Exploiting Molecular Dynamics of Adsorbed CO₂ Species in Amine-Modified Porous Silica by Solid-State NMR Relaxation

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ABSTRACT: Previous studies on CO₂ adsorbents have mainly addressed the identification and quantification of adsorbed CO₂ species in amine-modified porous materials. Investigation of molecular motion of CO₂ species in confinement has not been explored in depth yet. This work entails a comprehensive study of molecular dynamics of the different CO₂ species chemi- and physisorbed at amine-modified silica materials through the determination of the rotating frame spin–lattice relaxation times (T₁ρ) by solid-state NMR. Rotational correlation times (τRC) were also estimated using spin relaxation models based on the Bloch, Wangness, and Redfield and theBloembergen– Purcell–Pound theories. As expected, the τRC values for the two physisorbed CO₂ species are considerably shorter (32 and 20 μs) than for the three identified chemisorbed CO₂ species (162, 62, and 123 μs). The differences in molecular dynamics between the different chemisorbed species correlate well with the structures previously proposed. In the case of the physisorbed CO₂ species, the τRC values of the CO₂ species displaying faster molecular dynamics falls in the range of viscous liquids, whereas the species presenting slower dynamics exhibit T₁ρ and τRC values compatible with a CO₂ layer of weakly interacting molecules with the silica surface. The values for chemical shift anisotropy (CSA) and H–13C heteronuclear dipolar couplings have also been estimated from T₁ρ measurements, for each adsorbed CO₂ species. The CSA tensor parameters obtained from fitting the relaxation data agree with the experimentally measured CSA values, thus showing that the theories are well suited to study CO₂ dynamics in silica surfaces.

1. INTRODUCTION

Global warming and associated climate change are a major concern for scientists, politicians, and general public, becoming one of the most important challenges of humankind in the 21st century. Different reports and studies from Intergovernmental Panel on Climate Change, among others, have identified CO₂ emissions to be primary responsible for global warming. Among many of the identified sources, flue gas emissions have played a major role contributing to the rising of CO₂ levels in the atmosphere. Therefore, its scavenging from post-combustion gases combined with other greenhouse gas removal strategies is compulsory to curtail CO₂ emissions.

Different materials have been proposed, with amine-modified porous silica (AMPS) sorbents emerging as a promising alternative to the use of liquid amines for CO₂ capture. These materials show advantageous features for CO₂ capture in post-combustion applications, such as high selectivity and capture capacity toward CO₂ at low partial pressures even in the presence of moisture. In order to improve the design and optimization of these materials, gathering knowledge on the nature and dynamics of physi- and chemisorbed CO₂ species formed is crucial. Several studies have been published in recent years addressing the structure of the different types of CO₂-amine adducts formed in amine-modified silicas (AMPS), mainly performed by Fourier transform infrared (FT-IR) spectroscopy and nuclear magnetic resonance (NMR). However, the unambiguous assignment of CO₂ species under certain conditions is still a challenge wherein the tandem use of solid-state NMR and density functional theory (DFT) has provided some of the most prolific results. These contributions confirmed the formation of chemisorbed CO₂ species of several types in CO₂-adsorbed materials containing distinct amine loadings, in which the carbamic acid and alkylation amine carbamate are the predominant CO₂ species. Recently, our group was able to identify, at least, three new physiosorbed CO₂ species in SBA-15 mesoporous silica functionalized with a primary amine, 3-aminopropytriethoxysilane (APTES@sBA-15) combining relaxation and quantitative NMR.

