

Molecular-Level Understanding of Translational and Rotational Motions of C_2H_6 , C_3H_8 , and $n-C_4H_{10}$ and Their Binary Mixtures with CO_2 in ZIF-10

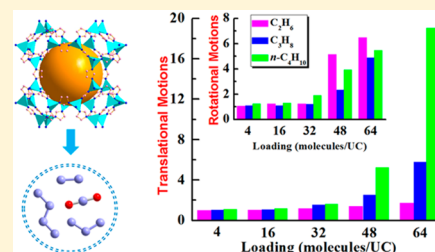
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Supporting Information

ABSTRACT: Molecular dynamics simulations have been employed to investigate the translational and rotational motions of C_2H_6 , C_3H_8 , and $n-C_4H_{10}$ and their binary mixtures with CO_2 in ZIF-10 at a molecular level. Our simulation results reveal that the translational motions of pure alkanes in ZIF-10 decrease monotonically with the increasing loading partly due to the competition between the enhanced alkane–alkane and the weakened alkane–ZIF interactions. Also, the increasing collision frequency with loading can hinder their translational motions considerably. However, their rotational motions are found to be initially accelerated and then decelerated gradually beyond a critical loading for all studied alkanes. The initial acceleration of their rotational motions is due to more alkane molecules not being adsorbed at the internal surfaces but into the free central regions of cages in ZIF-10 as the loading increases. Furthermore, a loading higher than the corresponding critical value can result in a considerable decrease in free spaces in whole ZIF-10 so that more restrictions hinder their rotational motions. On the other hand, the presence of CO_2 molecules promotes both the translational and rotational motions of alkanes in ZIF-10 for all studied alkane/ CO_2 mixtures, most significantly for $n-C_4H_{10}/CO_2$. Besides the small size of CO_2 molecules, the strong hydrogen bonds with the imidazolate rings can cause CO_2 molecules to preferentially occupy the adsorption sites of ZIF-10 compared to alkanes, leading to the weakened interactions between alkanes and ZIF-10. More importantly, such competitive adsorption with CO_2 in the mixture cases also results in a noticeable decrease in the collision frequency for alkanes in ZIF-10, which is in turn favorable to the enhanced translational and rotational motions of alkanes in ZIF-10. In addition, the confinement of ZIF-10 is also found to significantly promote the acceleration effect of CO_2 molecules on the translational and rotational motions of alkanes.



1. INTRODUCTION

Light alkanes are commonly regarded as the most important chemical raw materials for commodity production in the fuels and chemical industry.^{1–3} Actually, light alkanes often contain impurities in production processes, such as N_2 , CO_2 , H_2S , and H_2O .⁴ In particular, CO_2 is one of the most widespread impurities and can often be corrosive to gas pipelines.⁵ Meanwhile, C_2H_6 can form a maximum-pressure azeotrope with CO_2 , which will hinder CO_2 removal via distillation or other effective natural gas treatments.⁶ Therefore, efficiently removing CO_2 from light alkanes is still a great challenge in fully utilize light alkanes, such as natural gas purification,⁷ biogas and landfill gas upgrading,^{8,9} and enhanced oil recovery.¹⁰ In past decades, adsorption- and membrane-based separations by nanoporous materials have been widely accepted as promising cost-efficient techniques.^{11–19} The separation performance is mainly determined by the differences in both selective adsorption and diffusion properties between different components in nanoporous materials.^{19–25} Therefore, it is critical to gain a molecular-level understanding of the relevant adsorption

and diffusion mechanism of gas mixtures in nanoporous materials.

Until now, many experimental and simulation studies have focused on the adsorption and diffusion behavior of light alkanes and their mixtures with CO_2 in various porous materials.^{12,13,25–35} Experimentally, Patankar et al.³² investigated the properties of C_2H_6 and the C_2H_6/CO_2 mixture confined in mesoporous controlled pore glass (CPG) silica, showing that CO_2 has a stronger affinity for the CPG silica than for C_2H_6 , which should be responsible for the increasing mobility of C_2H_6 due to the displacement of C_2H_6 molecules from adsorption sites by CO_2 . On the contrary, Luo et al.³³ found that C_3H_8 molecules have an adsorption preference in small-pore zeolites (i.e., zeolite T, SSZ-13, and SAPO-34) compared to CO_2 , where C_3H_8 can displace some CO_2 from the adsorption site and hinder the permeation of CO_2 . On the

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other hand, Borah et al.³⁴ used molecular dynamics (MD) simulations to investigate the diffusion properties of pure CH₄, C₂H₆, C₃H₈, and C₄H₁₀ as well as their binary mixtures with CH₄ in six MOFs with different topologies and pore sizes. The diffusion coefficients of the alkanes follow the order CH₄ > C₂H₆ > C₃H₈ > C₄H₁₀ in the study of MOFs and decrease gradually with increasing chain length. Le and Striolo³⁵ employed MD simulations to investigate the relationship between the structure and dynamics of CO₂/C₄H₁₀ mixtures in fully protonated silica slit nanopores, where the presence of CO₂ molecules can enhance the self-diffusion motions of *n*-C₄H₁₀ because the preferential CO₂ adsorption to the pore walls can reduce the diffusion activation energy of *n*-C₄H₁₀.

Recently, zeolitic imidazolate frameworks (ZIFs), as a new subfamily of metal–organic frameworks (MOFs), have attracted considerable attention in practical gas storage and separation due to their exceptional chemical and thermal stabilities in both aqueous and organic media compared to other MOFs.^{36–45} For example, Gücüyener et al.⁴³ showed that ZIF-7 exhibits excellent selective adsorption of C₂H₆ over C₂H₄ in their mixture through the gate-opening effect. Keskin⁴⁴ employed grand canonical Monte Carlo (GCMC) and MD simulations to study the adsorption and diffusion properties of CH₄/H₂, CO₂/CH₄, and CO₂/H₂ mixtures in ZIF-3 and ZIF-10, respectively, showing that both ZIF-3 and ZIF-10 exhibit considerably higher adsorption selectivity compared to many common MOFs. Sholl and co-workers⁴⁵ have calculated the self- and transport diffusion coefficients of CH₄, C₂H₆, C₃H₈, *n*-C₄H₁₀, and other light hydrocarbons in fully flexible ZIF-8 by dynamically corrected transition-state theory. Most of their self-diffusion coefficients show an increase with loading, which is attributed to the larger decrease in the diffusion free energy barrier compared to the reduction of the transmission coefficient due to the increased number of gas–gas collisions.⁴⁵ Despite great effort, however, the diffusion mechanism of light alkanes and their mixtures with CO₂ in ZIFs is far from a complete understanding.

Besides the diffusion motions, which are essentially the translational motions, the rotational motions of light alkanes in ZIFs should also play an important role in the relevant separation processes as the chain length of alkanes increases, which is more unclear at present. Actually, the rotational motions of molecules confined in porous media have been confirmed to be closely related to their translational motions.^{46–48} For example, Reimer and co-workers⁴⁶ combined NMR and MD simulation to explore different xylene isomers in MOF-5. Paraxylene was experimentally observed to have the fastest translational motions at all temperatures but the slowest rotational motions. Their MD simulations confirmed that the construction of rotational freedom in an isotropically confined geometry leads to a faster translational motion of the most rodlike molecules (i.e., paraxylene). However, neither meta-xylene nor orthoxylene experienced comparable restrictions for in-plane rotations when adsorbed in MOF-5. Maurin and co-workers⁴⁷ explored the loading-dependent diffusion mechanism for light alkanes including C₂H₆, C₃H₈, and *n*-C₄H₁₀ in the flexible MOF MIL-53(Cr) by combining quasi-elastic neutron scattering measurements (QENS) and MD simulations. According to their results, the diffusion rates of C₂H₆ and C₃H₈ molecules decrease monotonically with the increasing loading, while that of *n*-C₄H₁₀ follows an unusual increase at a higher concentration due to the reopening of a flexible MOF. Moreover, they also found that the global translational

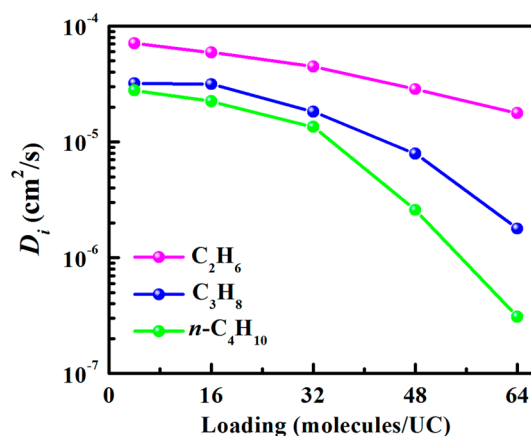


Figure 1. Variation of the self-diffusion coefficients D_i with loading for pure alkanes of C₂H₆, C₃H₈, and *n*-C₄H₁₀ molecules in ZIF-10. The relevant values and standard deviations are listed in Table S4 of the Supporting Information.

motion is associated with rotational dynamics, where *n*-C₄H₁₀ follows uniaxial rotational motions within the pore while C₂H₆ displays random rotational reorientation. Kolokolov et al.⁴⁸ employed experimental (QENS and NMR) and computational (MD) tools to investigate the diffusion behavior of benzene in MIL-53(Cr). They found that benzene uses a 1D-jump translational diffusion mechanism, which is combined with a fast uniaxial rotational motion around the C₆ axis. In this way, benzene can be thought of as a rotating disc that diffuses rapidly through the central part of the MIL-53 channel by short jumps between neighboring low-energy basins.

