Adsorption Forms of CO₂ on MIL-53(Al) and NH₂-MIL-53(Al) As Revealed by FTIR Spectroscopy

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Supporting Information

ABSTRACT: Adsorption of CO₂ on MIL-53(Al) and NH₂-MIL-53(Al) has been studied by Fourier transform infrared (FTIR) spectroscopy at different temperatures and equilibrium pressures. For better interpretation of the spectra, 13CO₂ was also utilized. It is established that with both samples at low coverages CO₂ forms O-bonded complexes with the structural OH groups (OH···O⁻²⁻CO). These species are characterized by ν₁(12CO₂) at 2337–2338 cm⁻¹ and two ν₂(12CO₂) modes around 662 and 650 cm⁻¹. Simultaneously, the ν(OH) modes of the hydroxyl groups are red-shifted, while the δ(OH) modes are blue-shifted. At higher coverages (OH···O⁻²⁻CO) dimeric species are formed and this leads to a decrease of the ν₁(CO₂) frequency by 2–4 cm⁻¹. This change is due to vibrational interaction as proven by the observation that the frequency remains practically unaffected for (OH···O⁻²⁻CO) (OH···O⁻³⁻CO) dimeric species. Interaction between dimers leads to additional slight decrease of the value of ν₁(CO₂). In parallel with the CO₂ adsorption a partial transformation of the material from large-pore to narrow-pore form occurs. Far before CO₂ interacts with all hydroxyl groups, polymeric CO₂ species are produced within the MIL-53(Al) sample. They are characterized by a split ν₁(CO₂) mode with a pronounced component at 2340 cm⁻¹. The formation of these species involves some of the dimers and is accompanied by a reopening of the MIL-53 structure. Analysis of the shift of the OH modes led to the conclusion that the polymeric moiety interacts strongly with one OH group and more weakly with several other hydroxyls. No polymeric species were observed with the NH₂-MIL-53(Al) sample which is associated with the more stable narrow-pore structure of this material. However, evidence of interaction between CO₂ and the hydroxyls H-bonded to amino groups was found.

1. INTRODUCTION

Presently, one of the most widely used methods for CO₂ capture is its absorption in liquids. However, the process suffers from some drawbacks, e.g., contamination of the gas flow with solvent vapor and fast degradation of the absorbent. Porous materials, such as amine-functionalized silica, have been alternatively proposed. Recently, many hopes are concentrated on the development of metal–organic frameworks (MOFs) as materials for CO₂ capture.†

To be efficient, the adsorbent should bind CO₂ strongly enough, but on the other hand, the strength of adsorption should not be very high in order to allow easy regeneration. Therefore, detailed knowledge of the way of CO₂ interaction with different MOFs is of crucial importance. The problem is usually tackled by using complementary experimental in situ techniques (e.g., X-ray and neutron diffraction, Fourier transform infrared (FTIR), Raman, and solid state NMR spectroscopies, adsorption measurements) with theoretical modeling. Among the numerous investigations, valuable information can be obtained from vibrational spectroscopy studies. Irrespective of the serious achievements, however, many questions are still disputable and need resolving.

Carbon dioxide is a linear triatomic molecule with a D₁h symmetry (d₁₋₋O = 0.1163 nm). Although CO₂ has a zero dipole moment, it is a charge-separated molecule with significant nonzero bond dipole moments and a large quadrupole moment.² The CO₂ molecule possesses four fundamental modes:²⁻³ ν₁ (symmetric stretchings); ν₂ (doubly degenerated bending vibrations), and ν₃ (antisymmetric stretching vibration). The ν₂ and ν₃ modes are infrared active, while ν₁ is only Raman active. For the free molecule in gas phase these modes appear at 1388.3 (ν₁), 667.3 (ν₂), and 2349.3 (ν₃) cm⁻¹.² In solid CO₂ ν₁ is detected by IR around 2344 cm⁻¹² while ν₂ splits into two components (659.8 and 695.7 cm⁻¹).
Table 1. Spectral Data Reported after Interaction of CO2 with OH Groups in MOFs

