xylene molecule while it actually has the fastest out-of-plane rotational motion.

Introduction

MOFs are a type of porous media under investigation for applications that require molecular specificity.¹ Since the initial discovery of MOF-5 (also known as IRMOF-1),² 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 synthesis³ enables modularity in MOFs achieving adsorbent characteristics.^{4,5} More recently, MOFs have been investigated for many liquid separation processes that requires a distinctive difference in the transport behavior of small molecules.⁶

To determine the suitability of these adsorbents for particular applications, transport phenomena are commonly investigated by performing macroscopic measurements (e.g. break-

through measurements) that characterize effective values containing contributions from both the intercrystalline and the intracrystalline regimes.⁷ 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 is well-defined.⁸ 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,⁹ in quantifying rotational motion of adsorbates in MOF systems.¹⁰⁻¹³ 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.^{12,13}

The separation of xylene isomers poses a lucrative scientific challenge, as distillation of these isomers accounts for a significant amount of global energy consumption.¹⁴ Composed of a conjugated ring perturbed by two methyl groups, xylene isomers have similar kinetic diameters (less than 1 Å differences) and similar chemical interaction energies which makes the design of a selective adsorbent difficult. The selectivity of MOFs such as MIL-47¹⁵⁻¹⁷ and MIL-53¹⁸⁻²¹ for xylene isomers has been studied and attributed to framework anisotropy that affects π - π 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 slower than the other isomers.²² Previous descriptions of how C8 aromatics diffuse in a porous environment postulate that entropy may play a greater role in determining the molecular mobility,²³⁻²⁶ yet present very little systematic experimental evidence.

We have chosen to employ magnetic resonance methods to quantify D_s to characterize 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 manifest 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 hours at 90 °C, resulting in an typical crystal size of 425 μ 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 3,565 m² g⁻¹. A flow of argon gas at a temperature of 150 °C degassed the samples overnight. Afterwards a 425 μ m sieve separated approximately 100 mg of the larger crystals, which were activated

overnight at 150 °C and 10 mtorr 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 on a separate high field (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 ensures that all adsorbed xylene molecules were in the high-density liquid-like phase based on theoretically-determined vapor-liquid phase diagrams provided previously.²⁷ The samples were flame sealed using a cold bath and liquid nitrogen, giving a minimal headspace of approximately 0.018 cm³. The linear stray-field of a 0.3 T single sided magnet²⁸ equipped with a temperature controlling dewar, was used for all NMR experiments (Fig. 1). The magnet field gradient strength was confirmed to be 7 T m⁻¹ through liquid diffusion calibrations. In order to increase sensitivity we constructed a home built probe using a solenoid copper coil oriented perpendicularly to the magnetic field direction, combined with a remote tuning box (Fig. 1). A Magritek Kea II Spectrometer was used with Prospa[®] operating software for the data acquisition. Power modulation was used to control the pulsed angle during all experiments.

The Carr-Purcell-Meiboom-Gill (CPMG) Sequence²⁹ was used to measure the transverse relaxation time (T_2), as shown in Fig. 2A. Further basic pulse sequences employed a CPMG acquisition train. The Saturation Recovery pulse sequence (Fig. 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 tables³⁰ (Fig. 2C) were used to determine the apparent D_s . These were interpreted as the intracrystalline diffusivities due to the large crystal size (450 μm) and small diffusion time, τ_2 ,

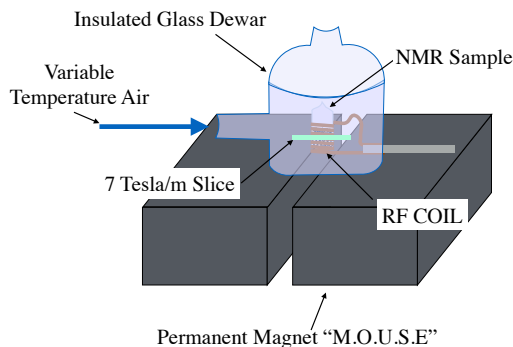


Figure 1: A schematic representing the custom homebuilt probe and temperature control setup used to make measurements. A volumetric coil is centered in the 1 mm selective slice inherent to xylene. A glass dewar was placed on top of the permanent magnet and was used to insulate the sample and electronics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

(10 to 100 ms). 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 relaxation due to longitudinal relaxation time constant. The resulting signal was T_2 -corrected during post-processing for the transverse relaxation experienced during the intervals of τ_1 and τ_3 . The signal intensity as a function of τ_1 was analyzed using Numerical Non-Negative Linear ‘Inverse’ Laplace Transformation (NNL) with Tikonov regularization to yield a spectrum of self-diffusion coefficients.^{30,31} This algorithm was provided with the Prospa[®] software from Magritek.