Although the study of CO₂ speciation in AMPS has been reported, information on CO₂ molecular dynamics properties is still scarce. FT-IR or X-ray diffraction methods are...
Figure 1. (a) Schematic molecular representations correspond to the three different chemisorbed species (A–C) found in APTES@SBA-15 silica loaded with $^{13}$CO$_2$ ($p = 770$ Torr) as proposed by previous studies. The drawing scheme on the right is a simplified picture of a CO$_2$-filled pore of the silica after adsorption, as proposed by our recent work. The different physisorbed species D, E, and F are represented in black, red, and orange colors, respectively. The chemisorbed species are represented by the simplified structures in white. (b) $^{13}$C CPMAS (purple) and MultiCP (blue) NMR spectra of dry APTES@SBA-15 loaded with $^{13}$CO$_2$ at $p = 770$ Torr. The intensity of the resonance associated to the physisorbed species is low in CPMAS but clearly polarized by MultiCP, contributing to the peak at around 125 ppm.

useful to investigate structural features but have limitations when seeking to understand the molecular dynamics of adsorbates confined in porous systems. Our group has recently investigated CO$_2$ dynamics in silicas for the first time by NMR relaxation. Solid-state NMR relaxation techniques have proven to be one of the most valuable approaches, particularly in probing the dynamics of biomolecular systems, to observe fluctuations of local environments in adsorbed molecules, often yielding information about local interactions and the motional behavior of molecular moieties. For amorphous materials (like silicas) and non-rigid solids, the correlation times of molecular motions measured by NMR are expected to be in the range of the $\mu$s–ms timescale. Therefore, the dynamics of adsorbed CO$_2$ in AMPS may be investigated by rotating frame spin–lattice relaxation ($T_{1p}$) measurements. Recent theoretical developments provide the analytical treatment of $T_{1p}$ as a function of the sample rotation frequency to estimate actual correlation times and amplitudes of motion in solids, particularly in the study of slow protein dynamics.

In this article, we take inspiration on the NMR relaxation studies demonstrated in protein dynamics and perform for the first time $T_{1p}$ measurements to explore the dynamics of physically and chemisorbed CO$_2$ species formed at the silica surface, applying the theoretical model proposed by Kurbanov et al. This formalism estimates average $^{13}$C–H distances and $^{13}$C chemical shift anisotropy (CSA) parameters. The study of $T_{1p}$ allows assessing the correlation times for each $^{13}$CO$_2$ species, thus providing a molecular level insight into the dynamics of each CO$_2$ species formed in AMPS materials.

2. MATERIALS AND METHODS

2.1. Material Preparation. SBA-15 was synthesized according to a procedure reported previously by our group. First, (EO)$_{20}$(PO)$_{20}$(EO)$_{20}$ copolymer (4.0 g; Aldrich) was dissolved in a 1.6 M solution of HCl (126 cm$^3$). Next, tetraethyl orthosilicate (9.1 cm$^3$; Aldrich) was added to this solution with constant stirring. The solution was then stirred at 40 °C for 20 h and subsequently heated at 100 °C for 24 h, under static conditions. Afterward, the solution was filtered, and the obtained solid was washed with deionized water and dried in an oven at 40 °C. The solid was calcined at 550 °C for 5 h with a heating ramp of 1 °C/min. The resulting SBA-15 product was stored in a desiccator for future use.

The calcined SBA-15 was functionalized with a primary amine, APTES (Sigma-Aldrich, purity > 98%). 2 g of SBA-15 was introduced in a closed reflux apparatus connected to a vacuum line and heated to 150 °C for 2 h. After cooling, nitrogen was introduced into the system prior to the opening of the reflux apparatus, and SBA-15 was refluxed with 100 cm$^3$ of dry toluene (Alfa Aesar, 99.8%) containing 9 mmol of APTES for 24 h in a nitrogen atmosphere. The resulting material (APTES@SBA-15) was purified by Soxhlet extraction with dry toluene, to remove the unreacted amino-alkoxysilane, and finally dried under vacuum, at 120 °C for 24 h.

2.2. $^{13}$CO$_2$ Sorption Procedure. The sorption apparatus comprises a laboratory-made high-vacuum line, connected to a turbomolecular pumping station (HiCube 80, Pfeiffer Vacuum), capable of vacuum greater than $10^{-3}$ Pa. A borosilicate glass cell was connected to the vacuum line and served as an enclosure for an NMR rotor to allow degassing and heating zirconia NMR rotors up to 300 °C under high vacuum. The heating was performed with a laboratory-made oven connected
to a power controller (Eurotherm 3116), and the temperature
was measured with a thermocouple. The desired gas was
introduced into the system from the canister connected to the
vacuum line and the cell. The pressure inside the cell was
measured with a capacitance transducer (MKS instruments,
Baratron 722B).