<table>
<thead>
<tr>
<th>Sample</th>
<th>OH group, cm⁻¹</th>
<th>Δν(OH), cm⁻¹</th>
<th>ν(CO2), cm⁻¹</th>
<th>other CO2 bands, cm⁻¹</th>
<th>Note</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-53(Cr)</td>
<td>3655</td>
<td>−19 to −22</td>
<td>2335</td>
<td>662, 653</td>
<td>up to 4 bar, NP form</td>
<td>25, 27, 28</td>
</tr>
<tr>
<td>MIL-53(Al)</td>
<td>3720</td>
<td>−13</td>
<td>2338</td>
<td>659</td>
<td>5–10 bar, LP form</td>
<td>16</td>
</tr>
<tr>
<td>MIL-53(Fe)−X, X = CH2ClBr</td>
<td>3650−3648</td>
<td>−28</td>
<td>2334.5</td>
<td>−</td>
<td>monomer dimer</td>
<td>29</td>
</tr>
<tr>
<td>NH2-MIL-53(Al)</td>
<td>3700°</td>
<td>−28°</td>
<td>−</td>
<td>661, 649</td>
<td>OH−O==C==O species + weak donor−acceptor interaction</td>
<td>31</td>
</tr>
<tr>
<td>MIL-125(Ti)</td>
<td>3686°</td>
<td>−54</td>
<td>ca. 2340</td>
<td>μ2(O−O)==C==O</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>NH2-MIL-125(Ti)</td>
<td>3686°</td>
<td>−41°</td>
<td>ca. 2340</td>
<td>−</td>
<td>−</td>
<td>30</td>
</tr>
</tbody>
</table>

*Experiments performed with deuterated samples. The values of ν(OH) and Δν(OH) are calculated from the respective ν(OD) and Δν(OD) values.

654.7 cm⁻¹) due to highly ordered structures (Davydov splitting).3

Because of the fact that the overtone of ν1 almost coincides with the ν1 mode, a Fermi resonance occurs and two bands of almost equal intensity are observed in the Raman spectrum at 1388 and 1285 cm⁻¹. The combination modes of these two bands with ν1 give rise to two other bands at 3714 and 3612 cm⁻¹.4

Typical of CO2 are also the so-called “hot” bands (excitation of already excited states) which are located at the low-frequency sides of the principal bands.6 The relative intensity of these bands increases with temperature.

Upon coordination the molecule of CO2 is affected thus producing changes in its spectral features. From a chemical point of view, CO2 can act as an electron donor (through one or the two O atoms) and/or as electron acceptor (through the C atom). Upon coordination through the C atom the CO2 molecule changes to a bent configuration. As a result, the ν3 mode is significantly red-shifted, down to 1700 cm⁻¹.5 At the same time, the ν1 mode becomes IR active and is detected at 1400−1100 cm⁻¹.5 It is also considered that, because of the degeneration removal, two ν3 bands are observed: in-plane (lower frequency) and out-of-plane (higher frequency) bending modes.6,8−9 As will be discussed below, this statement needs some refinement.

When CO2 is bonded through one of its oxygen atoms, the linearity of the molecule is preserved and the ν1 mode remains IR silent. The reported data on the spectral performance of O-bound species are controversial. There is strong evidence that formation of such complexes leads to a small red shift of the ν1 mode (down to 2200 cm⁻¹).5,10 However, matrix-isolation studies have indicated a moderate blue shift of ν4 in M−−O−CO moieties (up to 2380 cm⁻¹).11 Similar but less pronounced shift values have been reported when linear O-bounded species are formed with metal cations exchanged in zeolites.12,13 These observations suggest that the increase of the C−O stretching frequency of the CO2 molecule results from an electrostatic interaction (Stark effect). Indeed, the electrostatic interaction is expected to be strong in matrix-isolated cationic species as well as with CO2 interacting with highly electrolyphlic cations in zeolites. When the electron transfer is essential, the ν3 frequency should decrease.

