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Revisiting Anisotropic Diffusion of Carbon Dioxide in the Metal–Organic Framework $\text{Zn}_2(\text{dobpdc})$ Alexander C. Forse,^{†,‡,§,||} Stephen A. Altobelli,^{||} Stefan Benders,[⊥] Mark S. Conradi,^{||} and Jeffrey A. Reimer^{*,‡,§,||}[†]Department of Chemistry, [‡]Department of Chemical and Biomolecular Engineering, and [§]Berkeley Energy and Climate Institute, University of California, Berkeley, Berkeley, California 94720, United States^{||}ABQMR, Inc., 2301 Yale Blvd SE, Suite C2, Albuquerque, New Mexico 87106, United States[⊥]Institut für Technische und Makromolekulare Chemie (ITMC), RWTH Aachen University, Worringerweg 2, D-52074 Aachen, Germany[#]Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

S Supporting Information

ABSTRACT: The diffusion of gases confined in nanoporous materials underpins membrane and adsorption-based gas separations, yet relatively few measurements of diffusion coefficients in the promising class of materials, metal–organic frameworks (MOFs), have been reported to date. Recently we reported self-diffusion coefficients for $^{13}\text{CO}_2$ in the MOF $\text{Zn}_2(\text{dobpdc})$ ($\text{dobpdc}^{4-} = 4,4'$ -dioxidobiphenyl-3,3'-dicarboxylate) which has one-dimensional channels with a diameter of approximately 2 nm [Forse, A. C.; et al. *J. Am. Chem. Soc.* **2018**, *140*, 1663–1673]. By analyzing the evolution of the residual ^{13}C chemical shift anisotropy line shape at different gradient strengths, we obtained self-diffusion coefficients both along ($D_{\parallel}$) and between ($D_{\perp}$) the one-dimensional MOF channels. The observation of nonzero $D_{\perp}$ was unexpected based on the single crystal X-ray diffraction structure and flexible lattice molecular dynamics simulations, and we proposed that structural defects may be responsible for self-diffusion between the MOF channels. Here we revisit this analysis and show that homogeneous line broadening must be taken into account to obtain accurate values for $D_{\perp}$. In the presence of homogeneous line broadening, intensity at a particular NMR frequency represents signal from crystals with a range of orientations relative to the applied magnetic field and magnetic gradient field. To quantify these effects, we perform spectral simulations that take into account homogeneous broadening and allow improved $D_{\perp}$ values to be obtained. Our new analysis best supports nonzero $D_{\perp}$ at all studied dosing pressures and shows that our previous analysis overestimated $D_{\perp}$.

■ INTRODUCTION

Diffusion in nanoporous materials underpins their technological applications in adsorbents and membranes.¹ The wider deployment of these separation technologies alongside traditional distillation approaches could be facilitated by the development of new nanoporous materials. Metal–organic frameworks (MOFs) are one such class of materials that have shown promise for gas separations, as pore chemistries, shapes, and sizes can be designed for the separation of target gas mixtures.^{2–6} The incorporation of these materials in mixed-matrix membranes is also a promising route for energy-efficient gas separations that can alleviate the permeability–selectivity trade-off observed for traditional polymer materials.⁷ Relatively few studies have been carried out to date to characterize the diffusion of sorbate molecules in MOFs to date,^{8–16} despite its importance for their technological application. Numerous experimental and computational methods are available for the characterization of molecular diffusion in nanoporous materials.¹ Pulsed field gradient nuclear magnetic resonance

spectroscopy (PFG NMR) allows measurement of self-diffusion and has been applied in initial studies of sorbates in MOFs.^{17–25}