All samples of APTES@SBA-15 were packed in zirconia
NMR rotors, enclosed into the sorption apparatus, and dried
by degassing and heating (150 °C, 3 h, ramp of 2.5 °C/min)
under vacuum. After cooling down under vacuum, 13CO2
(Cortecnet, 99 atom % 13C; <3 atom % 13O) was introduced
into the system at a partial pressure of 770 Torr and allowed to
equilibrated for 4.5 h. Finally, the NMR rotor was closed inside
the cell, and only then, the cell was opened to remove the rotor
for NMR measurements.

2.3. Solid-State NMR Measurements. All 13C NMR
spectra were acquired on a Bruker Avance III 400 spectrometer
operating at B0 field of 9.4 T, with a 13C Larmor frequency of
100.6 MHz. All experiments were performed on a double-
resonance 4 mm Bruker magic-angle-spinning (MAS) probe at
a MAS frequency of 10 kHz and under room temperature
conditions. Samples were packed into ZrO2 rotors with Kel-F
caps. 13C chemical shifts are quoted in parts per million (ppm)
from α-glycine (secondary reference, C==O at 176.03 ppm).

The 13C cross-polarization MAS (CPMAS) spectrum, as shown
in Figure 1, was acquired under the following experimental conditions:
the 1H π/2 pulse length was set to
3.0 μs corresponding to a radio frequency (rf) of ~83 kHz; the
CP step was performed with a contact time (CTc) of 3000 μs
using a 50–100% RAMP shape pulse in the 1H channel and using a 55 kHz square shape pulse on the 13C channel; the
recycling delay (Dt) was 7.5 s. During the acquisition, SPINAL-64
decoupling was employed at a rf-field strength of
70 kHz. The total number of scans was 256. The multiple cross
polarization (multiCP) sequence, as shown in Figure S1, was
acquired under the following experimental conditions: the 1H π/2 pulse length was set to
3.0 μs corresponding to a radio frequency (rf) of ~83 kHz; the
CP step was performed with a contact time (CTc) of 3000 μs
using a 50–100% RAMP shape pulse in the 1H channel and using a 55 kHz square shape pulse on the 13C channel; the
recycling delay (Dt) was 7.5 s. During the acquisition, SPINAL-64
decoupling was employed at a rf-field strength of
70 kHz. The total number of scans was 256.

13C T1p times were measured using the NMR experiments,
as shown in Figure S1. These two different approaches were
used depending on the type of adsorbed CO2 species. The conventional method (Figure S1a) was based on CP-MAS
for chemisorbed species and a modified version of multiple
cross polarization (multiCP, Figure S1b) for the physisorbed
fraction. The labels used for the chemisorbed (A–C) and
physisorbed (D–F) species are the same as reported in our
previous work. The species F was found to exhibit relaxation parameters (T1) compatible with a highly dynamic
environment confined in a porous media.

To measure the 13C T1p after generating 13C magnetization by
CPMAS (species A, B, C, and D) or multiCP (species D
and E), the 13C spins were locked in the x,y-plane of
the rotating frame for a variable time (τ) (Table S2) by applying a
locking pulse. Under these conditions, the total locked magnetization in the transverse plane (Mt) decays exponentially
with a specific time constant T1p influenced by the modulation of the transverse relaxation Hamiltonian induced
by molecular motions. The remaining Mt magnetization after
different locking-field τ durations is fitted by the equation

\[ M_t = \sum_{i=1}^{n} M_{0,i} e^{-t/T_{1p,i}} \]  
(2.1)

where \( M_{0,i} \) is the initial locked magnetization in the transverse
plane at thermal equilibrium of each 13CO2 species, \( T_{1p,i} \) is the total number of 13CO2 species, and \( T_{1p,i} \) is the spin–lattice
relaxation time in the rotating frame of each 13CO2 species. During the application of the locking field, 1H decoupling
was not applied to avoid interferences on the relaxation mechanism. In our study, to facilitate the analysis, eq 2.1 was
linearized as

\[ \ln(M_t) = \sum_{i=1}^{n} \ln(M_{0,i}) - \tau/T_{1p,i} \]  
(2.2)

The T1p values (Table S3) were extracted by fitting the
linearized eq 2.2 to the experimental data (Figures S4–S9). The estimated fitted errors are below 10%.