Molecular Dynamics Simulation Details

Molecular dynamics simulations were conducted with LAMMPS³² in the NVT ensemble using a timestep of 0.5 fs, the Nosé-Hoover chain thermostat^{33,34} and a rigid-body time integrator.³⁵ The Lennard-Jones potential, shifted and truncated at 12.0 Å, was used to describe dispersive interactions. Framework

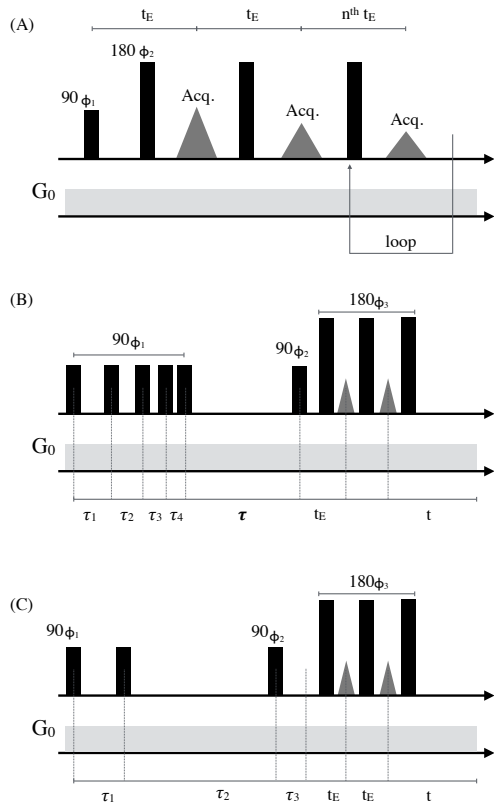


Figure 2: The standard NMR schematic for (A) the CPMG pulse sequence, (B) the Saturation Recovery pulse sequence with CPMG acquisition for inhomogeneous fields and (C) the Stimulated Echo sequences with CPMG acquisition for inhomogeneous fields.

atoms were modeled with a previously published force field,³⁶ adsorbate molecules were modeled with the TraPPE force field,³⁷ 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-5.³⁶ 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 shown³⁸ that framework flexibility does not have an effect on adsorbate diffusion in MOF-5. and the experimental crystal structure³⁹ was used.

The frameworks were loaded with guest molecules at densities corresponding to the saturated liquid densities found by simulations in a previous study.²⁷ 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)	o-xylene	m-xylene	p-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^{40,41} to collect MSD data.

Rotational Calculation of Spatial and Orientational Probability Distributions

Spatial density distributions of xylenes were generated from MD simulations Fig. 4, 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 Fig. 4, these data are presented in the form of a probability maps. 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 Fig. 7, 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 $u(t' + dt') \times u(t')$.⁴² 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, $D_r = \frac{1}{4} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\langle \left[\hat{\psi}(t) - \hat{\psi}(0) \right]^2 \right\rangle$ to the linear portion of the rotational MSD versus time plot, defined as $\langle \psi^2(\Delta t) \rangle = \left\langle \left[\hat{\psi}(t + \Delta t) - \hat{\psi}(t) \right]^2 \right\rangle$.

Results and discussion

Translational Motion

The self-diffusion coefficients of (p,m,o)-xylene were measured as a function of diffusion time (τ_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 of the inter-crystalline environment. The characteristic length (l_D) travelled by the adsorbed molecule was estimated using $l_D = \sqrt{D_{app}\tau_2}$; varying diffusion times from 10 to 100 ms yielded a range of characteristic lengths from 100 to 0.1 μm , 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, τ_2 (see Supporting Information). All the 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 τ_2 value (10 ms). In this way the values of translational activation energy ($E_{a,trans}$) and the entropic pre-exponential coefficient ($D_{0,trans}$) of the xylene isomers were determined (Fig 3 and Table 2).