An attractive feature of PFG NMR is that diffusion anisotropy can be measured.^{26–28} This is possible since molecular displacements are monitored only in the direction of the magnetic gradient field. Four main situations for measuring anisotropic diffusion in materials may be considered. (i) If very large single crystals are available, one can directly measure anisotropic diffusion by performing experiments for different crystal orientations (relative to the gradient field), as has been performed for diffusion of lithium ions in the layered material Li_3N .^{29,30} (ii) Relatedly, one may align several single crystals using an alignment medium such as capillaries.³¹ (iii) More commonly experiments are performed

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on powder samples with a large number of crystallites. Here the molecular displacements in the gradient direction depend on the crystallite orientation, and the overall NMR signal decay as a function of the applied gradient field then represents a distribution of effective diffusion coefficients. Such composite data may be fitted to obtain anisotropic self-diffusion values with analytical solutions available for uniaxial self-diffusion tensors.^{26,32–34} However, it is not always straightforward to assign the different obtained self-diffusion values to the different crystallographic directions with this approach,¹⁸ and the approach relies on a powder average that can be invalid for samples with preferred crystal orientations. (iv) In systems where the nuclear spins have anisotropic NMR interactions such as chemical shift anisotropy or the quadrupole interaction, experiments performed on powder samples give rise to spectra where the chemical shifts are dependent on the crystallite orientation.^{18,22,35–37} In this scenario one can obtain the anisotropic diffusion coefficients by analyzing the decay of NMR signal at different NMR frequencies. However, this approach relies on the *homogeneous* line width of the spectral contributions from single crystals/crystallites being small compared to the overall *heterogeneous* line width.

We recently used this latter approach to study the anisotropic diffusion of CO₂ in the MOF Zn₂(dobpdc) (Figure 1) (dobpdc^{4−} = 4,4′-dioxidobiphenyl-3,3′-dicarboxylate),²² a

Figure 1. A portion of the crystal structure of Zn₂(dobpdc) at 298 K, as determined by single-crystal X-ray diffraction in our previous work.²² Light blue, red, gray, and white spheres represent Zn, O, C, and H atoms, respectively. Self-diffusion coefficients parallel ($D_{||}$) and perpendicular ($D_{\perp}$) to the one-dimensional channels are shown schematically.

material from a wider MOF family that has shown promise for CO₂ capture from power station flue gases.^{2,38–47} The residual chemical shift anisotropy for pore-confined CO₂ rendered the chemical shift dependent on crystal orientation,²² as in several other NMR studies of CO₂ in MOFs.^{18,48–56} By analyzing the line shape changes as a function of the applied pulsed field gradient, we obtained values for the self-diffusion parallel ($D_{||}$) and perpendicular ($D_{\perp}$) to the MOF channels.²² The obtained nonzero value of $D_{\perp}$ was unexpected given the one-dimensional channels in the crystal structure obtained by single-crystal X-ray diffraction, and we suggested that structural defects are responsible. In our previous work we noted, “The dominant source of error in our analysis is most likely systematic error arising from the finite peak line widths that

arise from homogeneous broadening, such that for a given δ , crystals at a range of θ values contribute to the signal,”²² where θ is the angle between the crystallographic c -axis and the applied magnetic field, B_0 . This point has also been made elsewhere.^{28,36} Here we assess this issue by performing spectral simulations that take into account homogeneous broadening, which, as mentioned above, cause the signal at a given NMR frequency to arise from crystals with a range of orientations. We show that it is crucial to account for homogeneous broadening when $D_{\perp} \ll D_{||}$ (or vice versa). Our new analysis of the PFG NMR data for CO₂ in Zn₂(dobpdc) provides more accurate $D_{\perp}$ values, which are smaller than those from our previous analysis, but still nonzero.