To this end, a series of MD simulations have been carried out to systematically investigate at a molecular level the translational and rotational motions of light alkanes (including C₂H₆, C₃H₈, and *n*-C₄H₁₀) and their equimolar mixtures with CO₂ in ZIF-10. Herein, we mainly focus on the loading-dependent translational and rotational motions of light alkanes confined in ZIF-10 and how the presence of CO₂ molecules affects these dynamic properties. This article is organized as follows. In section 2, we present the details of MD simulations. Then, the simulation results for the pure and binary mixture components will be discussed and analyzed in section 3. Finally, we offer a few general conclusions and remarks in section 4.

2. SIMULATION DETAILS

In this work, the crystal structure of ZIF-10 for MD simulations was constructed from the experimental X-ray diffraction data of the Cambridge Structural Database (CSD).⁴⁹ In the framework of ZIF-10, each Zn atom is tetrahedrally bridged by four imidazolate linkers, resulting in a merlinoite (MER) zeolite-type cage of ~12.1 Å in diameter connected by large windows of 8.2 Å in diameter, and there are two MER cages in each unit cell (UC). The recent force field proposed by Zheng et al.⁵⁰ was employed for ZIF-10. Although the flexible force fields are more reasonable than the rigid ones in general, it should be noted that the ZIF-10 structure was rigid during the following MD simulations as a result of the limitations of the available force field.^{51,52} Actually, when the window sizes of nanoporous materials are comparable to the kinetic diameter of gas molecules, the free-energy barrier from the windows will dominate the diffusion of gas molecules, and the corresponding diffusion coefficients often increase with loading.^{20,45} In this

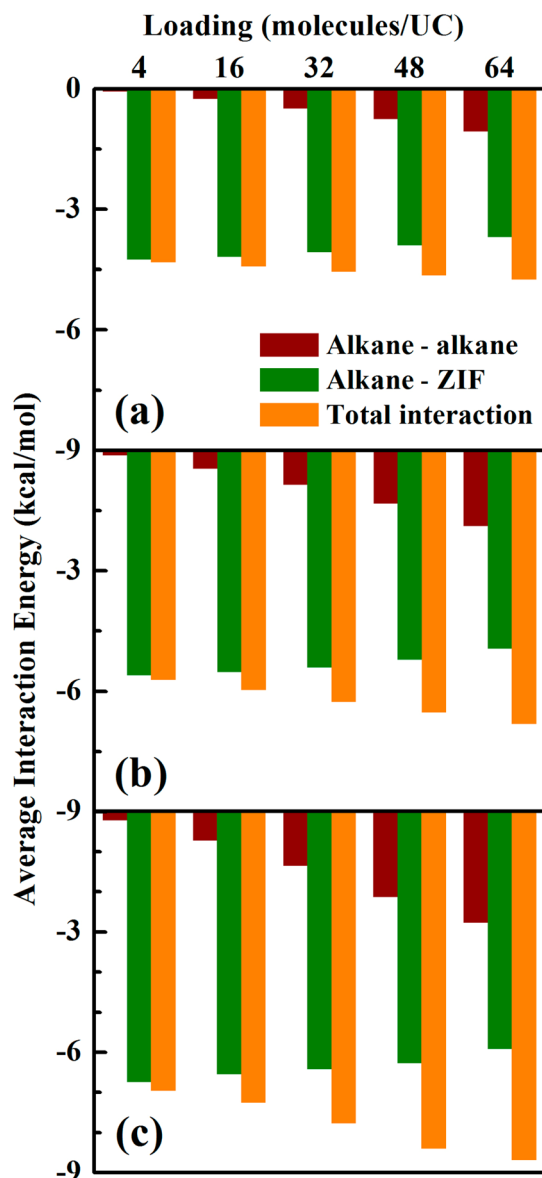


Figure 2. Average interaction energies of alkane–alkane, alkane–ZIF, and the total interaction energy for pure (a) C_2H_6 , (b) C_3H_8 , and (c) $n\text{-C}_4\text{H}_{10}$ molecules in ZIF-10 at different loadings. All standard deviations here are less than ± 0.02 kcal/mol. The error bars are smaller than the symbol size, so they are not shown.

case, the flexible force fields used for ZIFs are necessary, but when the window sizes are larger than the kinetic diameter of a gas molecule, the diffusion of the gas molecule is determined by the steric hindrance between diffusing molecules and the corresponding diffusion coefficients decrease with loading.^{21,22,34,53} In this work, the window openings of ZIF-10 (8.2 Å) are much larger than the kinetic diameters of CO_2 (3.3 Å),³⁹ C_2H_6 (4.0 Å),⁴¹ C_3H_8 (4.3 Å),⁵⁴ and $n\text{-C}_4\text{H}_{10}$ (4.3 Å).⁵⁴ In the following section, the diffusion coefficients are found to decrease with loading, suggesting that the flexibility of ZIF-10 may have a negligible influence on the confined properties of the studied gas molecules. Meanwhile, the TraPPE united atom model was used for the C_2H_6 , C_3H_8 , and $n\text{-C}_4\text{H}_{10}$ molecules,⁵⁵ while a three-site model was used for CO_2 and partial point charges are centered at each site to present the quadrupole moment.⁵⁶ Herein, the nonbonded interactions were described by the combination of electrostatic

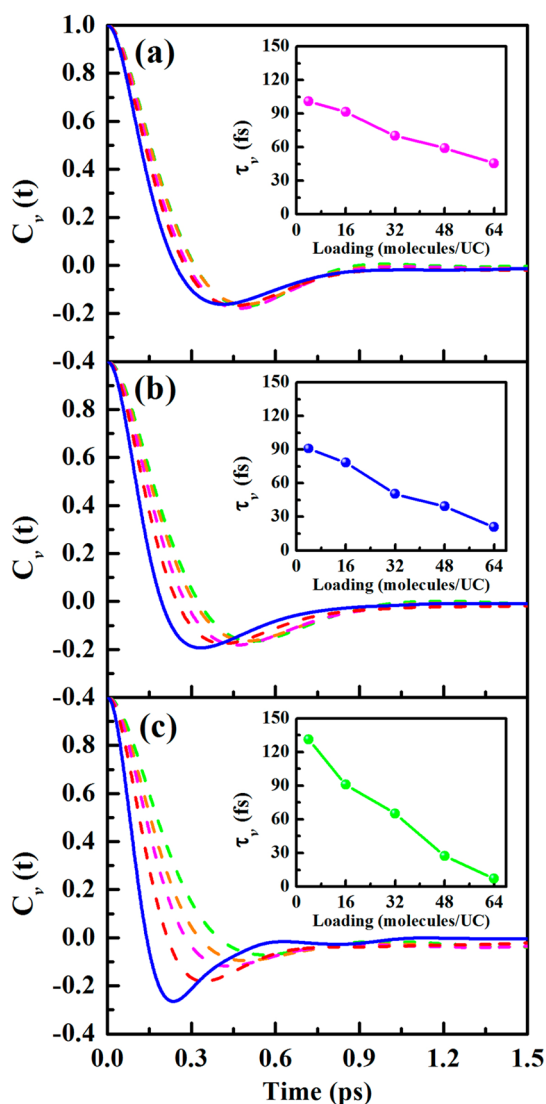


Figure 3. VACF curves for light alkanes (a) C_2H_6 , (b) C_3H_8 , and (c) $n\text{-C}_4\text{H}_{10}$ molecules in ZIF-10 at different loadings. Lines colored green, orange, magenta, red, and blue correspond to loadings from 4 to 64 molecules/UC in turn. The inset shows the corresponding relaxation times. All standard deviations here are less than ± 1.5 fs. The error bars are smaller than the symbol size, so they are not shown.

and Lennard-Jones (L-J) interactions. All L-J parameters and partial atomic charges used in this work were summarized and listed in Tables S1 and S2 in the Supporting Information. Then, the Lorentz-Berthelot mixing rules were employed to calculate the crossing L-J interaction parameters.