For experimentally measured values, paraxylene displays the fastest self-diffusion coefficient at all temperatures (Fig. 3) and lowest experimental calculated activation energy for translational motion, as shown in Table 2. **The simulated D_s are on the same order of magnitude as the experiment and display an Arrhenius trend. The relative magnitudes of the simulated D_s are closer in magnitude than measured by NMR at higher temperatures.** Paraxylene deviates from bulk behavioral trends⁴³ by having the smallest pre-exponential factor; this is surprising because when measured in bulk it has the largest.⁴⁴

We further explored the guest molecule configurations by calculating the spatial probability distributions from the MD simulations. **These figures reveal the preferential adsorption sites of each xylene isomer. Metaxylene has a**

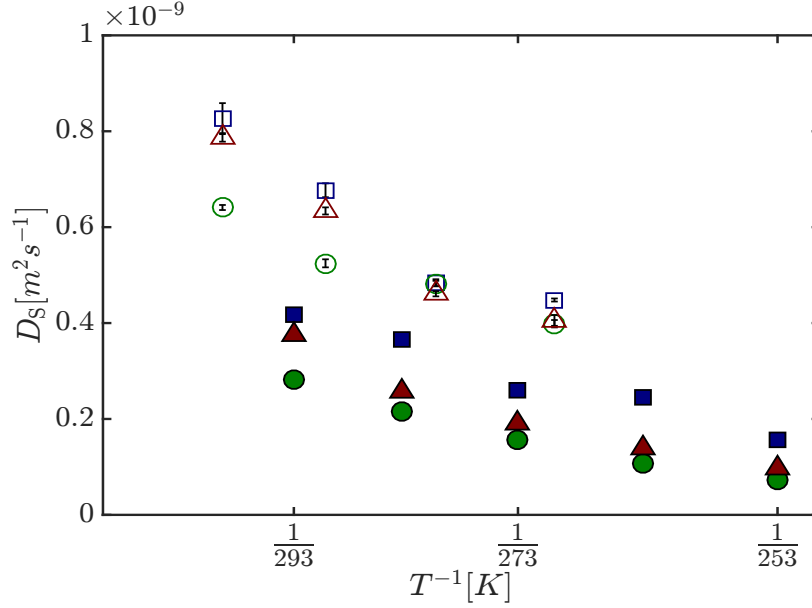


Figure 3: A plot of the experimental inverse temperature dependence of the self-diffusion coefficient for each xylene (para ■ , ortho ● , meta ▲) isomer at constant loading of 6 to 7 molecules/cage, and the simulated self-diffusion coefficients, (para □ , ortho ○ , meta △). All error is calculated as the standard deviation of the measurement and is contained within the demarcation.

Table 2: Translational activation energy ($E_{a,trans}$) calculated from an Arrhenius fit to the experimental data in Fig. 3. The actual $D_{0,trans}$ were taken from the intercept of the linear fit with inverse temperature.

	p-xylene	m-xylene	o-xylene
$E_{a,trans}$ (kJ mol ⁻¹)	15.3	19.7	21.2
$D_{0,trans}$ (m ² s ⁻¹)	1.8×10^{-7}	1.68×10^{-6}	2.45×10^{-6}
$E_{a,trans}$ (kJ mol ⁻¹)	15.3	16.1	10.3
$D_{0,trans}$ (m ² s ⁻¹)	3.79×10^{-7}	3.93×10^{-8}	5.06×10^{-7}

preference to adsorb in the center of the pore, while orthoxylene prefers to adsorb closer to the metal clusters located at the corners of the pore (Fig. 4 A and B shown by the darker shades areas). Paraxylene, by contrast, shows a more uniform distribution (Fig. 4 C). The presence of preferential adsorption sites of orthoxylene and metaxylene suggests that their translational diffusion mechanism involves the hopping of molecules between sites. These results demonstrate that orthoxylene and metaxylene must overcome a larger free energy barrier to move translationally compared to paraxylene, and 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 $R_1 \propto J(\omega) + 4J(2\omega)$,^{45,46} where R_1 is the inverse of T_1 , J is the spectral density function, and ω is the Larmor frequency. We employ the simplified Lipari-Szabo model^{47,48} as the descriptor for the spectral density function to separate the contributions of rotational molecular motion and the effective internal molecular 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 τ_m is the isotropic rotational correlation time of the molecule, $\tau = \frac{\tau_m \tau_e}{\tau_m + \tau_e}$, and τ_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.⁴⁶