METHODS

Spectral simulations were performed following an approach very similar to that published previously¹⁸ in order to calculate ¹³C NMR spectra for simulated crystallites for pulsed field gradient NMR experiments. In our Matlab simulations, we consider 28 656 crystallites with different orientations (φ , θ), relative to B_0 , according to the Zaremba, Conroy, and Wolfsberg scheme for sampling the spherical coordinate space, as implemented in Simpson software.⁵⁷ θ is the polar angle between the crystallite and B_0 , and φ is the azimuthal angle. Note that with the gradient field applied parallel to B_0 (as was performed here) the angle φ does not impact the experiment and analysis, though for experiments with gradients along x or y this angle does matter.¹⁸ Simulations with different numbers of crystallites confirmed that 28 656 crystallites are sufficient for converged results for typical parameters considered in this work (see Supporting Information, Figure S1). To account for the preferred crystal orientations in our experiments and the resulting, nonideal powder line shapes, we weighted the crystal orientations, such that crystals close to $\theta = 0$ had greater intensities. For this a weighting function of the form θ^{-n} was used, where n may be adjusted from sample to sample to account for different amounts of preferred orientation. In the simulations, values are chosen for $D_{||}$, $D_{\perp}$, $\delta_{||}$, $\delta_{\perp}$, and the full width at half-maximum (FWHM) of the Gaussian functions used to represent the line shapes of the spectral contributions of individual crystals, and a weighting function must also be selected. Values for $\delta_{||}$, $\delta_{\perp}$, and the FWHM, and a choice of the weighting function, are obtained by comparison of the experimental and simulated spectrum at the lowest b value, while $D_{||}$ is set to the values obtained in our previous work,²² and different $D_{\perp}$ values are considered. We additionally considered Lorentzian homogeneous broadening in initial simulations (as opposed to Gaussian), though best fits between experimental and simulated line shapes were seen with Gaussians, which were then used for all simulations reported here. The b values for the simulations were chosen to match the experimental ones. In the PFG NMR simulations, the weights of the spectral contributions from crystallites with different orientations are adjusted according to eqs 2 and 3 (see above), as described elsewhere.¹⁸

To determine a best fit $D_{\perp}$ value, simulated and experimental integrated signal intensities are compared for data at large b values. The value that minimizes the root-mean-square deviation between the experimental and simulated integrated intensities is considered the best-fit value. We then performed a series of simulations with different subsets of the data in order to obtain a mean value and an error, which was

Figure 2. (a) Static ^{13}C PFG NMR (7.0 T, 25 $^{\circ}\text{C}$) for $\text{Zn}_2(\text{dobpdc})$ crystals dosed at 2026 mbar of $^{13}\text{CO}_2$. The experimental data are from our previous study,²² though are reprocessed here with exponential line broadening applied in the time domain for improved signal-to-noise ratio. PFG NMR parameters can be found in our previous work.²² (b, c) Normalized integrated intensities at $\delta_{\parallel}$ and $\delta_{\perp}$, respectively. Integration ranges were ~ 2 ppm. The blue line shows the simulated result from the global fits in our previous study.²² The agreement is reasonable at $\delta_{\parallel}$ but shows systematic deviations at $\delta_{\perp}$.

determined as twice the standard error in the mean of the results of the different simulations.

To determine the errors in experimental integrated signal intensities, the following method was employed. First, the noise was quantified by obtaining the root-mean-square deviation in the intensity in a region of the spectrum with no signal and only baseline noise. We then assumed that the positive and negative errors at a single point in the spectrum may be estimated as twice this root-mean-square deviation. Finally, we propagated this error over the integrated signal intensity region, taking into account the number of points used in the integration, which was performed as a running sum.

Experimental details regarding PFG NMR experiments (experimental parameters, gradient calibration, etc.) can be found in our previous work.²²