A series of NVT MD simulations were conducted to explore the diffusion behavior for the pure components of C_2H_6 , C_3H_8 , $n\text{-C}_4\text{H}_{10}$, and their equimolar mixtures with CO_2 in ZIF-10 with a variety of loadings (i.e., 4, 16, 32, 48, and 64 gas molecules were initially arranged into a single UC by using the configuration-biased insertion technique⁵⁷). Then, each initial configuration was obtained by making a supercell from the corresponding unit cell (ZIF-10 with gas molecules) in three directions. The compositions of alkane/ CO_2 mixtures in bulk phases corresponding to the counterparts confined in ZIF-10 were calculated via grand canonical Monte Carlo (GCMC) calculations and have been summarized in Table S3 in the Supporting Information. It is worth noting that our simulation setup is to have a predefined loading in ZIF-10 and that the

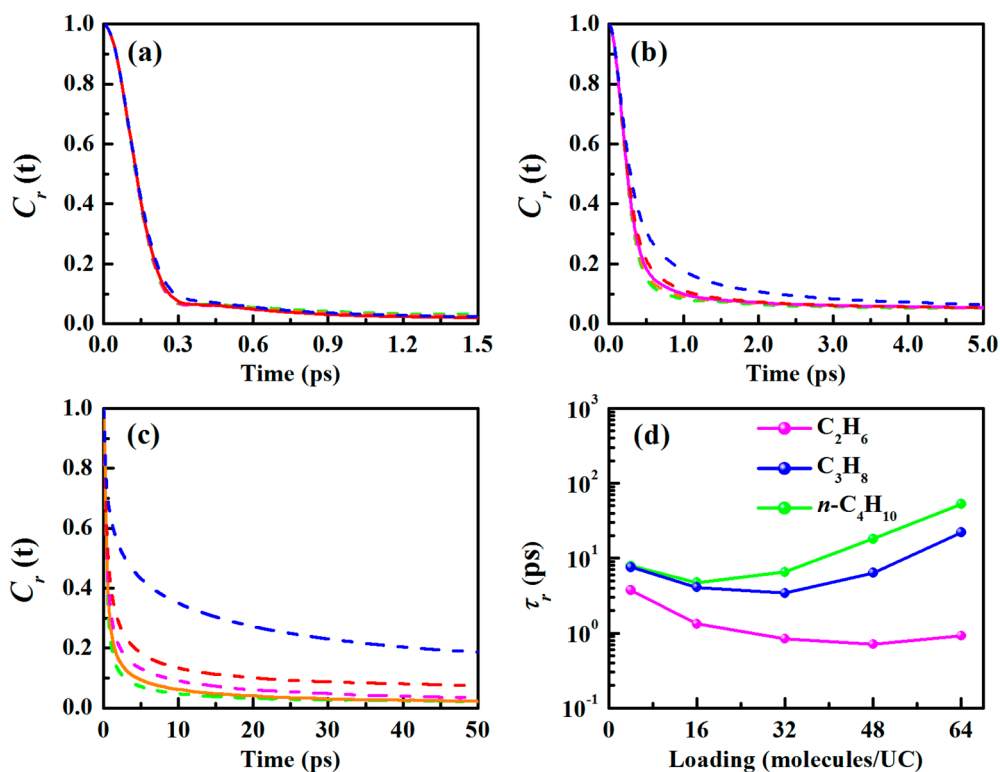


Figure 4. Rotational TCFs of (a) C_2H_6 , (b) C_3H_8 , and (c) $n-C_4H_{10}$ molecules in ZIF-10 at different loadings as well as (d) the corresponding rotational relaxation times. Green, orange, magenta, red, and blue lines correspond to the loadings from 4 to 64 molecules/UC in turn. Here the rotational TCFs are constructed using the second-order Legendre polynomial. The relevant values and standard deviations are listed in Table S6 of the Supporting Information.

corresponding bulk-phase pressure could be as high as a few hundred atmospheres, which is unlikely to represent a real separation application. As shown in the previous work,^{58,59} the size of the simulation box has a considerable influence on the diffusion coefficients due to the particle numbers and the calculation of long-range electrostatic interactions. To accommodate enough gas molecules,⁶⁰ two larger simulation boxes were composed of $4 \times 4 \times 4$ and $3 \times 3 \times 3$ UCs for the low loadings of 4 and 16 molecules/UC, respectively, which should be able to better eliminate the statistical uncertainties of diffusion coefficients. It should be noted that there are 34 816 atoms in the framework of ZIF-10 when the simulation box is $4 \times 4 \times 4$ UCs. Meanwhile, a smaller simulation box of $2 \times 2 \times 2$ UCs was used for other higher loadings. Therefore, the dimensions of these simulation boxes with the periodic boundary conditions in three directions are $54.12 \times 54.12 \times 38.81 \text{ \AA}^3$ for $2 \times 2 \times 2$ UCs, $81.18 \times 81.18 \times 58.22 \text{ \AA}^3$ for $3 \times 3 \times 3$ UCs, and $108.24 \times 108.24 \times 77.62 \text{ \AA}^3$ for $4 \times 4 \times 4$ UCs.

For each loading, at least three MD simulations with independent initial configurations were carried out in the canonical (NVT) ensemble, where the temperature was fixed at 303.0 K and controlled by the Nosé–Hoover algorithm. Newton's equation of motion was integrated by the velocity-Verlet algorithm with a time step of 1.0 fs. A cutoff of 10 Å was applied for the nonbonded interactions, and the long-range electrostatic interactions were treated by the particle–particle particle-mesh (PPPM) method.⁶¹ In each MD simulation, we ran the first 20 ns for equilibration, and then the next simulation from 30 to 100 ns was performed for trajectory analyses, with the trajectories stored every 100 fs. Subsequently, an additional NVT MD simulation of 500 ps (following the corresponding final configuration attained from the above calculation)

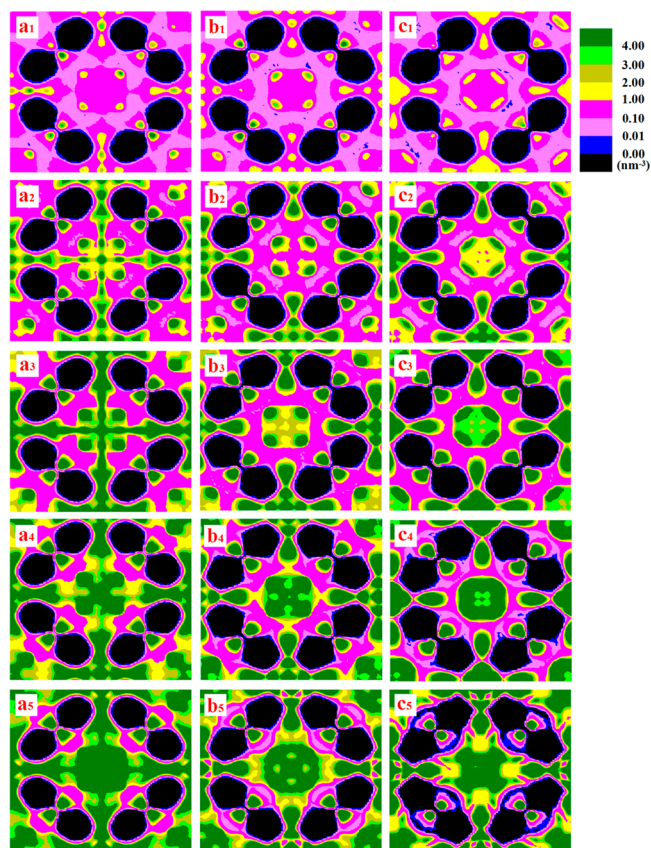


Figure 5. Two-dimensional density distribution in the x – y plane of pure (a) C_2H_6 , (b) C_3H_8 , and (c) $n-C_4H_{10}$ molecules in ZIF-10. Loadings from 4 to 64 molecules/UC corresponding to a_1 – a_5 , b_1 – b_5 , and c_1 – c_5 .