The overlapping resonances of the chemisorbed 13CO2
species centered at 164, 160, and 154 ppm were deconvoluted
as shown in Figure S1. These two different approaches were
used depending on the type of adsorbed CO2 species, T1p was measured as a function of the rf locking field strength (ωr). For each
measurement, the 13C rf field strength during spin-lock was
carefully calibrated using a nutation experiment in glycine. The values of \( ωr \) used for the correlation time study of each
adsorbed component were chosen around the condition \( ωr = γB_L \) where \( B_L \) is the local magnetic field amplitude driving the
relaxation mechanism in the rotating frame. The main interaction driving the T1p relaxation is CSA since homonuclear and heteronuclear dipolar couplings are negligible for physisorbed CO2 species E and F due to their high
mobility. Therefore, for E and F species, Bloembergen–
Parcell–Pound theory (BPP theory) can be applied. The
used \( ωr \) frequencies for each CO2 species are listed in Table S2.

The dependence of R1p with respect to τc for the fast
components E and F falls within the fast motional regime (τc ≪ T1).
In this case, the expression for R1p is given by

\[ R_{1p} = \frac{1}{T_{1p}} = \frac{3/4(γωrδ)^2}{(1 + 4ωr^2τ_c^2)} \]  
(2.3)

where γ is the gyromagnetic ratio of 13C, δ is the reduced anisotropy δ = δx = (1/3) (δxy + δy + δz), and the rest of the
parameters are the same as defined above. For species E, the data obtained at different \( ωr \) (Table S3) was fitted with eq 2.3
to extract τc. In the case of species F, weak locking field pulses to measure T1p are needed to assess its fast motional regime,
which is currently not possible with our NMR spectrometer.

For the chemisorbed CO2 species A, B, C, and D their
dynamical behavior falls within the intermediate case (τc ≫ T1).
Considering the 13C nuclei of these species are isolated,
that is, without covalently bonded protons and that they
involve sp/sp2-hybridized carbons with considerable CSA
contribution, the most suitable model to explain the 13C
relaxation of these species combines CSA and 13C–1H
heteronuclear dipolar coupling contributions. The expression
used to fit the experimental data is derived from the Bloch,
Wangness, and Redfield theory (BWR theory) accounting for the considerations from Kurbanov et al., in which the MAS frequency and the rf offset contributions are included. In fact, the MAS dependence of $R_{1p}(1/T_{1p})$ was crucial to obtain good fittings of our experimental data, which provide molecular dynamic processes in the range of microseconds to milliseconds.13,38,47,48

The $^{13}$C relaxation rate associated to CO$_2$ chemisorbed species, considering an off-resonant $\omega_1$ locking-field and MAS frequency ($\omega_M$), is given by

$$R_{1p(\text{off})} = R_{1p}^{\text{CSA}} + R_{1p}^{\text{IS}}$$

(2.4)

Equation 2.4 is the sum of the relaxation rates under CSA and heteronuclear dipolar mechanisms. According to Rovo, the $R_{1p}^{\text{CSA}}$ is given by

$$R_{1p}^{\text{CSA}} = \cos^2 \theta R_{1p}^{\text{CSA}} + \sin^2 \theta R_{1p}^{\text{CSA}}$$