An important question is the ν1 reference value. It has been noted that the gas-phase frequency is not appropriate in this respect for the cases of porous materials because dispersion forces with the surrounding framework cause a red shift of the ν1 mode. Consequently, a value of 2338 cm⁻¹, i.e. the ν3 frequency of CO2 adsorbed on silicalite and corrected for the interaction with silanols, is proposed as a reference.4 A complication here is that the real reference value seems to depend on the pore dimensions. Thus, a significant effect was suggested for CO2 in the small sodalite-like cages of Ni3(BTP)2, where weakly adsorbed CO2 was detected at 2335 cm⁻¹.12 In any case, considering a reference value differing from the gas phase frequency requires revision of many published data.

Usually CO2 is weakly adsorbed on MOFs and the interaction is mainly electrostatic. Typical CO2 adsorption sites are exposed metal cations and hydroxyl groups. Although with a lower interaction energy, CO2 can be bound to other MOF sites, usually atoms from the organic linkers. When CO2 interacts with the exposed metallic sites in MOFs, ν3 frequencies in the range between 2353 (CPO-27-Mg) and 2334 cm⁻¹ (Cu-BTC) have been reported.7,14,17−25 When interacting with OH groups, ν3 is observed in a narrow spectral interval, i.e. 2340−2353 cm⁻¹ (see Table 1).16,25,27−31

Among different MOFs, these from the MIL-53 series (MIL stands for Matériaux de l’Institut Lavoisier) have been considered as promising materials for CO2 storage and separation.14,16,20−26 MIL-53 materials represent metal hydroxyterephthalates and are build up by infinite trans chains of corner-sharing Me3O3(OH)2 octahedra linked by 1,4-benzenedicarboxylate ligands.31,35,38,39 They possess a three-dimensional skeleton structure with large pores up to 0.85 nm and are among the so-called breathing MOFs.31,32 i.e. they switch between large-pore (LP) and narrow-pore (NP) forms upon adsorption or temperature changes. With the aim of developing more effective CO2 adsorbents, NH2-MIL-53(Al) MOF was synthesized.35 This material exhibits the same topology as MIL-53(Al), but in this case the linker is the 2-aminoterephthalate anion.31,35,38,39 Due to the H-bonding between the NH2 and OH groups NH2-MIL-53(Al) is in a very narrow-pore form.31,39

French authors studied in detail the adsorption of CO2 on MIL-53(Cr).26−28 They followed the process in a large pressure range at 305 K and compared the IR results with X-ray diffraction (XRD) data.26,28 The activated material was in a LP form (diagnosed by the band at 1022 cm⁻¹), and CO2 adsorption up to a pressure of 4 bar provoked transition to a NP form (band at 1017 cm⁻¹). At these conditions the ν1 mode was observed at 2335 cm⁻¹ and two ν2(CO2) bands were detected at 662 and 650 cm⁻¹.26,28 Simultaneously, a red shift by −22 cm⁻¹ was observed for the ν(OH) band at 3655 cm⁻¹ while the δ(OH) mode at 920 cm⁻¹ appeared blue-shifted by 30 cm⁻¹. These spectral changes were associated with an
electron donor–acceptor interaction; the electron donor was identified as the oxygen atom from the OH group and the electron acceptor was the C atom from the CO₂ molecule. A complementary Raman study²⁷ registered the presence of the ν₁ and 2ν₁ bands at 1383 and 1281 cm⁻¹, respectively.

At higher CO₂ pressure (6–10 bar) the material was converted into the LP pore form (diagnostic band at 1022 cm⁻¹) and a new ν₂(CO₂) band appeared at 659 cm⁻¹.²⁶,²⁸ Another set of shifts of the OH modes was associated with this band: Δν(OH) = −13 cm⁻¹ and Δδ(OH) = 15 cm⁻¹. Subsequent decrease in the pressure down to 2 mbar restored the spectrum initially recorded at low CO₂ pressure.

According to others,³³ at pressures lower than 6 bar one CO₂ molecule interacts with two OH groups on MIL-53(Cr), which explains the low ν₁ frequency of CO₂.