RESULTS AND DISCUSSION

Figure 2a shows static ^{13}C PFG NMR data for $\text{Zn}_2(\text{dobpdc})$ crystals dosed at 2026 mbar of $^{13}\text{CO}_2$ from our previously published work,²² with the pulsed gradient field applied in the same direction as the static magnetic field, B_0 . Under these conditions CO_2 molecules exchange rapidly between different adsorption sites within a given crystal; i.e., exchange in the intracrystalline space is in the fast limit.²² At the same time, CO_2 exchange between crystals with different orientations is in the slow exchange limit.²² Therefore, the NMR spectrum

represents a histogram of crystallite orientations. The position of the spectral contribution of a given crystal depends on its orientation, θ , between the crystal long axis (c -axis) and B_0 (note: the same angle, θ , describes the angle between the crystal and the gradient direction here). Intensity at the left-hand edge of the spectrum at a NMR frequency of $\delta_{\perp}$ arises from $^{13}\text{CO}_2$ in crystals oriented approximately perpendicular to the applied magnetic field, B_0 , while intensity at the right-hand edge at $\delta_{\parallel}$ arises from $^{13}\text{CO}_2$ in crystals oriented approximately parallel to the applied magnetic field. Additional intensity is observed at the right-hand side of the spectrum compared to that expected for an ideal powder with random crystallite orientations, which is due to the large size of the crystals here (up to ~ 750 μm in length)²² that results in preferred orientations. These preferred orientations do not impact the analysis of the effects of homogeneous broadening that follow in this study and rather only affect the absolute intensities observed in different regions of the NMR spectrum.

The faster decay at $\delta_{\parallel}$ as a function of the gradient strength (compared to $\delta_{\perp}$) arises from the faster self-diffusion along the one-dimensional channels of the MOF ($D_{\parallel}$), while the more gradual decay at $\delta_{\perp}$ indicates a slower diffusion between the one-dimensional channels of the MOF ($D_{\perp}$) (see Figure 1). The data in Figure 2a, with the gradient field applied in the same direction as B_0 , may be modeled using the following equations:

$$\delta = \delta_{\parallel} \cos^2 \theta + \delta_{\perp} \sin^2 \theta \quad (1)$$

$$D_{\text{eff}} = D_{\parallel} \cos^2 \theta + D_{\perp} \sin^2 \theta \quad (2)$$

$$I(b)/I(b_0) = \exp(-bD_{\text{eff}}) \quad (3)$$

where $I(b)$ is the signal intensity for a given b value and $I(b_0)$ is the signal intensity at the smallest studied b , where b is a parameter that depends on the square of the applied pulsed field gradient strength, g , the gyromagnetic ratio, and a number of pulse sequence parameters.^{22,58} In our previous work we performed a global fit of the PFG NMR data to eqs 1–3 to obtain the two free parameters, $D_{\parallel}$ and $D_{\perp}$, the determined values $D_{\parallel} = 6.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $D_{\perp} = 1.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 2026 mbar of $^{13}\text{CO}_2$.

Integrated signal intensities at approximately $\delta_{\parallel}$ are shown in Figure 2b and show reasonable agreement with the simulated curve based on the fitted $D_{\parallel}$ value (from the global fit in our previous work). In contrast, similar data at approximately $\delta_{\perp}$ (Figure 2c) show some systematic differences between the experimental and the fitted data, and it appears that a single exponentially decaying function is an inadequate model at $\delta_{\perp}$. For example, at high b values the model generally underestimates the experimental data, while at low b values the model generally overestimates the experimental data. Similar effects are observed at gas-dosing pressures of 1010 and 625 mbar (Supporting Information, Figures S2 and S3, respectively). This suggests that the analysis associated with the determination of $D_{\perp}$ in our previous work was incomplete.

The reason for deviation from monoexponential behavior at $\delta_{\perp}$ may be understood by inspecting the variation of D_{eff} with θ in eq 2 and by considering the effects of homogeneous line broadening. D_{eff} tends to plateau (on a logarithmic scale) as $\theta = 0^\circ$ is approached but shows significant variation close to $\theta = 90^\circ$ when $D_{\perp} \ll D_{\parallel}$ (Figure 3). If zero homogeneous line broadening were present (i.e., with Dirac delta function line shapes arising from the $^{13}\text{CO}_2$ signal from each crystal), then each NMR frequency would correspond to unique θ and D_{eff} values. However, in practice, this is *not* the case. Homogeneous line broadening is present (i.e., the spectral contribution from an individual crystal has a finite line width) which is evident

Figure 3. Plots of D_{eff} as a function of θ from eq 2 for $D_{\parallel} = 6.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Note only the range $\theta = 0$ to 90° is plotted, and the function is symmetric about $\theta = 90^\circ$.

from the limited sharpness of the spectral features. Each NMR frequency then represents signal intensity from $^{13}\text{CO}_2$ in crystals with a range of orientations, θ .