(2.5)

with

$$R_{1p}^{\text{CSA}} = \frac{2}{15} (\delta \omega_1)^2 f(\omega_1)$$

(2.6)

and $R_{1p}^{\text{IS}}$ written as

$$R_{1p}^{\text{IS}} = \frac{(\delta \omega_1)^2}{135} (2f(\omega_1 - 2\omega_1) + 4f(\omega_1 - \omega_1)
+ 4f(\omega_1 + \omega_1) + 2f(\omega_1 + 2\omega_1) + 9f(\omega_1)$$

(2.7)

$\delta$ is the reduced CSA, $\omega_1$ is the resonant frequency of the $^{13}$C spin in question, and $\theta$ is the off-resonance angle (the angle between the $B_0$ and $B_1$ fields). $f(\omega)$ is the spectral density functions where $\omega$ can be replaced by different frequency arguments.

Analogous expressions for the heteronuclear dipolar relaxation mechanism can be derived

$$R_{1p}^{\text{IS}} = \cos^2 \theta R_{1p}^{\text{IS}} + \sin^2 \theta R_{1p}^{\text{IS}}$$

(2.8)

with

$$R_{1p}^{\text{IS}} = \frac{b_{13}^2}{10} \left( f(\omega_1 - \omega_1) + 3f(\omega_1) + 6f(\omega_1 + \omega_1) \right)$$

(2.9)

and

$$R_{1p}^{\text{IS}} = \frac{b_{13}^2}{10} \left( \frac{2}{3} f(\omega_1 - 2\omega_1) + \frac{4}{3} f(\omega_1 - \omega_1) + \frac{4}{3} f(\omega_1 + \omega_1)
+ 2f(\omega_1 + 2\omega_1) + f(\omega_1 + \omega_1) + 3f(\omega_1) + 6f(\omega_1) \right)$$

(2.10)

where $b_{13}$ is the $^{13}$C–$^1$H dipolar coupling constant and $\omega_1$ is the $^1$H resonant frequency.

Considering the simplest model with a bond vector motion with only one correlation time and an axially symmetric CSA tensor, $f(\omega)$ both for the dipolar and CSA relaxation mechanisms can be written as

$$f(\omega) = \frac{2}{5} \left( 1 - S^2 \right) \tau_1$$

(2.11)

$S^2$ is the generalized order parameter describing the amplitude of the motion, and it satisfies the condition $0 \leq S^2 \leq 1$, where $S^2 = 0$ and $S^2 = 1$ represent the fully disordered and completely rigid states, respectively.32,45 In the present work, considering the amorphous character of the silica as fully disordered, condition $S^2 = 0$ has been used. We have used these equations to fit the experimental $T_{1p}$ dependence on the $\omega_1$ spin-lock field. For the case of A, B, and C, the off-resonance (eq 2.4) was used to fit their $T_{1p}$ evolution with $\omega_1$, while for species D, data were fitted considering only the on-resonance part. As a result, correlation times and $b_{13}$ and $\delta$ values are extracted for these four $^{13}$CO$_2$ species.

3. RESULTS AND DISCUSSION

3.1. CO$_2$ Speciation after Adsorption in APTES@SBA-15. Figure 1 shows the $^{13}$C CPMAS (purple) and multiCP (blue) spectra of APTES@SBA-15. Both spectra display four peaks, corresponding to the chemisorbed and physisorbed CO$_2$ species, which have been addressed in previous studies.15,16,20,22–24,28,31,53 Nevertheless, we provide a brief overview of their assignment for the sake of simplicity. The peak at $\sim$125 ppm arises from physisorbed $^{13}$CO$_2$ at the silica surface, corresponding to confined CO$_2$ in the pore. The full characterization of the three physisorbed CO$_2$ species, dubbed D, E, and F, contributing to this resonance ($\sim$125 ppm) has been performed previously using quantitative CSA and $T_1$ relaxation analyses.14 The other three resonances at $\sim$154 ppm (species A), $\sim$160 ppm (species B), and $\sim$164 ppm (species C) are assigned according to our previous studies,20–24,31 that is, to carboxylic acid species (A, B) and ammonium carbamate species (C). In the next sections, we employ $T_{1p}$ to assess correlation times for each CO$_2$ species, which are more facile to determine for an accurate estimation of the dynamics of the adsorbed CO$_2$ species.