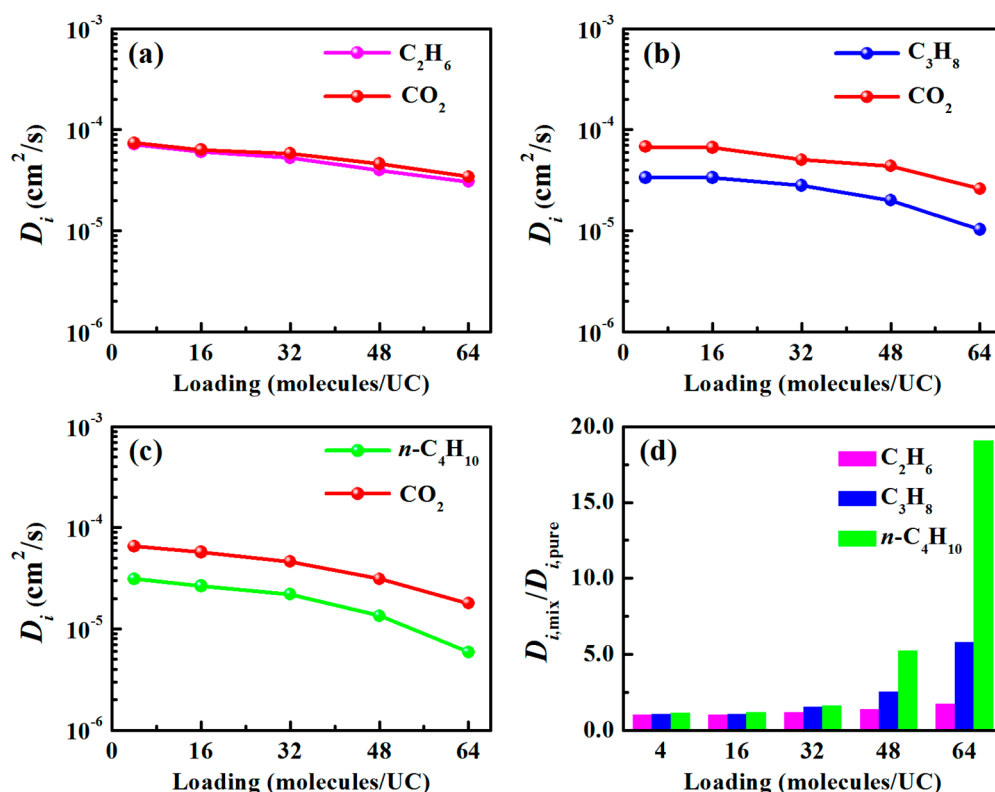


Figure 6. Variation of self-diffusion coefficients D_i with loading for binary (a) $\text{C}_2\text{H}_6/\text{CO}_2$, (b) $\text{C}_3\text{H}_8/\text{CO}_2$, and (c) $n\text{-C}_4\text{H}_{10}/\text{CO}_2$ mixtures as well as (d) the $D_{i,\text{mix}}/D_{i,\text{pure}}$ ratio. The relevant values and standard deviations are listed in Table S5 of the Supporting Information.

was performed for each simulation system, but their trajectories and velocities were saved every time step (i.e., 1 fs) to better calculate the velocity autocorrelation functions. In this work, all NVT MD simulations were performed by using the large-scale atomic/molecular massively parallel simulator (Lammps) software package.⁶² It should be noted that all standard deviations reported in this work are the population standard deviation, calculated by $\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - \bar{x})^2}$, where N is the block number of each system. After equilibrium, the trajectory of a production run was divided into 3 to 10 blocks to guarantee that each block covers 10 ns of data.

3. RESULTS AND DISCUSSION

3.1. Pure Alkanes in ZIF-10. First, the translational motions of pure light alkanes in ZIF-10 can be well specified with the self-diffusivity of the center of mass (COM), and the corresponding self-diffusion coefficients D_i can be calculated via the relevant mean square displacement (MSD) based on Einstein's formulation^{63,64}

$$D_i = \lim_{t \rightarrow \infty} \frac{\langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle}{6t} \quad (1)$$

where $\langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle$ is the MSD of the i th kind of gas molecule at a certain time t . The angular bracket means that the ensemble average is taken over all tagged gas molecules at different reference initial times. The calculated MSD curves of C_2H_6 , C_3H_8 , and $n\text{-C}_4\text{H}_{10}$ molecules are shown in Figure S1 of the Supporting Information, where C_3H_8 and $n\text{-C}_4\text{H}_{10}$ molecules in ZIF-10 are found to have obvious subdiffusive behavior at the highest loading of 64 molecules/UC. Then, Figure 1 presents the calculated self-diffusion coefficients D_i of

pure alkanes in ZIF-10 as a function of the loading. We can observe that all values of D_i for different pure alkanes in ZIF-10 decrease monotonically with increasing loading and their diffusion rates always follow the order $\text{C}_2\text{H}_6 > \text{C}_3\text{H}_8 > n\text{-C}_4\text{H}_{10}$ at the same loadings. In particular, the D_i of $n\text{-C}_4\text{H}_{10}$ ($3.10 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) is far less than that of C_2H_6 ($1.77 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) by around 60 times at the highest loading of 64 molecules/UC. A larger D_i difference between C_2H_6 ($2.57 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) and $n\text{-C}_4\text{H}_{10}$ ($8.85 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$) molecules can be observed in ZIF-8⁴⁴ due to the smaller window of ZIF-8 ($d_w = 3.8 \text{ \AA}$) compared to that of ZIF-10 ($d_w = 8.2 \text{ \AA}$). Meanwhile, the self-diffusion coefficients D_i for pure alkanes in ZIF-10 are found to have a slight decrease at low loadings, followed by a rapid decrease as the loading increases, especially for the C_3H_8 and $n\text{-C}_4\text{H}_{10}$ molecules.

Generally, the loading-dependent diffusion behavior of gas molecules in ZIFs is determined by the competition between both the gas–gas and gas–ZIF interactions. Figure 2 shows the average alkane–alkane and alkane–ZIF interaction energies for C_2H_6 , C_3H_8 , and $n\text{-C}_4\text{H}_{10}$ molecules in ZIF-10 over the studied loading range, as well as the corresponding total interaction energies. All average interaction energies are found to be negative, and their absolute values correspond to the magnitude of the interaction strength. As shown in Figure 2, there is an obvious competition between both the alkane–alkane and alkane–ZIF interactions, where the average interaction strength between alkanes and ZIF-10 always decreases while that between alkanes themselves increases as the loading increases. By comparison, the predominant one is the increased interaction between alkanes themselves in all cases so that the total interaction strength always increases with the increasing loading, which is unfavorable to the diffusion motions of pure alkanes in

ZIF-10 (shown in Figure 1). Furthermore, the absolute values of total interaction energies follow the order $n\text{-C}_4\text{H}_{10} > \text{C}_3\text{H}_8 > \text{C}_2\text{H}_6$ at the same loadings, meaning that the total interaction strength of pure alkanes in ZIF-10 gradually increases as the chain length increases. In other words, longer alkanes will suffer more restrictions from ZIF-10, which is consistent with the D_i order of $\text{C}_2\text{H}_6 > \text{C}_3\text{H}_8 > n\text{-C}_4\text{H}_{10}$ in Figure 1.

On the other hand, longer alkanes and higher loadings can also increase the collision frequency among alkanes in ZIF-10. A higher collision frequency can change the velocity directions of alkanes more frequently, which is significantly unfavorable to the diffusion motions. Meanwhile, it should be noted that the alkane collisions in ZIF-10 occur among alkanes themselves and also between alkanes and ZIF-10. In fact, the translational motions of small gas molecules are mainly determined by the relevant interaction energies at the low loadings while those of large gas molecules are dominated by their relevant collision frequency at the high loadings because the interaction energies mainly refer to the long-range attractive interactions while the collision behavior mainly refers to the short-range repulsive interactions. Then, the insight into such microscopic collisions can be gained by the COM velocity autocorrelation functions (VACFs) of alkanes because both kinds of effective collisions can change the magnitude and direction of their velocities, which are favorable to losing the correlation of initial velocities. Therefore, less relaxation time implicitly specifies a higher collision frequency. The normalized VACFs and the relevant relaxation times τ_v can be expressed as^{65,66}

$$C_v(t) = \frac{\langle v_i(0) v_i(t) \rangle}{\langle v_i(0) v_i(0) \rangle} \quad (2)$$

and then

$$\tau_v = \int_0^\infty C_v(t) dt \quad (3)$$

where $v_i(t)$ is the velocity of gas molecule type i at time t . The angular brackets denote the ensemble average. As shown in Figure 3, all VACF curves are found to cross the axis and then become negative. The negative regions in all VACF curves mean that the alkane molecules are moving in the direction opposite to that at $t = 0$ due to the collision effect, which is the characteristic of rattling motion of alkanes in ZIF-10. Accordingly, the variations of relaxation times as a function of the loading are shown in the insets of Figure 3. A shorter relaxation time means a higher collision frequency for alkanes in ZIF-10, which is unfavorable to the relevant diffusion motions. Therefore, we can find the same loading-dependent behavior between the relaxation time of VACF and the diffusion coefficients D_i . In this way, we can capture the diffusion behavior qualitatively during a short simulation time, and the VACF is more sensitive and convenient than the MSD in identifying the diffusion motions of longer alkanes in porous media.

