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Study of Xenon Mobility in the Two Forms of MIL-53(Al) Using Solid-State NMR Spectroscopy

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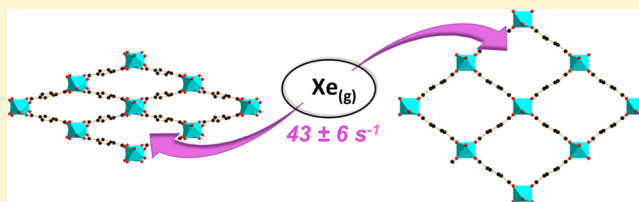
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Supporting Information

ABSTRACT: The Al-based metal–organic framework (MOF) MIL-53(Al) exhibits a structural transition between a large-pore (*lp*) form and a narrow-pore (*np*) one. Such change is induced by temperature, external pressure, or the adsorption of guest molecules. ¹²⁹Xe solid-state NMR experiments under static and magic-angle spinning (MAS) conditions have been used to study the *lp*–*np* transition in MIL-53(Al) initially loaded with xenon gas under a pressure of 5×10^4 Pa (at room temperature). The conversion of the *lp* form into the *np* one when the temperature decreases from 327 to 237 K and the reopening of the pores below 230 K are then observed. Furthermore, ¹H → ¹²⁹Xe cross-polarization under MAS (CPMAS) experiments demonstrate the possibility to observe the *np* phase at $T \leq 230$ K, while the *lp* one is unseen because the xenon residence time is too short for successful cross-polarization transfer. Moreover, even for the *np* phase at 199 K, the xenon atoms still exhibit significant motion on time scale faster than a few milliseconds. We prove the exchange of Xe atoms between the *lp* and *np* forms at room temperature with the two-dimensional (2D) ¹²⁹Xe EXchange Spectroscopy (EXSY) NMR method. Using ¹²⁹Xe selective inversion recovery (SIR) experiments, the rate for this exchange has been measured at 43 ± 6 s⁻¹.



I. INTRODUCTION

During the last two decades, metal–organic framework (MOF) materials have been widely studied because of their possible use in various applications ranging from gas storage to drug delivery. These compounds are hybrid materials built up from the three-dimensional association of metal clusters and organic ligands and exhibit interesting properties owing to their modular architecture and porosity.^{1,2} Among the large MOFs family, the specific case of the terephthalate-based MIL-53 [M(III)(1,4-benzendicarboxylate)] MOFs with M = Al, Fe, Ga, Cr, Sc, or In^{3–10} is of particular interest as these materials present massive flexibility and dynamic properties called the breathing effect. This latter is induced by changes in temperature¹¹ or external pressure^{12,13} as well as upon the presence of guest molecules (including xenon, water molecules, CO₂, or hydrocarbons)¹⁴ and strongly depends on the nature of the linker^{7,15,16} and the metal.^{17,18} This structural transition has been interpreted as a variation of MIL-53 structure between a large-pore (*lp*) form and a narrow-pore (*np*) one (see Figure 1).

In this study, we focus on MIL-53(Al) since it combines low cost, density, and toxicity, and good thermal stability; it is already produced at the industrial scale under the name of Basolite A100.^{19,20} The lattice framework of MIL-53(Al) and its structural transition have been investigated by powder X-ray diffraction (PXRD)^{19,21,11,22} and one-dimensional (1D) ¹H, ¹³C, and ²⁷Al solid-state NMR experiments.^{19,23–28} Furthermore, we have demonstrated recently how the measurement of the dephasing of ¹³C signals under ¹³C–²⁷Al dipolar couplings validates the crystal structures of the *lp* and *np* forms obtained from PXRD and confirms their rigidity.²⁸ The *lp*–*np* transition as a function of the Xe pressure and the temperature has also been studied by ¹²⁹Xe NMR in MIL-53(Al)²⁹ and very recently in Cu-based MOF material (DUT-49).³⁰ This technique allows one to distinguish the *lp* and *np* forms of MIL-53(Al) and