Under the conditions in which the internal motion of methyl groups is extremely fast,⁴⁹ $\tau \ll \tau_m$, 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 $R_1 \propto \frac{1}{S^2 \tau_m}$ and to employ an Arrhenius analysis to

determine the activation energies for restricted rotational motion of the xylenes adsorbed in MOF-5 (see Figure 5 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 Rotational activation energy ($E_{a,rot}$) were all on the same order of magnitude.⁵⁰

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 Fig. 5.

	p-xylene	m-xylene	o-xylene
$E_{a,rot}$ (kJ mol ⁻¹)	47.26	12.88	11.55

MD simulations were performed at the aforementioned loadings and support of paraxylene’s restricted rotational motion comes from rotational self-diffusion coefficients. 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 the slowest in-plane rotation and the fastest out-of-plane rotation Fig. 6. The trend in the in-plane rotational activation energies show that paraxylene’s activation energy is greater than that of both metaxylene and orthoxylene (Table 4). It is possible that restricted in-plane rotation of paraxylene leads to the higher experimental rotational activation energy.

To further explore the effect of confinement on the orientation sampled during rotational motion, the angle between the methyl bond and the bond connecting the nearest neighboring carboxylate group to the aromatic part of organic linker was tracked. The probability of finding a molecule oriented at a particular angle was then calculated for each xylene and the results are displayed in Fig. 7. The observed probability distribution shown in solid

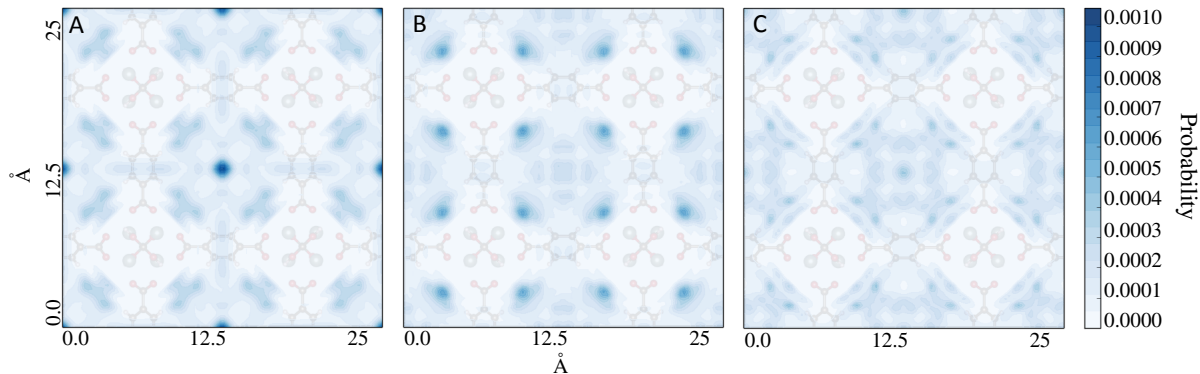


Figure 4: Results of the MD simulations at 280 K and loadings shown in Table 1 displaying the spatial probability distribution of liquid phase xylene molecules in the MOF-5 structure (A) metaxylene, (B) orthoxylene, (C) paraxylene.

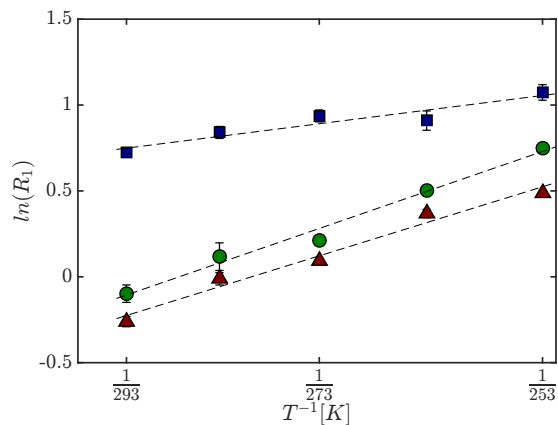


Figure 5: A plot of the experimental inverse temperature dependence of the T_1 for each xylene (para ■, ortho ●, meta ▲) isomer at constant loading of 6 to 7 molecules/cage.