A series of studies on NH₂-MIL-53(Al) revealed two CO₂ adsorption forms.¹⁶,³¹,³⁴,³⁵ The first form is associated with interaction of CO₂ with the OH groups that are not involved in H-bonding with NH₂ groups. In this case, two ν₂ bands were observed, at 661 and 649 cm⁻¹. In order to follow precisely the changes in the hydroxyl spectra, i.e. to prevent the hindering from the CO₂ combination modes, deuterated samples were investigated.³¹ Upon CO₂ adsorption the OD band at 2726 cm⁻¹ (corresponding to free hydroxyls observed at 3700 cm⁻¹) was shifted to 2705 cm⁻¹. The band at 2715 cm⁻¹ (OD groups D-bonded to amino groups) was hardly affected. It was considered that these sites were occupied after breaking the preexisting D-bonds. In addition, only a negligible part of the NH₂ groups were affected by CO₂, presumably those located at the external surface.³⁵ Two ν₂(CO₂) bands were identified for this adsorption form, at 669 and 653 cm⁻¹.³⁸

In the pilot communication of this study,²⁶ we reported that low-temperature CO₂ adsorption on MIL-53(Al) leads, at low coverages, to formation of OH–OCO species characterized by a ν₂(CO₂) band at 2338 cm⁻¹ and causing a shift of the 3720 cm⁻¹ ν(OH) band by −38 cm⁻¹. At higher coverages (OH…OCO) dimers are produced which leads to a red shift of the ν₂(CO₂) by ca. −4 cm⁻¹. However, only one ν₂(¹³CO₂) band (arising from the ¹³C natural abundance) was registered at 2272 cm⁻¹ for the two adsorption forms. This indicated that the shift of the ν₂(CO₂) was due to vibrational interaction. Moreover, we found that even at ambient temperature dimeric species could be formed.

In this work we explore our previous findings showing that the process is not restricted to MIL-53(Al) but can occur with different MOFs, in particular NH₂-MIL-53(Al). Moreover, here we demonstrate that at higher coverage polymers are formed with MIL-53(Al) and lead to opening of the structure. In contrast, no polymers are produced with NH₂-MIL-53 due to the relatively high stability of the narrow-pore form. We also provide detailed analysis of the whole spectral region, including the changes in the ν(OH) and δ(OH) regions as well as in the region of ν₂(CO₂) modes and offer more detailed information on the adsorbent–adsorbate and adsorbate–adsorbate interaction. For better assignment of the spectra, isotopically labeled CO₂ (¹³CO₂) was used in the experiments.

2. EXPERIMENTAL SECTION

The MIL-53(Al) sample was a commercial BASF product Basolite A100. Before the experiments it was evacuated at 623 K for 30 min in order to remove the residual free acid. The amino-functionalized sample, NH₂-MIL-53(Al), was home-prepared, and synthesis details are reported elsewhere.³⁸ The sample was acid-free and was activated under vacuum at 473 K for 30 min.

The IR measurements were performed using Nicolet Avatar 360 and Nicolet 6700 FTIR spectrometers accumulating up to 128 scans at a spectral resolution of 2 cm⁻¹ and accuracy of 0.01 cm⁻¹. Specially designed IR cells were used for the experiments. One of them, equipped with CaF₂ windows, allowed registering the spectra at low (100 K) and ambient temperatures. Another cell, equipped with KBr windows, allowed obtaining the spectra at a preset temperature in the range between 100 and 300 K. The cells were directly connected to a vacuum-adsorption apparatus with a residual pressure lower than 10⁻³ Pa.

To obtain the IR spectra the sample was spread onto a KBr pellet. This technique ensured optimal intensity of the IR bands. Parallel experiments were performed with a self-supporting pellet in order to verify the lack of interaction with KBr. During the low-temperature experiments helium was introduced in the cell before CO₂ adsorption in order to keep a constant temperature. Then CO₂ was introduced to the system and allowed to diffuse to the pellet. The background and gas-phase corrections were performed using Omnic software. For the low-temperature CO₂ experiments a spectrum registered in the presence of He was used as background.

Carbon dioxide (99,998% purity) was supplied by Messer. Labeled ¹³CO₂ (¹³C isotopic purity of 99 atom %) was provided by Aldrich. Helium was supplied by Messer and had a purity of 99.999%.