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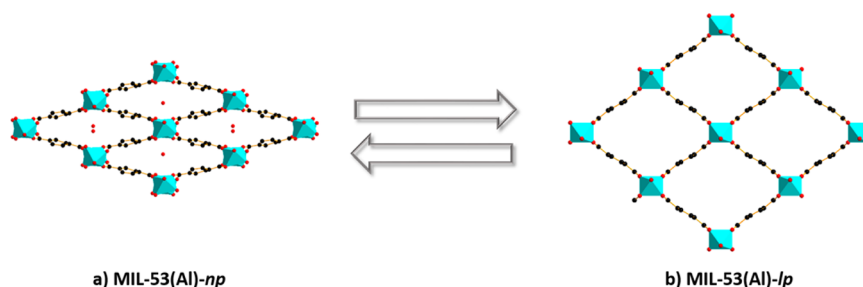


Figure 1. Views of the 3D structures of MIL-53(Al) materials in (a) the *np* form and (b) the *lp* one.¹⁹

determine their relative proportion. However, the spectral resolution of the reported 1D ^{129}Xe NMR spectra was limited by the NMR data acquisition under static conditions. Additionally, the motions of Xe atoms in the MIL-53(Al) pores and the exchange of Xe atoms between *lp* and *np* forms have not been investigated so far.

Here, the *lp*–*np* transition of MIL-53(Al) loaded with xenon is investigated using variable-temperature ^{129}Xe NMR under static and magic-angle spinning (MAS) conditions, and $^1\text{H} \rightarrow ^{129}\text{Xe}$ cross-polarization under MAS (CPMAS) experiments are used to study the mobility of Xe atoms with respect to the pore walls. Finally, the exchange of Xe atoms between the *lp* and *np* forms is investigated using two-dimensional (2D) EXchange Spectroscopy (EXSY) experiments with the rate of exchange obtained by performing selective inversion recovery (SIR) experiments.

II. EXPERIMENTAL SECTION

II.1. Sample Preparation for NMR Measurements.

MIL-53(Al) was synthesized according to the procedure reported in the literature.¹⁹ An amount of 13 mg of MIL-53(Al) was activated under vacuum at 423 K overnight in a capillary. Xenon gas was added in the tube and condensed under liquid nitrogen. Then the tube was sealed, which gives an equilibrium pressure of ca. 5×10^4 Pa at room temperature. It should be noted that the powder was not squeezed into the capillary, and the sealing was performed as symmetrically as possible so that the rotor remains balanced and spins evenly. According to the adsorption isotherms,²⁹ the xenon pressure inside the capillary varies very significantly with the temperature. For instance, the pressure is 4×10^2 Pa at 195 K and 1.25×10^5 Pa at 323 K. Even at high temperature, there is no risk of overpressure and explosion of the capillary with 0.3 mm thick walls. We chose a capillary with an outer diameter of 3 mm, which exactly fitted into the 4 mm rotor. The rotor containing the capillary was spun without taking any special precaution.

II.2. NMR Experiments. NMR spectra were recorded at 9.4 T (400 MHz for ^1H) using wide-bore Bruker BioSpin spectrometer equipped with either (i) an AVANCE-II console and a static double resonance HX probe or a 4 mm triple resonance HXY MAS probe (used in a double resonance mode) or (ii) an AVANCE-III HD console equipped with a 4 mm HXY triple resonance MAS probe (used in a double resonance mode). For all variable temperature NMR experiments, the samples were allowed to equilibrate at the targeted temperature for 10 min. The temperature of the sample was controlled using a BCU-X Bruker system.

1D ^{129}Xe NMR spectra under static and MAS conditions at a rate $\nu_R = 10$ kHz were acquired using a Direct Excitation sequence and a radio frequency (rf) pulse at a nutation

frequency of 62.5 kHz. The relaxation delay was $\tau_{RD} = 5$ s and the number of scans was 512, which led to an experimental time of $t_{\text{exp}} = 43$ min. These experiments are quantitative since the ^{129}Xe longitudinal relaxation time, $T_1(^{129}\text{Xe})$ is shorter than 1 s for all the temperatures and hence $\tau_{RD} > 5T_1(^{129}\text{Xe})$. The molar fractions of Xe atoms adsorbed in the *lp* and *np* forms were calculated from the integrated intensities of their NMR signals in the 1D ^{129}Xe direct excitation NMR spectra under static conditions.

$^1\text{H} \rightarrow ^{129}\text{Xe}$ CPMAS were recorded at a MAS frequency of $\nu_R = 8$ kHz using a recycle delay of $\tau_{RD} = 3$ s, a 83 kHz $\pi/2$ ^1H excitation pulse, a contact time of $\tau_{CP} = 8$ ms, and rf nutation frequencies of 52 and 60 kHz for ^{129}Xe and ^1H nuclei, respectively. SPINAL-64 (Small Phase Incremental Alternation with 64 steps)³¹ ^1H decoupling of 83 kHz was applied during the acquisition of ^{129}Xe spectra. The number of scans was 800, which led to $t_{\text{exp}} = 40$ min.