3.2. $T_{1p}$ of CO$_2$ Species Formed in $^{13}$CO$_2$-Adsorbed APTES@SBA-15. The measured $T_{1p}$ values of CO$_2$ species A–F are listed in Table 1. The first clear observation is that $T_{1p}$ values for physisorbed species D–F are considerably longer than the values for chemisorbed species A–C. This is expected since the mobility of the former species is higher than the latter ones. The motional averaging of relaxation mechanisms (mainly heteronuclear dipolar couplings and CSA) causes long $T_{1p}$ relaxation times for the species D–F. Particularly, long $T_{1p}$ is obtained for species E and F (Table 1), which according to our previous work41 are confined CO$_2$ phases with liquid-like and gas-like $T_1$ relaxation rates. CO$_2$ species D is engaged in H-bonds with the chemisorbed CO$_2$ layer formed on the silica surface.20,23,31 These interactions are sufficient to restrict the mobility of this species opening routes for a more efficient spin relaxation through dipolar and CSA mechanisms. CO$_2$ species F undergoes faster dynamics compared to CO$_2$ species D–F.
species D and E; thus, a much longer $T_{1p}$ value is expected for this species (Table 1).

As for the chemisorbed CO$_2$ species A–C, larger $T_{1p}$ differences are found between A and B/C though. These discrepancies can be explained invoking the strength of interactions and the different molecular dynamics. Because species B and C refer to paired amines, the density of coupled $^1$H spins surrounding these species is higher. The magnitude of the heteronuclear dipolar couplings of B and C is presumably larger than that in the case of species A, offering a more efficient $^{13}$C relaxation route for B and C.

In addition, A interacts with silanol groups at the silica surface through hydrogen bonds, leading to a strong restriction in motion, which therefore translates in a higher $\tau_c$ value as it will be discussed ahead.
3.3. Correlation Times ($\tau_c$) of the Adsorbed $^{13}$CO$_2$ Species in APTES@SBA-15. Relaxation rates ($R_1p$) were evaluated by acquiring $T_{1p}$ as a function of the spin-lock field. The resulting curves were fitted (Figure 2) using the relaxation models described in Section 2.4. In the case of the chemisorbed CO$_2$ species A, B, and C, the data were fitted using eq 2.4. For the physisorbed CO$_2$ species D, the on-resonance part of eq 2.4 was employed, whereas for the physisorbed species E, eq 2.3 was used to fit the data. Detailed parameters obtained from data fittings including estimated correlation times for each CO$_2$ species can be found in Table 1 and Figure 3. In the case of CO$_2$ species F, the correlation times could not be retrieved due to the difficulties in measuring $T_{1p}$ at different $\omega_1$ spin-lock field values. Particularly, when the spin-lock field values are several orders of magnitude higher than the size of the interaction driving the relaxation mechanism, or when the locking field is weak, it renders strongly inhomogeneous pulses.

As expected, the shortest $\tau_c$ is obtained for the physisorbed CO$_2$ species D ($32 \mu$s) and E ($20 \mu$s). The obtained values agree with the mobile character of these species as they are weakly interacting inside the pores. However, the obtained $\tau_c$ values are much longer than the values reported in the literature for CO$_2$ in liquid and gas states (typically in the range of picoseconds to nanoseconds). These discrepancies in correlation times between bulk and confined CO$_2$ reveal the dramatic effect on the dynamics of gases adsorbed in porous materials. The $\tau_c$ value for D is slightly longer than for E, most likely due to the effect of H-bond interactions hindering the motion of CO$_2$ species D.