Besides the translational motions, the rotational motions are also an important dynamics property of C_2H_6 , C_3H_8 , and $n\text{-C}_4\text{H}_{10}$ molecules in ZIF-10, especially for longer alkanes. Herein, the relevant rotational dynamics is studied through the corresponding time correlation function (TCF) $C_r(t)$,^{67,68}

$$C_r(t) = \left\langle P_l \left(\frac{1}{N} \sum_{i=1}^N \mathbf{u}_i(t) \cdot \mathbf{u}_i(0) \right) \right\rangle \quad (4)$$

where P_l is the l th rank Legendre polynomial ($l = 1$ and 2), N is the number of alkanes in ZIF-10, and $\mathbf{u}_i$ is the unit vector of

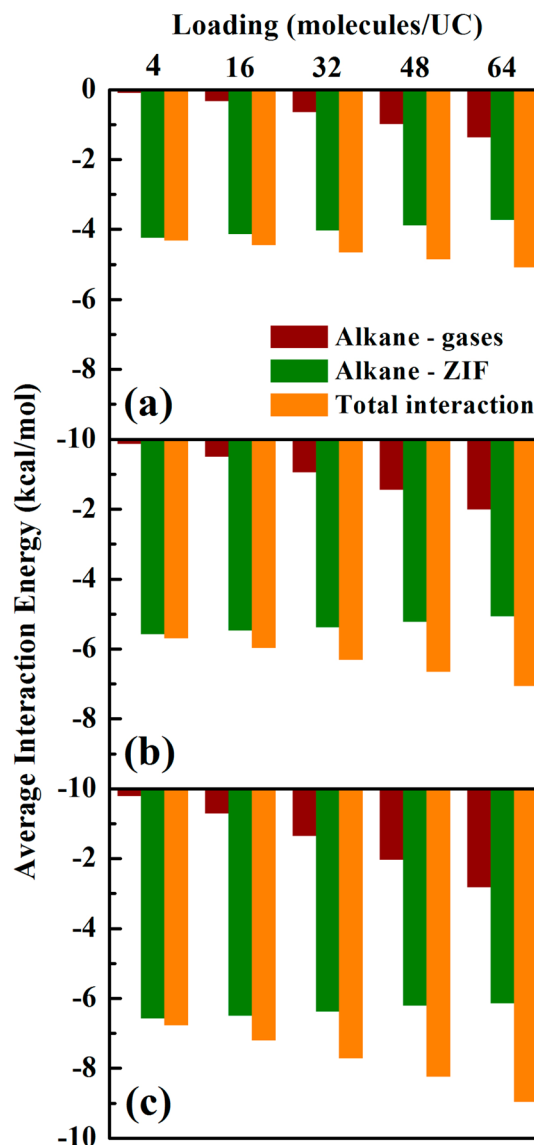


Figure 7. Average interaction energies of alkane-gases (containing alkane-alkane and alkane- CO_2 interactions) and alkane-ZIF and total interaction energy for (a) C_2H_6 , (b) C_3H_8 , and (c) $n\text{-C}_4\text{H}_{10}$ molecules of their mixtures with CO_2 in ZIF-10 at different loadings. All standard deviations here are less than ± 0.02 kcal/mol. The error bars are smaller than the symbol size, so they are not shown.

the i th alkane at time t . The angular brackets mean that the ensemble averaging is taken over the tagged alkanes at different reference initial times. In this work, the orientation of each alkane molecule is represented by a vector pointing from the terminal carbon group to the other terminal carbon group. Figure 4 shows that the rotational $C_r(t)$ curves ($l = 2$) of the $n\text{-C}_4\text{H}_{10}$ molecules decay more slowly than those of C_2H_6 and C_3H_8 molecules as the loading increases, suggesting that $n\text{-C}_4\text{H}_{10}$ molecules rotate more slowly than both the C_2H_6 and C_3H_8 molecules in ZIF-10. In order to gain the rotational relaxation times τ_r , these $C_r(t)$ curves are fitted by a three-parameter exponential function (with a total weight of 1, i.e., $A + B + C = 1$),^{65,68,69}

$$C_r(t) = A \exp(-t/\tau_a) + B \exp(-t/\tau_b) + C \exp(-t/\tau_c) \quad (5)$$

and then

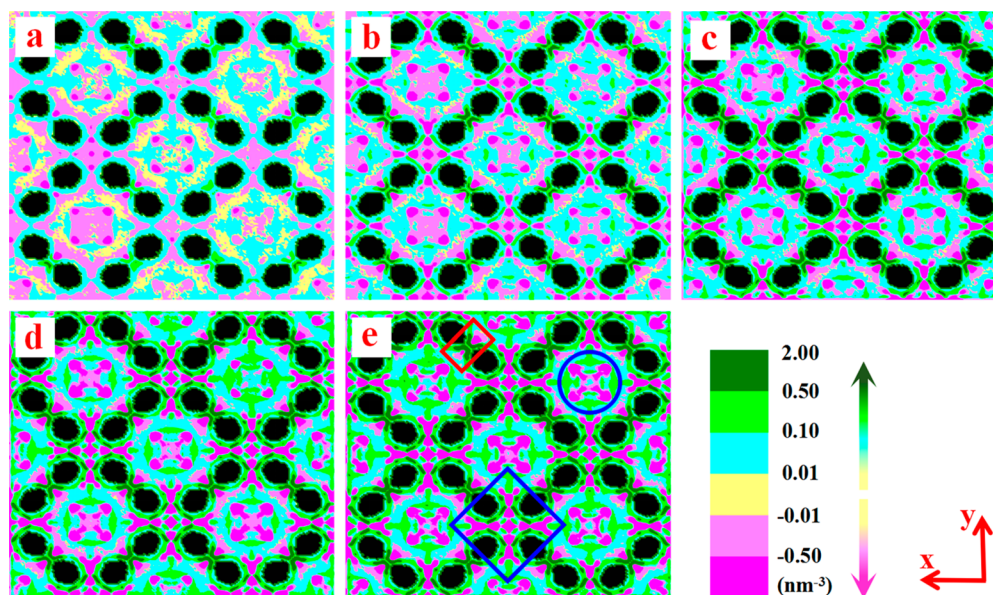


Figure 8. Two-dimensional different density distribution in the x - y plane between CO_2 and C_2H_6 in the $\text{C}_2\text{H}_6/\text{CO}_2$ mixture, where the positive region means that the density of CO_2 molecules is higher than that of C_2H_6 and the negative region means that the density of CO_2 molecules is lower than that of C_2H_6 . The black regions refer to the frameworks without both CO_2 and C_2H_6 molecules. The loadings from 4 to 64 molecules/UC correspond to a–e.

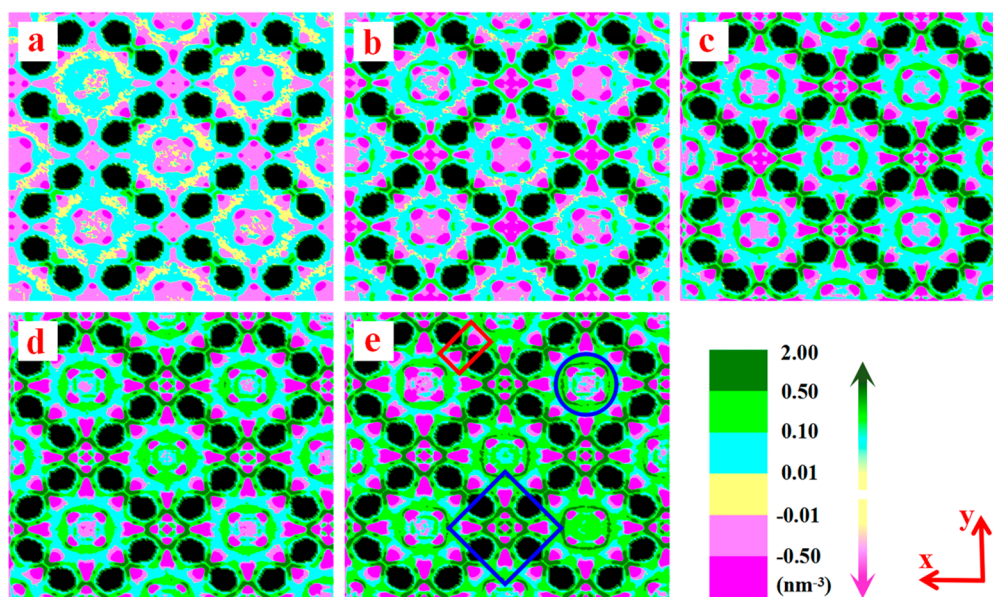


Figure 9. Two-dimensional different density distribution in the x - y plane between CO_2 and C_3H_8 in the $\text{C}_3\text{H}_8/\text{CO}_2$ mixture, where the positive region means that the density of CO_2 molecules is higher than that of C_3H_8 and the negative region means that the density of CO_2 molecules is lower than that of C_3H_8 . The black regions refer to the frameworks without both CO_2 and C_3H_8 molecules. The loadings from 4 to 64 molecules/UC correspond to a–e.