2D ^{129}Xe EXSY experiments were performed at room temperature with $\nu_R = 10$ kHz using rf pulses at a nutation frequency of 71 kHz. The 2D spectra result from averaging 512 transients for each of 30 t_1 increments with $\Delta t_1 = 50 \mu\text{s}$ and $\tau_{RD} = 2$ s. To ensure steady-state condition for the acquisition of the EXSY experiment, a train of pulses was applied prior the τ_{RD} delay to saturate the ^{129}Xe magnetization. This train used 20 pulses with rf-field amplitude of 81 kHz and a 20 ms delay between the consecutive pulses. The 2D EXSY spectra were acquired with mixing time (τ_{mix}) ranging from 5 μs to 1 s leading to experimental times ranging from $t_{\text{exp}} = 10$ h and 20 min to $t_{\text{exp}} = 14$ h and 40 min. The pulse sequence is displayed in Figure S1 in the Supporting Information (SI).

The $T_1(^{129}\text{Xe})$ times were measured at room temperature using standard nonselective inversion–recovery (NIR) experiments at $\nu_R = 10$ kHz. The rf nutation frequency of ^{129}Xe $\pi/2$ and π pulses was 71 kHz and the relaxation delay was $\tau_{RD} = 10$ s. The variable relaxation delay, τ , between the π and $\pi/2$ pulses was varied from 10 μs up to 5 s. The number of scans for these experiments was 512, which led to an experimental time of $t_{\text{exp}} = 32$ h and 16 min. Selective Inversion Recovery (SIR) experiments were also conducted using the sequence shown in Figure S3. A shaped π pulse selectively inverts one resonance.^{32,33} Here, we employed a Gaussian π pulse, with an rf peak amplitude of 1.6 kHz, a full width at half-maximum of 6 kHz and a duration of 585 μs . This Gaussian pulse was truncated at 5% of its maximum rf peak amplitude. It was applied on-resonance with the signal of the *np* form and the *lp* form in Figure S4. The other parameters for the SIR experiments are identical to those of NIR ones.

The ^1H and ^{129}Xe chemical shifts were externally referenced to tetramethylsilane and gaseous xenon extrapolated to zero pressure, respectively, and both set to 0 ppm. The sample temperature under MAS conditions was measured from the

isotropic chemical shift of ^{207}Pb nuclei in $\text{Pb}(\text{NO}_3)_2$,³⁴ and all temperatures reported are actual sample temperatures.

The chemical shift parameters are defined according to the Haeberlen notation³⁵

$$\delta_{\text{iso}} = 1/3(\delta_{\text{XX}} + \delta_{\text{YY}} + \delta_{\text{ZZ}}) \quad (1)$$

$$\delta_{\text{aniso}} = \delta_{\text{ZZ}} - \delta_{\text{iso}} \quad (2)$$

$$\eta_{\text{CSA}} = \frac{\delta_{\text{YY}} - \delta_{\text{XX}}}{\delta_{\text{ZZ}} - \delta_{\text{iso}}} \quad (3)$$

where δ_{iso} denotes the isotropic chemical shift; δ_{XX} , δ_{YY} , and δ_{ZZ} are the principal components of the chemical shift anisotropy (CSA) tensor ordered as $|\delta_{\text{YY}} - \delta_{\text{iso}}| \leq |\delta_{\text{XX}} - \delta_{\text{iso}}| \leq |\delta_{\text{ZZ}} - \delta_{\text{iso}}|$; δ_{aniso} corresponds to the anisotropic chemical shift, and η_{CSA} is the asymmetry parameter of the CSA tensor.

The simulation of the 1D spectra were performed using DMfit software.³⁶ The exchange constant of the process (k_{exch}) in the case of the SIR experiments is measured by modeling the experimental data with the CIFIT program.^{32,33}

III. RESULTS AND DISCUSSION

III.1. 1D ^{129}Xe NMR Spectra under Static Conditions.