The relatively small slope of D_{eff} close to $\theta = 0^\circ$ means that a reasonable value for $D_{\parallel}$ can straightforwardly be determined (Figures 2b and 3), either by fitting the signal by integration at $\delta_{\parallel}$ or by using the global fitting method.²² In contrast, the marked variation of D_{eff} close to $\theta = 90^\circ$, coupled with homogeneous line broadening (full width at half-maximum intensity, FWHM, is approximately 1.7 ppm for the data in Figure 2a), makes the determination of $D_{\perp}$ more challenging, as signal intensity at $\delta_{\perp}$ represents crystals with a range of θ values and therefore a range of D_{eff} values. This accounts for the poor agreement between the experimental and fitted data in Figure 2c and the apparent stretched exponential form of the data decay. The physical reason for this behavior is that crystal orientations with angles, θ , slightly different from $\theta = 90^\circ$ can give rise to significant molecular displacements in the gradient direction when $D_{\parallel} \gg D_{\perp}$ due to the projection of the relatively fast motion along the one-dimensional channels (c -axis). The question that then arises is, how can $D_{\perp}$ be accurately determined in the presence of homogeneous broadening?

To address this problem, we performed spectral simulations following an approach published previously¹⁸ (see Methods for details). Starting with a theoretical powder of 28 656 crystallites (see Methods), the relative weights of the different crystallites are adjusted to account for the preferred crystal orientations of the tube-packed sample as discussed above. (Note: this does not impact the core of our analysis on the effects of homogeneous broadening that follow, and the analysis is generally applicable regardless of preferred crystal orientation effects.) We then simulate the attenuation of the NMR spectrum as a function of the pulsed magnetic field gradient using eqs 1–3 for various $D_{\perp}$ values and with the $D_{\parallel}$ value fixed to the previously determined value.²² Homogeneous broadening of the spectral contributions from individual crystals was accounted for by using Gaussian line shapes with a FWHM for the NMR signal from each crystal. These single crystal line shapes are then summed for the 28 656 different crystal orientations to yield the final spectrum, with the NMR center frequency of each contribution determined by eq 1.

The key features of the experimental data (Figure 4a) are well reproduced by the simulations (Figures 4b–d). In these simulations the value of $D_{\parallel}$ was fixed to our previously determined value of $6.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, while $D_{\perp}$ was varied in different simulations. The simulations clearly demonstrate that only the spectra for large b values are sensitive to variations of $D_{\perp}$. Notably, even for a $D_{\perp}$ of zero, a significant apparent decay can be observed at $\delta_{\perp}$ as a function of b (Figure 4c), which arises from the homogeneous broadening effects described above. It can clearly be seen that a value of $D_{\perp} = 4.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Figure 4d) gives poor agreement with the experimental data at large b ; $D_{\perp} = 4.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ is too large. However, it is not immediately obvious whether a value of $D_{\perp} = 4.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ or a value of zero gives a better agreement with the experiment (see also Figure S4 for plots with directly overlaid data from simulations and experiments). Similar data for gas dosing pressures of 1010 and 625 mbar are shown in Figures S5 and S6, respectively.