$$\tau_r = A\tau_a + B\tau_b + C\tau_c \quad (6)$$

where A , B , and C are fitting parameters, while τ_a , τ_b , and τ_c are the time constants. The calculated τ_r values are illustrated in Figure 4d. It can be clearly observed that all τ_r values of $n\text{-C}_4\text{H}_{10}$ molecules in ZIF-10 are always much larger than those of C_2H_6 and C_3H_8 molecules at the same loadings. Moreover, the difference between these τ_r values among different alkanes is found to become larger and larger as the loading increases. For example, the τ_r values are 3.71, 7.56, and 7.91 ps in turn for C_2H_6 , C_3H_8 , and $n\text{-C}_4\text{H}_{10}$ molecules at 4 molecules/UC while the corresponding values are 0.92, 22.05, and 52.82 ps at

64 molecules/UC, respectively. More importantly, the τ_r values initially show a decrease with the increasing loading and then follow an increase at high loadings, especially for longer C_3H_8 and $n\text{-C}_4\text{H}_{10}$ molecules. Namely, their rotational motions are initially accelerated and then decelerated gradually beyond a critical loading regardless of the chain length, which is very different from the monotonic decrease in the diffusion rate with loading (Figure 1). Such different loading-dependent behavior between the translational and the rotational motions originates mainly from the fact that the translational motion is a kind of global dynamics property while the rotational motion is a kind

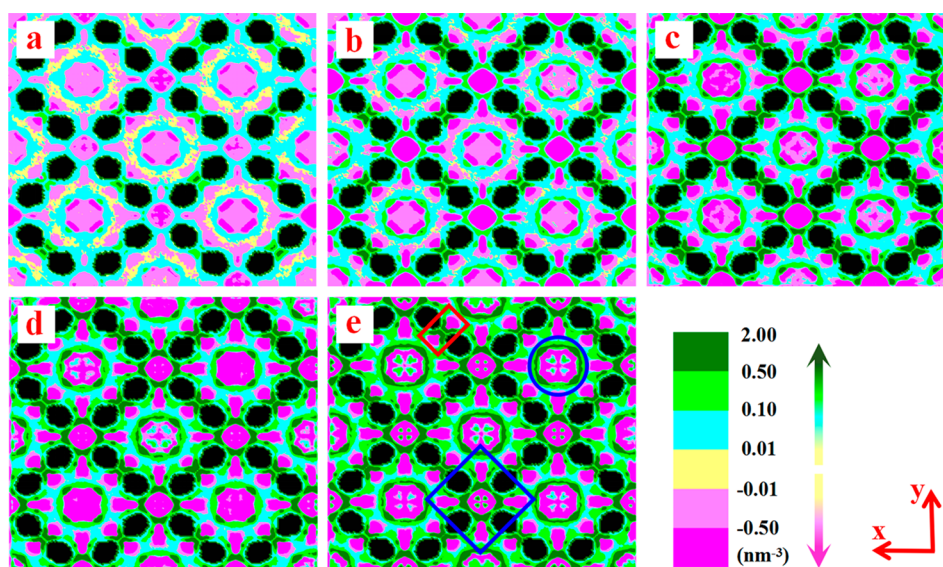


Figure 10. Two-dimensional different density distribution in the x - y plane between CO_2 and $n\text{-C}_4\text{H}_{10}$ in the $n\text{-C}_4\text{H}_{10}/\text{CO}_2$ mixture, where the positive region means the density of CO_2 molecules is higher than that of $n\text{-C}_4\text{H}_{10}$ and the negative region means the density of CO_2 molecules is lower than that of $n\text{-C}_4\text{H}_{10}$. The black regions refer to the frameworks without both CO_2 and $n\text{-C}_4\text{H}_{10}$ molecules. The loadings from 4 to 64 molecules/UC correspond to a–e.

of local dynamics property. The translational motions of alkanes refer to the migration among different cages of ZIF-10, i.e., the intercage dynamics. However, the rotational motions can occur in the same cages, i.e., the intracage dynamics, which are much more sensitive to the changes of local environment around the alkanes.

To further capture the changes in the local environment, Figure 5 illustrates the two-dimensional density distributions projected on the x - y plane with different loadings for C_2H_6 , C_3H_8 , and $n\text{-C}_4\text{H}_{10}$ molecules in ZIF-10. It can be seen from Figure 5a₁–c₁ that the adsorption sites of all alkane molecules are located at the internal surfaces of ZIF-10 when the loading is 4 molecules/UC. Accordingly, the average interaction strength between alkanes and ZIF-10 should be the largest at the adsorption sites compared to those at other loadings, which is well supported by the results in Figure 2. In this case, the rotational motions of alkanes in ZIF-10 would be considerably hindered by strong restrictions at the adsorption sites. As the loading increases, Figure 5a₂–c₄ shows that the internal surfaces have no space to accommodate more alkanes, and then more and more alkanes enter the free center regions of cages in ZIF-10 where these alkane molecules suffer from fewer restrictions and rotate faster than those at the adsorption sites. Therefore, we can find a decreasing process of the rotational relaxation times τ_r with the increasing loading at the beginning for C_2H_6 , C_3H_8 , and $n\text{-C}_4\text{H}_{10}$ molecules in ZIF-10. When the loading is beyond a critical value, however, the central regions of cages are gradually occupied by more and more alkane molecules so that no free space exists in ZIF-10, as shown in Figure 5a₅–c₅. Those additional alkanes in ZIF-10 cages result in the enhanced alkane–alkane interactions (Figure 2), leading to more restrictions for the rotational motions of all alkanes. Accordingly, we can observe an increasing process of the τ_r value from Figure 4d when the loading is beyond a critical loading regardless of the chain length. By comparison with Figure 4d, additionally, it is worth noting that the corresponding critical loading is found to decrease with the increasing chain length of alkanes. For example, the critical loading for the

C_2H_6 molecule is 48 molecules/UC, while the corresponding loadings for C_3H_8 and $n\text{-C}_4\text{H}_{10}$ molecules are 32 and 16 molecules/UC, respectively. This is because longer alkanes are larger than shorter ones so that longer alkanes need more free space to rotate. Therefore, they are sensitively subjected to restrictions from the increasing loading.

3.2. Equimolar Alkane/ CO_2 Mixtures in ZIF-10. Next, we focus on how the presence of CO_2 affects the translational and rotational motions of light alkanes in ZIF-10. For better comparisons, equimolar alkane/ CO_2 mixtures with the same loadings as pure alkanes in ZIF-10 are considered here. Figure 6 presents the variation in the self-diffusion coefficients D_i for alkane/ CO_2 mixtures with loading as well as the $D_{i,\text{mix}}/D_{i,\text{pure}}$ ratios for alkanes in ZIF-10 to evaluate the effects from the presence of CO_2 . Then, we can see from Figure 6a–c that all D_i values for C_2H_6 , C_3H_8 , and $n\text{-C}_4\text{H}_{10}$ molecules in the presence of CO_2 show a monotonically decreasing trend with loading and are smaller than that of CO_2 molecules, especially for C_3H_8 and $n\text{-C}_4\text{H}_{10}$ molecules. As shown in Figure 6d, meanwhile, all ratios of $D_{i,\text{mix}}/D_{i,\text{pure}}$ for alkanes are larger than 1 over all studied loadings and increase significantly with the increasing loading, where the $D_{i,\text{mix}}/D_{i,\text{pure}}$ value for $n\text{-C}_4\text{H}_{10}$ molecules in ZIF-10 is even up to around 20 at 64 molecules/UC. This clearly indicates that the presence of CO_2 molecules can promote the acceleration of the translational motions of alkanes in ZIF-10 for all mixtures and such promotion effects become more and more significant as the loading increases, especially for long $n\text{-C}_4\text{H}_{10}/\text{CO}_2$ mixtures.