The ^{129}Xe direct excitation NMR spectrum of MIL-53(Al) loaded with xenon under static conditions exhibits at 298 K two signals resonating at δ_{iso} of 128 and 90 ppm (Figure 2), which

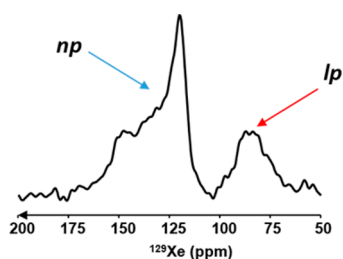


Figure 2. 1D ^{129}Xe direct excitation NMR spectrum of MIL-53(Al) loaded with xenon recorded under static conditions at 298 K.

are assigned to Xe atoms in the *np* and *lp* forms of MIL-53(Al), respectively.²⁹ This assignment agrees with the higher ^{129}Xe isotropic chemical shift in smaller pores for microporous solids.^{37–39} The simulation of the spectrum (Figure S5) yields the ^{129}Xe NMR parameters of the two forms (see Table 1). The

Table 1. ^{129}Xe δ_{iso} , δ_{aniso} , and η_{CSA} Parameters, Defined According to Eqs 1–3, of the Two Forms of MIL-53(Al) at Room Temperature^a

	δ_{iso} /ppm	δ_{aniso} /ppm	η_{CSA}
<i>np</i>	128 ± 5	25 ± 5	0.2 ± 0.1
<i>lp</i>	90 ± 5	N/A	N/A

^aValues were obtained from the simulation of the static lineshapes (Figure S5).

np signal exhibits a relatively large δ_{aniso} value since the pores of this form have a rhomboid shape. On the contrary, no anisotropy is found for the *lp* form owing to the square shape of its pores (Figure 1). The higher symmetry of the pore cross section in the case of the *lp* form induces a smaller constraint than in the *np* form (see Table 1).

Figure S6 shows the variable temperature 1D ^{129}Xe direct excitation NMR spectra of MIL-53(Al) loaded with xenon

between 327 to 237 K. When the temperature decreases from 301 to 237 K, the intensity of the *lp* signal decreases and almost totally vanishes at 237 K. Such variation in signal intensity shows the conversion of *lp* into *np* form for decreasing temperature. Conversely, when the temperature is increased from 301 to 327 K, the signal intensity of the *np* form decreases and that of the *lp* form increases. The evolution of the fractions of xenon atoms adsorbed in the *lp* and *np* forms as a function of the temperature is shown in Figure 3.

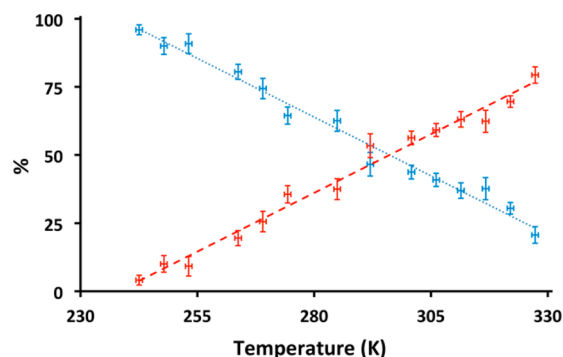


Figure 3. Molar fractions of xenon atoms adsorbed in the *np* (blue) and *lp* (red) forms for MIL-53(Al) loaded with gaseous xenon as a function of the temperature. These were determined from the integrated intensities of the 1D ^{129}Xe NMR signals recorded under static conditions (see Figure S6). The error bars were calculated according to eq S1 for the molar fraction while we estimated an error of 0.7 K for the temperature.

The coexistence of the two phases, for which a single phase is thermodynamically stable according to the phase diagram,⁴⁰ has already been observed²⁹ and is potentially related to the kinetics of xenon adsorption. The presence of xenon equilibrates first the outer shell of the MIL-53(Al) particles. But, the diffusion of xenon through this shell is supposed to be slow. The cores of the particles can be consequently away from thermodynamic equilibrium.⁴¹ Such phenomenon would also explain the hysteresis observed for the absorption and the desorption of xenon in MIL-53(Al).²⁹ This behavior is not taken into account in the osmotic thermodynamic model, which assumes an homogeneous system at complete equilibrium.