As for chemisorbed species A, B, and C, their $\tau_c$ values are 2–8 times longer than that for the physisorbed D and E species, thus highlighting the differences in mobility between both fractions. The comparison of the $\tau_c$ values among the different chemisorbed species reveals striking differences in their molecular dynamics. Species A exhibits the longest $\tau_c$...
(162 μs), which is in good agreement with rigid structures reported previously, where the formation of either carboxylic acid species stabilized by H-bonds with neighboring silanol groups or silylpropylcarbamate species are proposed. The formation of both species implies a strong interaction with the silica surface and, therefore, strong molecular rigidity that translates into long correlation times as found in the present work. Species C (\( \tau_c = 123 \mu s \)) is more rigid than B (\( \tau_c = 62 \mu s \)) since the former might be further stabilized by the formation of H-bond with neighbor silanol groups (Figure 1).

3.4. NMR Interactions Obtained from \( R_{1\rho} \) Analysis.

The curve fitting of relaxation rates allows extracting important parameters such as \( b_{\text{IS}} \) and \( \delta \), which provide further structural information regarding the different CO\(_2\) species (Table 1). This information is complementary to the determined correlation times further aiding to investigate the CO\(_2\) structure in confined spaces.

The fitted \( \delta \) values obtained for all the chemisorbed CO\(_2\) species (A: \( \delta = 71.9 \) ppm, B: \( \delta = 74.6 \) ppm, and C: \( \delta = 49.3 \) ppm) are in good agreement with previously measured values reported elsewhere\(^{22,23,26}\) (A: \( \delta = 78 \) ppm, B: \( \delta = 72 \) ppm, and C: \( \delta = 52 \) ppm). The similarity in the \( \delta \) values for A and B reflects the fact that both possess similar chemical structures (carboxylic acid). However, differences in molecular dynamics and structural flexibility exhibited by both species impose different modulation of the CSA relaxation pathways, giving rise to distinct \( \tau_c \) values. For C, the estimated \( \delta \) value is very different compared to both species A and B. This is expected as the CO\(_2\) species C contains a carbamate ion pair, instead of a carboxylic acid moiety. \( \tau_c \) values for species C and A show the same order of magnitude as both species are engaged in additional interactions supposedly with nearby silanol groups from the silica surface.\(^{22,23,26}\) In the case of species D, the estimated \( \delta \) was 57.7 ppm, which matches approximately the value measured previously (\( \delta = 57.0 \) ppm) by Vieira et al\(^3\) through \(^{13}\)C CSA MAS NMR. A \( \delta = 334.5 \) ppm has been measured for pure CO\(_2\) gas at low temperatures (10–20 K), under vacuum (2–4 \( \times \) \( 10^{-6} \) Torr)\(^{22,23,26}\) and has been used by other studies to estimate the \( \tau_c \) of CO\(_2\) confined in microporous solids.\(^{60}\) The discrepancy between the \( \delta \) value measured for CO\(_2\) species D (a gaseous like CO\(_2\) species judging from the \( \tau_c \) values) in the present work and the previously reported value\(^{60}\) can be ascribed to different reasons. First, in our work, we are dealing with mesoporous materials instead of microporous. Second, the temperature and pressure conditions in both studies are different. Finally, the importance of the intermolecular interactions established between the CO\(_2\) molecules with the silica surface in AMPS\(^{14}\) may have an impact.\(^{31}\) The estimated \( \delta \) value for the physisorbed CO\(_2\) species E was 0.2 ppm (Table 1), using eq 2.3 and considering the CSA interaction as the main relaxation source.

In addition to the CSA interaction, the relaxation model for CO\(_2\) species A–D also involves the \(^1\)H–\(^{13}\)C dipolar couplings as an extra relaxation pathway. Due to the proximity of these species to the \(^1\)H spins belonging to the grafted alkylamine chains, \(^{13}\)C spins from species A–D are thus strongly coupled with nearby protons. Therefore, the values of the \(^1\)H–\(^{13}\)C dipolar couplings for the A-D species with \(^1\)H in their vicinity were estimated from the \( R_{1\rho} \) curve fittings. For CO\(_2\) species A, a \( b_{\text{IS}} \) of 6949 Hz was obtained, which corresponds to an average \(^1\)H–\(^{13}\)C distance of 1.6 Å (Figure 3). In the case of B and C, the estimated \( b_{\text{IS}} \) values were 15,269 and 22,132 Hz, accounting for an average distance of 1.2 and 1.1 Å, respectively. These average \(^1\)H–\(^{13}\)C distances support the proposed models (Figure 1) for the chemisorbed species A, B, and C. B and C are species involving paired amines; therefore, their proton densities are higher compared to species A, which involves a single amine residue. The estimated \( b_{\text{IS}} \) for species D is 3962 Hz (average \(^1\)H–\(^{13}\)C distance of 2.2 Å), a much lower value compared to A, B, and C as this species is far more mobile (i.e., weaker dipolar coupling).