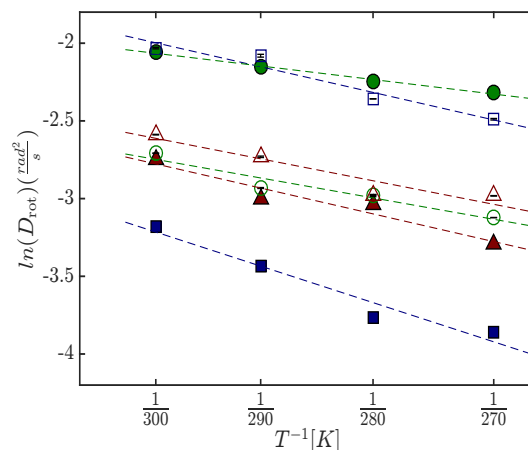


Figure 6: The inverse temperature dependence of the simulated rotational self diffusion coefficients for each xylene isomer at constant loading, where the filled symbols represent the in-plane rotation, (para ■, ortho ●, meta ▲), results and the empty symbols represent the out-of-plane results, (para □, ortho ○, meta △). The dashed lines represent the linear fit for an Arrhenius relationship.

Table 4: The simulated in-plane and out-of-plane rotational activation energies and the pre-exponential factors fitted from an Arrhenius relation in Fig. 6.

	p-xylene	m-xylene	o-xylene
$E_{a,rot,\parallel}$ (kJ mol ⁻¹)	17.03	11.37	6.0
$D_{0,rot,\parallel}$ (rad ² ps ⁻¹)	37.83	5.95	1.4
$E_{a,rot,\perp}$ (kJ mol ⁻¹)	10.84	10.06	9.05
$D_{0,rot,\perp}$ (rad ² ps ⁻¹)	10.43	4.2	2.44

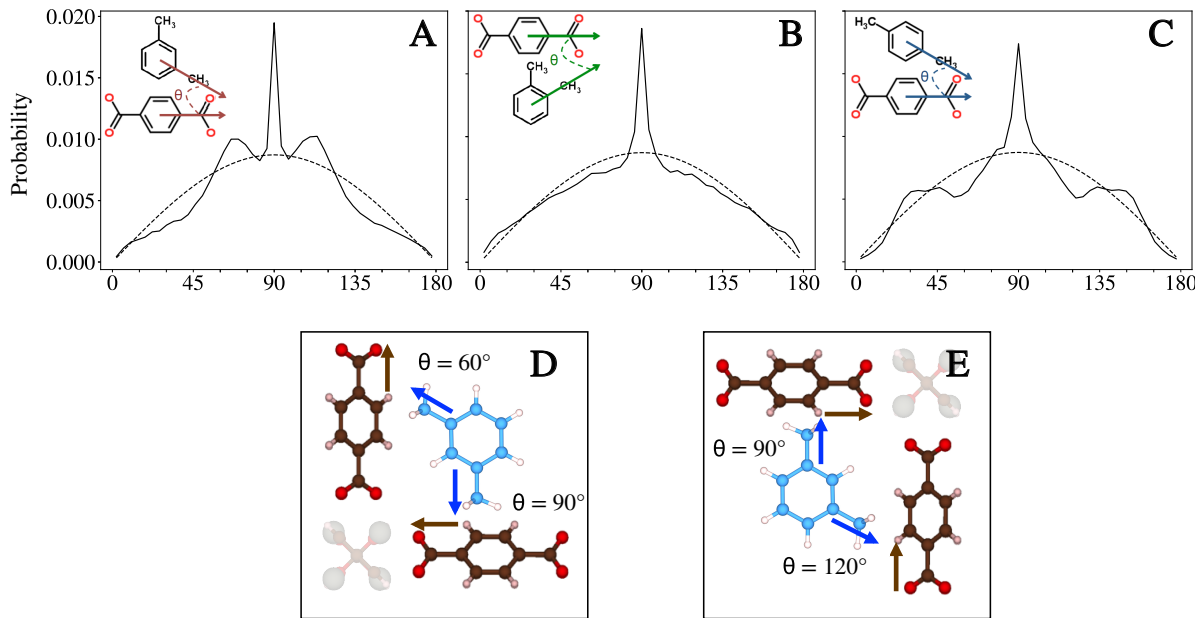


Figure 7: Probability density functions describing the likelihood of finding a methyl bond on a xylene molecule oriented at a range of angles relative to the nearest neighboring carboxylate group on a framework linker, demonstrated by (D) and (E), and the resulting distributions (A) metaxylene, (B) orthoxylene, (C) paraxylene. The dashed black lines reflect a random distribution of methyl orientations.