The δ_{iso} shift of ^{129}Xe nuclei in the *np* form increases when the temperature decreases (Figure S7). Such variation is typical for adsorbed xenon. The chemical shift originates from the interactions of xenon atoms with the pore surface and from the Xe–Xe interactions inside the pore.^{29,39,42} The isotropic chemical shift of Xe atoms increases due to the reducing of shielding when in contact with the pore walls. In a sealed tube, the amount of adsorbed xenon does not vary much with temperature; however, the residence time of the xenon atoms on the surface increases when the temperature decreases. Because the xenon mobility is reduced at lower temperature, the average chemical shift increases with decreasing temperature. This increase is generally more important for small pores than for large pores since the residence time on the surface of small pores is longer compared to that on the large pores. It is not observed in the present case. In particular, the chemical shift of Xe adsorbed in the *lp* channels slightly decreases with the temperature (Figure S7). This can be due to the slow exchange of Xe atoms between the *lp* and *np* channels. As the

mobility of Xe atoms increases with the temperature, the exchange between the two forms becomes faster.

III.2. 1D ^{129}Xe NMR Spectra under MAS Conditions.

Figure 4a shows the 1D ^{129}Xe direct excitation MAS spectrum

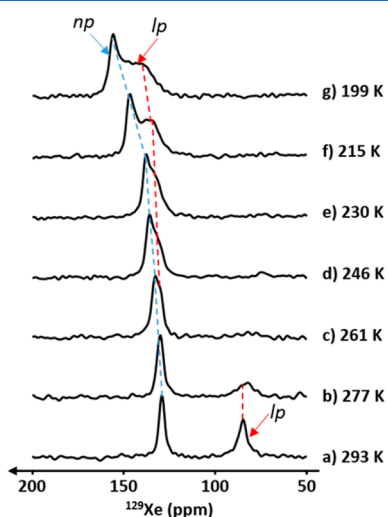


Figure 4. 1D ^{129}Xe direct excitation MAS NMR spectra of MIL-53(Al) loaded with xenon at $\nu_R = 10$ kHz and (a) 293, (b) 277, (c) 261, (d) 246, (e) 230, (f) 215, and (g) 199 K.

of MIL-53(Al) loaded with xenon at 293 K. The ^{129}Xe signals under MAS are narrower (especially for the *np* form) than those under static conditions (compare Figures 2 and 4a) since the MAS averages out the CSA. As observed in the static experiments, the intensity of the *lp* signal resonating around 90 ppm decreases with temperature and disappears at $T \leq 246$ K. Furthermore, the ^{129}Xe MAS spectra acquired at temperature ranging from 261 to 199 K exhibit two overlapping signals with $\delta_{\text{iso}} \geq 130$ ppm (Figure 4c–g). They are assigned to the *np* and *lp* forms for the most and the least shifted signals, respectively. For instance, at 199 K, the isotropic chemical shift of the *np* signal is 155 ppm while the broad signal attributed to *lp* channels resonates at 144 ppm. This new *lp* signal is due to the reverse transformation (*np* \rightarrow *lp*), that is consistent with the phase diagram of MIL-53(Al) in the presence of xenon gas which shows that the *np* form should transform back into *lp* one at low temperature.⁴⁰ This broad signal at 144 ppm is not observed in the static experiments because it is hidden by the broad anisotropic *np* signal. The evolution of the isotropic chemical shift of the *np* and the *lp* forms as a function of the temperature is reported in Figure 5. Values were obtained from the simulation of the spectra under MAS conditions (Figure S8).

III.3. 1D $^1\text{H} \rightarrow ^{129}\text{Xe}$ CPMAS Spectra. 1D $^1\text{H} \rightarrow ^{129}\text{Xe}$ CPMAS experiments have so far only been reported for clathrates and polymers.^{43–45} Here, this experiment has been employed to probe the mobility of xenon atoms in the channels of the MIL-53(Al) compound. The 1D $^1\text{H} \rightarrow ^{129}\text{Xe}$ CPMAS spectra of MIL-53(Al) loaded with gaseous xenon at temperature ranging from 230 to 199 K are shown in Figure 6. These spectra exhibit a single peak assigned to the *np* phase. As already seen in Figure 5, the isotropic chemical shift of the *np* signal increases as the temperature decreases owing to the increase of residence time of Xe atoms in the pores. Furthermore, as already observed in Figure 4, the *np* signal is broader at 215 and 199 K with respect to 230 K. Such

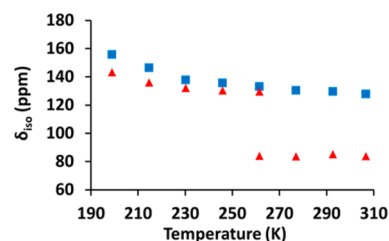


Figure 5. Evolution of δ_{iso} of the *np* form (blue squares) and *lp* form (red triangles) in MIL-53(Al) obtained from the 1D ^{129}Xe direct excitation NMR spectra of MIL-53(Al) loaded with xenon at $\nu_R = 10$ kHz.