To obtain a more quantitative comparison between experiment and simulation, we compared *total* integrated spectral intensities as a function of b . For this, we focused our

Figure 4. Experimental (a) and simulated (b–d) PFG NMR (7.0 T, 25 °C) spectra for $\text{Zn}_2(\text{dobpdc})$ crystals dosed at 2026 mbar of $^{13}\text{CO}_2$. The data in (a) are reproduced from Figure 2a for convenience. In the simulations, the experimental b values were used. Simulation parameters: $D_{\parallel} = 6.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $\delta_{\perp} = 133.0 \text{ ppm}$, $\delta_{\parallel} = 114.5 \text{ ppm}$, Gaussian line shapes with a FWHM of 1.7 ppm. $D_{\perp}$ was varied in the three different simulations (b–d).

analysis on data with $b \geq 8.2 \times 10^8 \text{ s m}^{-2}$, as the data at large b are most sensitive to the choice of $D_{\perp}$ and are also relatively insensitive to the choice of weighting function used to account for the preferred crystal orientations (because only signals from $^{13}\text{CO}_2$ in crystals with θ close to 90° remain at large b). Experimental and simulated total integrated intensities are shown for a number of different simulations in Figure 5a. The curves on this semilogarithmic plot follow an apparent stretched exponential-like form, as anticipated. We note for the data shown in Figure 5a there is not one simulated line that fits all of the data points perfectly, though somewhat better agreement was observed for analysis at different gas dosing pressures (see Figure S7). It is also possible that there is some distribution of $D_{\perp}$ values for CO_2 in our samples which could arise from sample heterogeneity (e.g., a heterogeneous defect distribution) within individual $\text{Zn}_2(\text{dobpdc})$ crystals or between different crystals. To obtain a single best-fit value of $D_{\perp}$, we find the value that minimizes the root-mean-square deviation between the experimental and simulated integrated total intensities (Figure 5b). For example, for the data shown in Figure 5b, a best-fit value is given by $D_{\perp} = 5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. This value is smaller than our previously determined value²² of $D_{\perp} = 1.4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

To estimate the error in values determined in this way, a series of five fits were performed, in which the first data point (b value) was discarded in successive fits; i.e., an analysis of the form shown in Figure 5b was performed first for $b \geq 8.2 \times 10^8 \text{ s m}^{-2}$, then for $b \geq 1.12 \times 10^9 \text{ s m}^{-2}$, and so on until $b \geq 3.29 \times 10^9 \text{ s m}^{-2}$ (see Figure S8). We then report in Table 1 the mean values from the five fits and their errors, estimated as twice the standard error from the five values where the interval spanned by the upper and lower limiting values approximates a 95% confidence interval, accounting for random errors such as

noise in the NMR data. Note that the fits were insensitive to the choice of FWHM of the Gaussian peaks used in the simulation, as we only consider total integrated intensities. Fits of the data at large b values were also insensitive (within error) to small variations in the weighting function used in generating the nonideal powder pattern line shape and also to variations of 10% of the $D_{\parallel}$ value used.

As can be seen from Table 1, the obtained $D_{\perp}$ values have large uncertainties. However, the values are nonzero within error; i.e., this new analysis is consistent with nonzero diffusion in the ab plane at all studied $^{13}\text{CO}_2$ gas pressures (see Figures S5–S8 for analysis at other pressures). The new $D_{\perp}$ values may be compared to values from our previous analysis²² of 1.4×10^{-10} , 2.3×10^{-10} , and $1.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at pressures of 2026, 1010, and 625 mbar, respectively. The new analysis gives values that are 3–9 times smaller than the old analysis (depending on the pressure). The new $D_{\perp}$ values (Table 1) should be considered more accurate than those in our previous work. Our findings show the importance of accounting for homogeneous broadening when analyzing pulsed field gradient spectra of “powder pattern” line shapes. Finally, we note that the calculated root-mean-square displacements in the ab plane are of the order of a 2–4 μm using the $D_{\perp}$ values from Table 1, supporting the translation of CO_2 between thousands of different MOF channels during the probed diffusion time of 0.08 s.