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° . This suggests the most favored orientation for a methyl group relative to the framework phenyl ring may be a *t*-configuration near π -pocket of the ligand. This is not the case for orthoxylene, as Fig. 4 shows that the molecules 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. Figures demonstrating the proposed metaxylene configurations are available in the Supporting Information. The peaks at 60° and 120° 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° or 120° angle with the nearest neighboring carboxylate group. The paraxylene distribution is unique because if 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° . The additional features at 140° and 40° 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 molecules translational and rotational motion, as observed using NMR techniques. The quantifi-

cation 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 that 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 indicated that neither metaxylene nor orthoxylene experienced comparable restrictions on in-plane rotations when adsorbed in MOF-5, supporting the experimental findings that paraxylene faces higher energy barriers for rotational motion

Acknowledgement This work was supported as part of the Center for Gas Separations Relevant to Clean Energy Technologies, as an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award DE-SC0001015 (Experimental and Characterization studies), by the National Science Foundation under Award DGE 1106400 (stipend VW, SJ), and this research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under the Contract No. DE-AC02-05CH11231.

Supporting Information Available

References

- (1) Rowsell, J. L.; Yaghi, O. M. Metal-organic frameworks: a new class of porous materials. *Microporous Mesoporous Mater.* **2004**, *73*, 3–14.
- (2) 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.
- (3) James, S. L. Metal-organic frameworks. *Chem. Soc. Rev.* **2003**, *32*, 276.
- (4) Furukawa, H.; Müller, U.; Yaghi, O. M. "Heterogeneity within order" in metal-organic frameworks. *Angew. Chem. Int. Ed. Engl.* **2015**, *54*, 3417–30.
- (5) 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.
- (6) Li, J.-r.; Sculley, J.; Zhou, H.-c. Metal-Organic Frameworks for Separations. **2012**, 869–932.
- (7) 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.
- (8) Davis, M. E. Ordered porous materials for emerging applications. *Nature* **2002**, *417*, 813–821.
- (9) 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. Engl.* **2006**, *45*, 2123–6.
- (10) Kolokolov, D. I.; Diestel, L.; Caro, J.; Freude, D.; Stepanov, A. G. Rotational and Translational Motion of Benzene in ZIF-8 Studied by ^2H NMR: Estimation of Microscopic Self-Diffusivity and Its Comparison with Macroscopic Measurements. **2014**, 4–10.

- (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 (Basel)*. **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.; Pantatosaki, 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.; Vos, D. E. D. 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.; Jobic, 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.* **2013**, *47*, 6293–6302.
- (17) Gabrienko, A.; Frick, B. 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**, *47*, 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**, *53*, 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. Engl.* **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) Trens, 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**, *21*, 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. Engl.* **2015**, *54*, 14349–52.
- (28) Chen, J. J.; Kong, X.; Sumida, K.; Manupil, M. A.; Long, J. R.; Reimer, J. a. Ex Situ NMR Relaxometry of Metal-Organic Frameworks for Rapid Surface-Area Screening. *Angew. Chemie Int. Ed.* **2013**, n/a–n/a.
- (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. *Comptes Rendus 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* **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 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 Isoreticular 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. *Open-Access J. Basic Princ. Diffus. Theory, Exp. Appl.* **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; 2002.
- (41) Dubbeldam, D.; Ford, D.; Ellis, D.; Snurr, R.; Dubbeldam, D.; Ford, D.; Ellis, D.; Snurr, R.; Perspective, A. N. 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. *Physical Review E* **2007**, *76*, 031203.

- (43) Rousseau, B.; Petracic, J. Transport coefficients of xylene isomers. *The Journal of Physical Chemistry B* **2002**, *106*, 13010–13017.
- (44) Kitchlew, A.; Rao, B. D. N. Temperature dependence diffusion in liquids. *Mol. Phys.* **1971**, *21*, 1145–1147.
- (45) L. Sudmeier, J.; E. Anderson, S.; S. Frye, J. 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. 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. *Chem. Phys.*; 2002; Vol. 284; pp 253–285.
- (50) Eades, R. G.; Jones, T.; Llewellyn, J. P. N.M.R. Investigation of Molecular Motions in Solid Xylene. *J. Chem. Soc. Faraday Trans. 2 Mol. Chem. Physics* **1972**, 1316–1322.