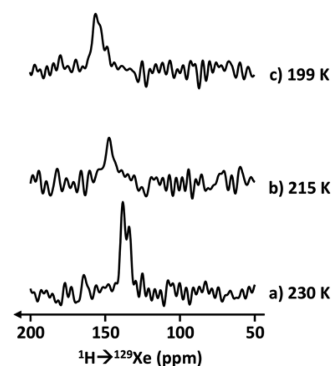


Figure 6. 1D $^1\text{H} \rightarrow ^{129}\text{Xe}$ CPMAS spectra of the *np* form of the MIL-53(Al) loaded with xenon and recorded at $\nu_R = 8$ kHz and (a) 230 K, (b) 215 K, and (c) 199 K.

broadening results in decreased signal intensity. The absence of the *lp* signal in the 1D $^1\text{H} \rightarrow ^{129}\text{Xe}$ CPMAS spectra indicates the high mobility of xenon atoms in the channels of the *lp* form since these motions average out the ^1H – ^{129}Xe dipolar couplings. Furthermore, the signal intensity of the 1D $^1\text{H} \rightarrow ^{129}\text{Xe}$ CPMAS signal of *np* site reaches a maximum after a 8 or 10 ms contact time (Figure S9). By comparison, it has been shown that CPMAS transfers between surface protons and adsorbed ^{129}Xe nuclei in the absence of motions only require contact time of approximately 2 ms.⁴⁶ The longer contact time required here suggests that the xenon atoms adsorbed in the channels of the *np* form of MIL-53(Al) exhibit significant motion on time scales faster than a few milliseconds at 199 K.

III.4. 2D ^{129}Xe EXSY Experiments. 2D ^{129}Xe EXSY experiments have already been employed to study the chemical exchanges between distinct ^{129}Xe environments in MOFs.⁴² Here, this experiment has been employed to investigate the exchange between the *np* and *lp* ^{129}Xe signals. Figure 7 shows the 2D ^{129}Xe EXSY spectrum of MIL-53(Al) loaded with xenon at room temperature. The presence of cross-peaks between the *np* and *lp* signals proves the exchange of xenon atoms between the two forms of the MIL-53(Al). Hence, at room temperature, the xenon atoms diffuse between the channels of *np* and *lp* domains of MIL-53(Al) for a time scale higher than hundreds of milliseconds.

By measuring the intensity of the NMR signals in the 2D EXSY MAS spectra recorded for different τ_{mix} values (see Figures S10 and S11), we estimate that the exchange rate of xenon atoms between the channels of the *lp* and *np* forms is in the order of 20 s^{-1} . This value is comparable to exchange rates of xenon atoms between the pores of NaX and NaY zeolite particles⁴⁷ and in zinc-based MOFs.⁴²

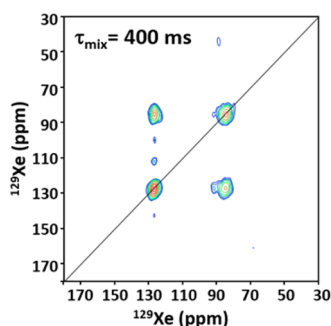


Figure 7. 2D ^{129}Xe MAS EXSY spectrum of MIL-53(Al) loaded with xenon and recorded at $\nu_R = 10$ kHz and room temperature with $\tau_{\text{mix}} = 400$ ms.

III.5. SIR 1D MAS Results. The SIR 1D MAS experiment is an accurate and rapid method to measure the exchange rate between two sites.^{32,33} Introduced for the study of chemical exchange in solution, it has been recently applied to probe the kinetics of lithium mobility in battery systems.⁴⁸ The determination of the exchange rate is faster using SIR experiments than 2D EXSY ones since the SIR experiment can be acquired in approximately the same time as a single 2D EXSY spectrum. Furthermore, the exchange rates determined from SIR experiments are usually more accurate than those extracted from 2D EXSY spectra as the EXSY intensities can be distorted by the t_1 ridge caused by the longitudinal relaxation during the EXSY sequence and these t_1 ridges cannot be eliminated by the phase cycling.^{49,50}