Crystal defects²² remain the most likely explanation of this unexpected diffusion, with missing groups presumably creating additional porosity that enables perpendicular diffusion. As detailed in our previous study,²² single-crystal X-ray diffraction and inductively coupled plasma optical emission spectroscopy (ICP-OES) indicate a slight deficiency of zinc compared to the amount anticipated from the ideal molecular formula of

Figure 5. (a) Experimental (blue data points, with error bars, 2026 mbar of $^{13}\text{CO}_2$) and simulated (black lines) integrated (total) intensities for simulations with various $D_{\perp}$ values. For determination of error bars, see [Methods](#) section. In the analysis shown here only the data with $b \geq 8.2 \times 10^8\ s\ m^{-2}$ were considered, and integrals were separately normalized to the simulated and experimental integrated intensities for $b = 8.2 \times 10^8\ s\ m^{-2}$. (b) Root-mean-square deviation between simulated and experimental integrated intensities as a function of $D_{\perp}$. The best-fit value is that which minimizes the root-mean-square displacement.

Table 1. Self-Diffusion Coefficients for $^{13}\text{CO}_2$ in $\text{Zn}_2(\text{dobpdc})$ at Different Gas Pressures^a

pressure/mbar	$D_{\perp}/m^2\ s^{-1}$	$D_{\parallel}/m^2\ s^{-1}$ (ref 22)
2026	$3.9\ (3.3) \times 10^{-11}$	$6.5\ (0.2) \times 10^{-9}$
1010	$4.6\ (1.4) \times 10^{-11}$	$6.2\ (0.2) \times 10^{-9}$
625	$1.6\ (0.8) \times 10^{-11}$	$5.8\ (0.1) \times 10^{-9}$

^a $D_{\perp}$ values are from our new analysis, while $D_{\parallel}$ values are reproduced from our previous work.²² The values shown in parentheses should be added or removed from the preceding value to obtain 95% confidence limits that account for random errors such as noise in the NMR data.

$\text{Zn}_2(\text{dobpdc})$. Additionally, in the Supporting Information of that study,²² the nitrogen uptake of our $\text{Zn}_2(\text{dobpdc})$ crystals at saturation (adsorption isotherm at 77 K) was $\sim 90\%$ of that observed in previous work for $\text{Zn}_2(\text{dobpdc})$ powder samples. These findings are consistent with the presence of defects in our $\text{Zn}_2(\text{dobpdc})$ crystal samples, though the chemical nature of these defects is currently unclear. We note that our measured diffusion data showed little variation as a function of the diffusion time in the range of 20–160 ms²² and that signal

decays from fast diffusing CO_2 molecules are not observed. These observations indicate that exchange of CO_2 between the MOF pores and the free gas phase (e.g., via micro/meso scale cracks) is negligible and cannot account for the observed unexpected diffusion behavior.²² Moving forward, experimental and computational work should be carried out to understand the nature of defects in the MOF-74 family of materials as well as their effects on adsorbate diffusion.

CONCLUSION

In summary, we have performed a more detailed analysis of our previously published PFG NMR data for $^{13}\text{CO}_2$ adsorbed in the metal–organic framework $\text{Zn}_2(\text{dobpdc})$. When extracting the diffusion anisotropy from static “powder pattern” spectra in systems with large diffusion anisotropy, one must take into account homogeneous line broadening in the analysis. By carrying out spectral simulations, we have shown that a failure to account for homogeneous line broadening in our previous work led to an overestimation of the self-diffusion coefficient between the one-dimensional channels ($D_{\perp}$). Our simulations and new analysis are consistent with nonzero $D_{\perp}$, though the values are 3–9 times smaller than previously reported. The generality of these diffusion phenomena in various one-dimensional metal–organic frameworks remains an active area of investigation in our laboratories.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b02843.

PFG NMR analysis at different pressures; additional details of simulations and analysis (PDF)

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Notes

The authors declare no competing financial interest.

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