4. CONCLUSIONS

This work demonstrates that relaxation studies based on \( T_{1\rho} \) measurements are a powerful tool to investigate the dynamics of chemi- and physisorbed CO\(_2\) species formed in AMPS. We observe that the three chemisorbed CO\(_2\) species (A, B, and C) possessing the highest rigidity give rise to the shortest \( T_{1\rho} \) values (4.7, 1.1, and 1.4 ms); a CO\(_2\) species with higher flexibility corresponding to the weakly interacting physisorbed CO\(_2\) species D exhibits an intermediate \( T_{1\rho} \) value (8.1 ms); finally, the highly dynamic physisorbed CO\(_2\) species E and F possess the longest \( T_{1\rho} \) values (10.0 and 44.0 ms).

Furthermore, the dependence of the \( T_{1\rho} \) with respect to the locking field was also studied allowing to retrieve correlation times (\( \tau_c \)) which provide further information on the dynamics of CO\(_2\) confined in AMPS. The variations in \( \tau_c \) values could eventually be correlated to the differences in desorption energy for the different species. We believe the knowledge about the dynamical properties of each CO\(_2\) species could then be used for the optimization of the regenerability of the sorbent material. The experimental data were fitted using either the BPP theory for the physisorbed CO\(_2\) species E or the BWR theory for the CO\(_2\) species A–D. This theoretical analysis also allowed us to extract \( b_{\text{IS}} \) and \( \delta \) values, providing further insights into CO\(_2\) dynamics and CO\(_2\) speciation. This analysis was impractical for CO\(_2\) species F due to its fast dynamics, which requires weak rf fields beyond the instrumental capability of a typical solid-state NMR spectrometer. The extracted NMR parameters obtained from \( R_{1\rho} \) curve fitting agree well with the ones obtained from previous studies combining solid-state NMR and DFT calculations,\(^{22,23,31}\) thus consolidating our knowledge concerning the structure of CO\(_2\) adsorbed in porous materials.

The obtained \( \tau_c \) values corresponding to physisorbed CO\(_2\) species D and E (32 and 20 μs) show typical molecular dynamics very close to a viscous liquid (Figure 4), whereas chemisorbed species A, B, and C present a higher rigidity and therefore longer \( \tau_c \) values (162, 62, and 123 μs), as typically observed in amorphous solids (Figure 4). The dispersion in the \( \tau_c \) values is also higher among chemisorbed than that in physisorbed CO\(_2\) species. The estimated \( \tau_c \) value for A indicates that this species has the strongest rigidity, owing to its engagement in multiple H-bonds with silanol groups. Furthermore, we show that the \( T_{1\rho} \) relaxation mechanism in the chemisorbed CO\(_2\) species is mainly driven by a combination of heteronuclear dipolar and CSA interactions. The largest \( b_{\text{IS}} \) values estimated for CO\(_2\) species B and C suggest they are surrounded by a dense protonated environment. On the other hand, species A possesses a smaller \( b_{\text{IS}} \) (6949 Hz) value compared to both B (15269 Hz) and C (22132 Hz), thus pointing toward the existence of a less protonated environment surrounding those CO\(_2\) species. The estimated \( b_{\text{IS}} \) value for physisorbed species D (3962 Hz) is also compatible with CO\(_2\) molecules weakly interacting with the silica surface.
The authors declare no competing financial interest.

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