Likewise, Figure 7 shows the average interaction energies of three different alkanes in their mixtures with CO_2 in ZIF-10 at all loadings. In the mixture cases, the total interaction energies of alkanes in ZIF-10 include the alkane–alkane, alkane– CO_2 , and alkane–ZIF interaction energies. By comparison, the absolute values of their total interaction energies are found to increase with the increasing loading, which mainly results from the increased alkane–gas interactions (including alkane–alkane and alkane– CO_2 interactions) over the decreased alkane–ZIF interactions. The increase in the total interaction

energies with loading leads to the decreased D_i values of alkanes in ZIF-10. As shown in Figure S2 of the Supporting Information, the absolute values of CO₂–ZIF interaction energies are larger than those of the corresponding alkane–ZIF interaction energies regardless of the loading and alkane chain length. This is because the oxygen atoms of CO₂ molecules with partially negative charges can form hydrogen bonds (HBs) with electron-deficient C–H groups of the imidazolate ligands in ZIF-10.^{60,70–73} As shown in Figure S3, the average number of HBs per CO₂ molecule in ZIF-10 is found to be more than 1.5. Therefore, CO₂ molecules should preferentially occupy the area around the imidazolate ligands in ZIF-10 compared to alkanes, which can be well supported by the density deviation distributions of alkane/CO₂ mixtures in ZIF-10. Similar phenomena have been reported for alkane/CO₂ mixtures in other confinements.^{32,35,74,75} Experimentally, Gautam et al.⁷⁵ found that CO₂ molecules can replace C₃H₈ molecules from the pore walls of nanoporous silica aerogel so that more C₃H₈ molecules become available and excitable. In other words, the addition of CO₂ molecules can enhance the jump rates of C₃H₈ molecules and then increase their diffusion coefficient.

Figures 8–10 show the density deviation distributions between alkanes and CO₂ molecules in ZIF-10, where the color is green when the density of CO₂ molecules is higher than that of alkanes and magenta otherwise. As illustrated in Figure 8, the interaction sites mainly correspond to the red rectangle and blue diamond regions, which are close to the imidazolate ligands of ZIF-10. As the loading increases, CO₂ molecules are found to accumulate at the four-membered window in the red rectangle due to the strong HB interactions between CO₂ molecules and imidazolate rings, while most of the C₂H₆ molecules are located in the larger space of the MER cage in the blue circle and the intercage region in the blue diamond. Larger available space is favorable to diffusion and rotational motions of C₂H₆ molecules. As shown in Figures 9 and 10 (i.e., mixtures of C₃H₈/CO₂ and *n*-C₄H₁₀/CO₂), CO₂ is initially distributed at the four-membered window in the red rectangle at 4 molecules/UC and then CO₂ molecules are gradually enriched and take up the interaction sites of C₃H₈ (or *n*-C₄H₁₀) in the blue diamond as the loading increases. Especially for the *n*-C₄H₁₀/CO₂ mixture, *n*-C₄H₁₀ molecules are found to be trapped by the surrounding CO₂ molecules, shown by the blue diamond in Figure 10. Also, the additional alkane molecules from the loading increase, generally stay away from the strong interaction sites, and are concentrated in the large center region of the MER cage, as labeled in the blue circled region. When most of the interaction sites of alkanes in ZIF-10 are replaced by CO₂ molecules, weakened interactions between alkanes and ZIF-10 can resulting, a situation that is favorable to the diffusive motions of alkanes. Furthermore, a larger amount of available free space should be able to reduce the collision frequency of alkanes in ZIF-10, promoting both diffusional and rotational motions of alkanes.

Figure 11 presents the relaxation times of VACF curves for alkane molecules in the pure and mixture cases. Accordingly, those detailed VACF curves at different loadings are shown in Figure S4 of the Supporting Information. The comparison results clearly demonstrate that the relaxation times in the mixture case are always larger than those in the pure case, indicating a decrease in the collision frequency of alkanes in ZIF-10 in the presence of CO₂. In particular, the collision relaxation times for *n*-C₄H₁₀/CO₂ mixtures are much larger than those for pure *n*-C₄H₁₀ in ZIF-10, meaning that the collision frequency of *n*-C₄H₁₀ in ZIF-10 is considerably reduced in the

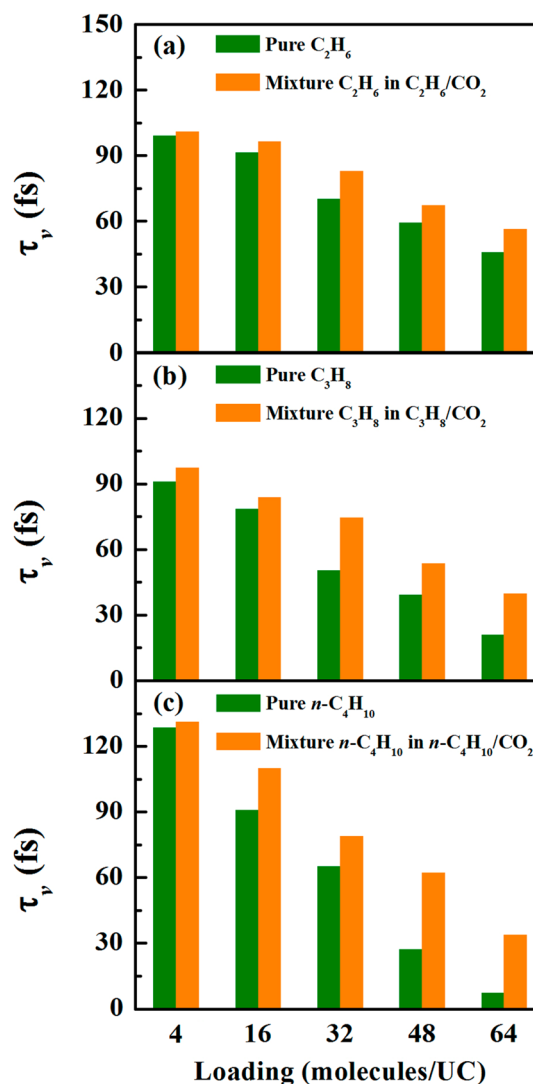


Figure 11. Contrast of the relaxation time from VACF curves for alkane molecules in the pure and mixture systems. All standard deviations here are less than ± 2.0 fs. The error bars are smaller than the symbol size, so they are not shown.

presence of CO₂, which is significantly favorable to their diffusion rate. Furthermore, the differences in relaxation time between pure alkanes and alkane/CO₂ mixtures in ZIF-10 are gradually increasing as the loading increases. Therefore, the presence of CO₂ molecules can promote the diffusion motion of alkanes in ZIF-10 for all mixtures, and such a promotion effect becomes more and more significant as the loading increases, as shown in Figure 11. Moreover, Figure 12 presents the rotational TCF curves and the corresponding τ_r values of alkanes molecules in ZIF-10 in the presence of CO₂. By comparison with Figure 12a–c, we find that the TCF curves of C₂H₆, C₃H₈, and *n*-C₄H₁₀ decay much faster in mixture cases than in pure cases. Similarly, Figure 12d shows that the $\tau_{r,pure}/\tau_{r,mix}$ ratio is larger than 1, indicating that the relaxation times of the mixture system are also smaller than those of the pure systems. Therefore, the presence of CO₂ molecules can also promote the rotational motions of alkanes for all studied mixtures due to the decreased collision frequency of alkanes in ZIF-10.