The $T_1(^{129}\text{Xe})$ values of np and lp signals of MIL-53(Al) loaded with xenon were determined at room temperature from NIR experiments (see Figure 8a). In order to estimate the exchange rate, we then carried out SIR experiments under similar conditions. As the lp resonance is broader than the np one, the selective inversion of the np signal is more efficient than the lp one (see Figure S4). The SIR data using a selective inversion of the np signal is shown in Figure 8b. The chemical exchange between the two ^{129}Xe environments causes (i) a rapid decrease of the lp signal as well as (ii) a simultaneous increase of the np one for short τ delay ($\tau < 0.2$ s). The fit of SIR data by fixing $T_1(^{129}\text{Xe})$ parameters to their values determined from NIR yields $k_{\text{exch}} = 43 \pm 6 \text{ s}^{-1}$. This value

agrees with the rough estimate derived from the 2D EXSY experiments.

IV. CONCLUSION

We have investigated the np – lp transition of MIL-53(Al) loaded with gaseous xenon and the mobility of the xenon atoms in this flexible MOF. ^{129}Xe direct excitation NMR experiments under static and MAS conditions have shown that as the temperature decreases, the amount of lp form decreases and almost vanishes at 237 K and increases again for $T \leq 230$ K. Such trends are consistent with the previously reported phase diagram.⁴⁰ Nevertheless, a major difference lies in the coexistence of the lp and np phases for most investigated temperatures. This heterogeneity of the system is ascribed to the kinetics of xenon adsorption. $^1\text{H} \rightarrow ^{129}\text{Xe}$ CPMAS experiments show the restricted mobility of xenon atoms in the np channels at $T \leq 230$ K. Nevertheless, the long required contact times indicates that xenon atoms in such environment move on time scale faster than a few milliseconds. 2D EXSY spectra demonstrate the exchange of xenon atoms between the two forms of MIL-53(Al) at room temperature. The rate for this exchange was measured by SIR and is equal to $43 \pm 6 \text{ s}^{-1}$.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b06006.

Pulse sequences used in the manuscript, 1D ^{129}Xe spectra of MIL-53(Al) recorded under static conditions, variation of the ^{129}Xe isotropic chemical shifts as a function of the temperature, 1D $^1\text{H} \rightarrow ^{129}\text{Xe}$ CPMAS build-up curves recorded at 153 K, 2D ^{129}Xe EXSY spectra and the corresponding theory (PDF)

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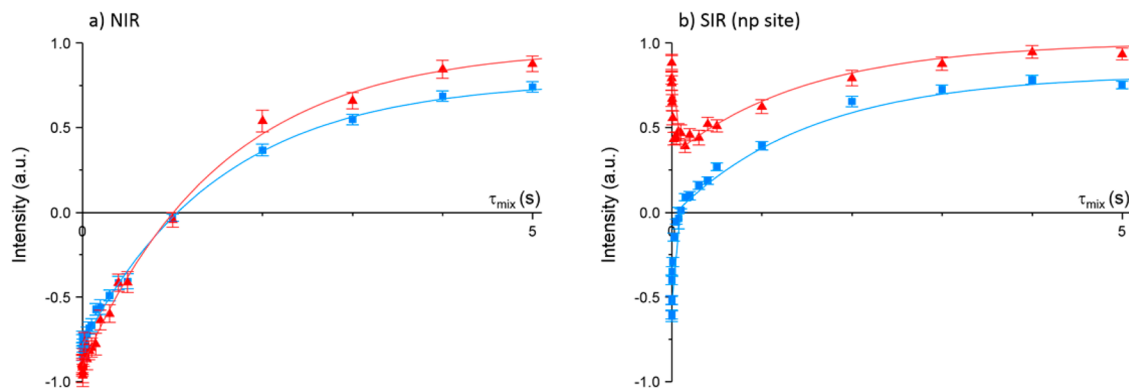


Figure 8. (a) NIR and (b) SIR experiments on MIL-53(Al) loaded with xenon at $\nu_R = 10$ kHz and room temperature. For SIR experiment, the np signal was selectively inverted. The experimental signal intensities are displayed as symbol (blue squares for np form and red triangles for lp one). The best fit curves are displayed as continuous lines (blue for np form and red for lp one). The error bars were taken as the noise standard deviation of the signals.

Notes

The authors declare no competing financial interest.

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