To better understand the role of confinement from ZIF-10, we have performed additional MD simulations for pure alkanes

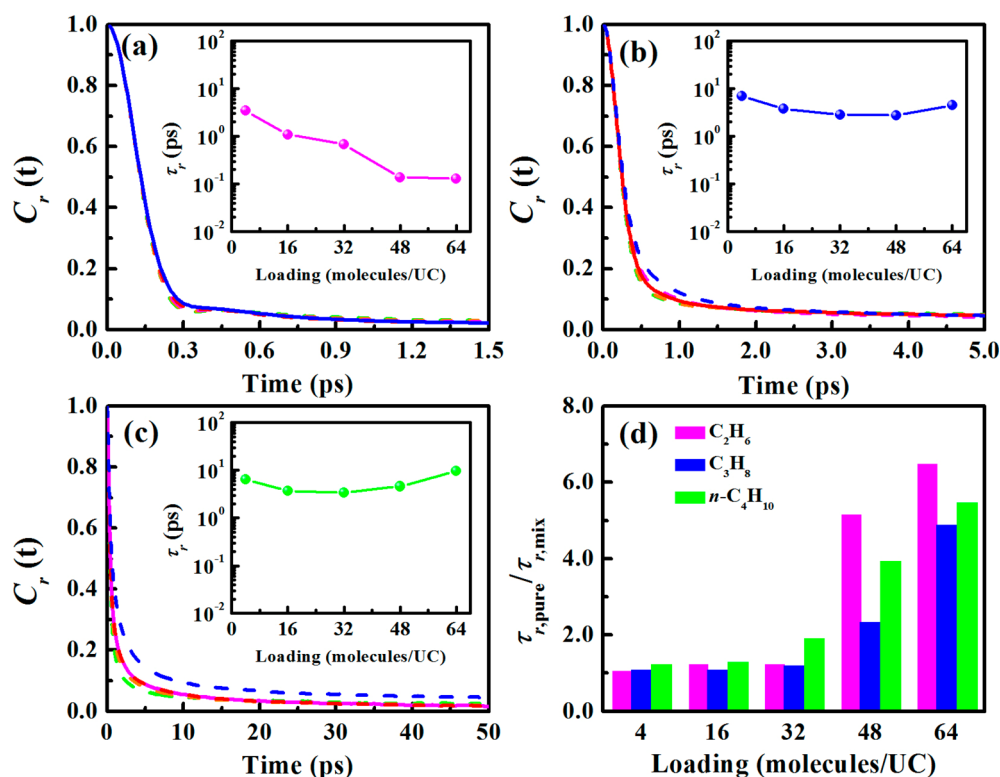


Figure 12. Rotational TCFs of (a) C_2H_6 , (b) C_3H_8 , and (c) $n-C_4H_{10}$ in their mixtures at different loadings and (d) the $\tau_{r,pure}/\tau_{r,mix}$ ratio. Green, orange, magenta, red, and blue lines correspond to the loadings from 4 to 64 molecules/UC in turn. The relevant values and standard deviations are listed in Table S6 of the Supporting Information.

and equimolar alkane/ CO_2 mixtures (including two loadings of 4 and 64 molecules/UC) in the same simulation box only without ZIF-10. Figure 13 presents the calculated $D_{i,mix}/D_{i,pure}$ and $\tau_{r,pure}/\tau_{r,mix}$ ratios in the system without ZIF-10. For the loading of 4 molecules/UC, both the $D_{i,mix}/D_{i,pure}$ and $\tau_{r,pure}/\tau_{r,mix}$ ratios for these three alkanes are smaller than 1, suggesting that the presence of CO_2 molecules restricts their translational and rotational motions at the lowest loading. On the contrary, the presence of CO_2 molecules can accelerate the translational and rotational motions of these three alkanes in ZIF-10, as shown in Figures 6 and 12. For the loading of 64 molecules/UC, the $D_{i,mix}/D_{i,pure}$ and $\tau_{r,pure}/\tau_{r,mix}$ ratios for these three alkanes are found to be a bit more than 1, which is much smaller than the corresponding values of $D_{i,mix}/D_{i,pure}$ and $\tau_{r,pure}/\tau_{r,mix}$ in ZIF-10 (Figures 6 and 12). Therefore, the confinement of ZIF-10 can significantly promote the acceleration effect of CO_2 molecules on the translational and rotational motions of alkanes.

4. CONCLUSIONS

In this work, the loading-dependent translational and rotational behavior of pure C_2H_6 , C_3H_8 , and $n-C_4H_{10}$ and their binary equimolar mixtures with CO_2 in ZIF-10 has been investigated by a series of classical MD simulations. Our simulation results show that self-diffusion coefficients D_i for pure alkanes in ZIF-10 decreased monotonically with increased loading partly due to the competition between the enhanced alkane–alkane and the weakened alkane–ZIF interactions, where the unfavorable contribution of the former increase dominates the favorable contribution of the latter decrease. Accordingly, the total interaction strength of all pure alkanes in ZIF-10 is also found to increase as the loading increases. Furthermore, the

corresponding collision frequency of pure alkanes in ZIF-10 obviously increases with loading, which can hinder their translational motions considerably. Nevertheless, the dependence of their rotational motions on the loading is found to be significantly different from that of their translational motions. Their rotational motions are initially accelerated and then decelerated gradually beyond a critical loading regardless of the chain length. Such different loading-dependent behavior between the translational and rotational motions is mainly due to the fact that the translational motion is a global intercage dynamics property relating to the migration among different cages while the rotational motion is a local intracage dynamics property occurring in the same cages. Therefore, the initial acceleration of their rotational motions can be attributed to the fact that more alkane molecules are not adsorbed at the internal surfaces of MER cages but rather are adsorbed into the free center regions of cages in ZIF-10, which can be clearly captured by the relevant two-dimensional density distributions. Furthermore, a loading higher than the corresponding critical value can result in a considerable decrease in free space within the whole ZIF-10 so that more restrictions hinder their rotational motions.

However, our simulation results reveal that the presence of CO_2 molecules can significantly accelerate both the translational and rotational motions for alkanes in ZIF-10 at the same loading partly due to the lower steric resistance of smaller CO_2 molecules compared to that of longer alkane molecules. Especially for $n-C_4H_{10}/CO_2$ in ZIF-10, the value of $D_{i,mix}/D_{i,pure}$ is up to around 20 at the highest loading of 64 molecules/UC. Meanwhile, the strong hydrogen bonds with the imidazolate rings can cause CO_2 molecules to preferentially occupy the adsorption sites in ZIF-10 compared to alkanes, leading to the

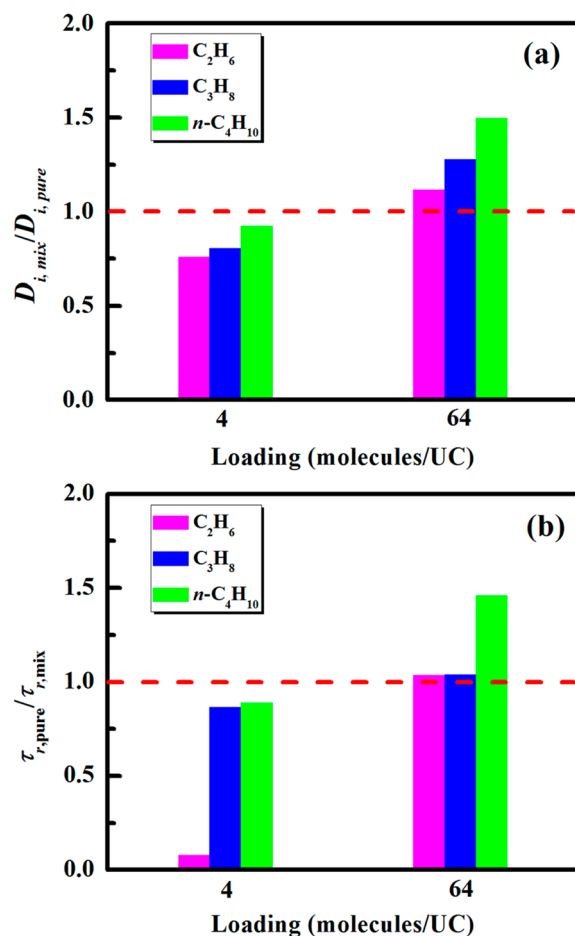


Figure 13. (a) $D_{i,mix}/D_{i,pure}$ and (b) $\tau_{i,pure}/\tau_{i,mix}$ ratios under loadings of 4 and 64 molecules/UC in the same simulation boxes without ZIF-10.

weakened interactions between alkanes and ZIF-10. Such competitive adsorption behavior can be observed at the molecular level from the density deviation distributions of alkane/ CO_2 mixtures in ZIF-10. More importantly, the competitive adsorption between alkanes and CO_2 molecules can also significantly reduce the collision frequency for alkanes in ZIF-10, which is quite favorable to both the translational and rotational motions of alkanes in ZIF-10. In addition, the confinement of ZIF-10 is also found to significantly promote the acceleration effect of CO_2 molecules with respect to the translational and rotational motions of alkanes. The simulation results in this work provide a molecular-level understanding of the translational and rotational motions of pure alkanes and alkane/ CO_2 mixtures in ZIF-10 and are of great benefit to experimental scientists in designing and preparing new ZIFs and their membranes for various gas separations.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.8b00651.

Lennard-Jones parameters and partial atomic charges used in this work; compositions of alkane/ CO_2 mixtures in corresponding bulk phases; MSD curves of pure alkane molecules in ZIF-10; interaction energies between gas molecules and ZIF-10 in three mixture systems; average HB number per CO_2 in ZIF-10; VACF curves of binary mixtures in ZIF-10; all rotational

relaxation times in this work; self-diffusion coefficients of alkane molecules without ZIF-10; and self-diffusion coefficients for gas molecules (PDF)

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Notes

The authors declare no competing financial interest.

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