3. EXPERIMENTAL RESULTS

3.1. Adsorption of CO₂ and ¹³CO₂ at Ambient Temperature. 3.1.1. Background Spectra. The background spectra of the MIL-53(Al) and NH₂-MIL-53(Al) MOF compounds are already described in the literature,¹⁶,³¹,³⁴,³⁵,³⁷ and here we will only concentrate on the bands under interest for this study. Some details for the other regions are provided in the Supporting Information (see Figure S1).

The activated MIL-53(Al) sample shows two bands, at 1025 and 1019 cm⁻¹, which are indicative of the LP and NP forms of the material, respectively (Figure S1, spectrum a).²⁶ In the OH region, one band at 3708 cm⁻¹ with a shoulder at 3702 cm⁻¹ is recorded (see the inset in Figure S1). This band is attributed to ν(OH) of the structural μ₃-hydroxyl groups of the sample.¹⁶ The heterogeneity is most probably associated with the coexistence of the LP and NP forms in the activated material. A component of the very intense (out of scale) band at ca. 986 cm⁻¹ is due to the respective δ(OH) modes.

The spectrum of NH₂-MIL-53(Al), although similar, shows some differences. Due to the fact that the material is considered to be in a (very) NP form, there are no bands proposed to follow the pore structure. In the OH region two bands, at 3701 and 3681 cm⁻¹, are detected (Figure S1, spectrum c). The former band is due to (almost) free structural hydroxyl as found with the MIL-53(Al) sample. The band at 3681 cm⁻¹ is attributed to structural hydroxyls involved in H-bonding with the amino groups.³⁵,³⁴,³⁵,³⁷ The respective δ(OH) band was monitored by a component of the out-of-scale band around 987 cm⁻¹. In addition, two intense bands at 3500 and 3388 cm⁻¹ are detected and assigned to the symmetric and antisymmetric N−H stretching modes of the amino groups.

3.1.2. Spectral Signatures of Adsorbed CO₂. First we compare the changes in the spectra occurring during adsorption of 50 mbar ¹²CO₂ or ¹³CO₂ at ambient temperature (298 K) on
the activated samples (Figure 1). Adsorption of $^{12}$CO$_2$ on MIL-53(Al) results in the appearance of a $\nu_3$ band at 2336.1 cm$^{-1}$.

![Figure 1](image-url) FTIR spectra recorded after ambient temperature adsorption of $^{12}$CO$_2$ (a, c) or $^{13}$CO$_2$ (b, d) (50 mbar equilibrium pressure) on MIL-53(Al) (a, b) and NH$_2$-MIL-53(Al) (c, d). The spectra are background and gas-phase corrected. Panel A, $\nu_3$(CO$_2$) region; panel B, $\nu_2$(CO$_2$) region; panel C, $\nu$(OH)/$\nu$(NH) region; and panel D, $\delta$(OH) region.

(Figure 1A, spectrum a). Because the exact position of this band is essential for the following discussion, we will present the maximum values with the first figure after the decimal point which is allowed by the accuracy of our instrument. The $\nu_3$ band has a pronounced shoulder at 2325 cm$^{-1}$ which is assigned to the so-called “hot” band. A weak and broad band around 2370 cm$^{-1}$ is most probably due to a combination mode. Another weak feature at 2271.3 cm$^{-1}$ arises from the natural $^{13}$C abundance and is attributed to the $^{13}$C satellite of the principal band at 2336.1 cm$^{-1}$.

After adsorption of $^{13}$CO$_2$, the principal $\nu_3$ band was detected at 2270.6 cm$^{-1}$ (Figure 1A, spectrum b). The isotopic shift factor ($i = 1.029$) is in good agreement with the theoretical expectation (1.023). Note that the maximum of the main band is at slightly lower wavenumber as compared to the satellite $^{13}$CO$_2$ band recorded after adsorption of $^{12}$CO$_2$ at the same conditions. Comparison of the two bands after normalizing the intensity reveals a well-pronounced lower frequency component in the case of $^{13}$CO$_2$ adsorption (Figure S2, spectra a,b). The $^{13}$CO$_2$ “hot” band was detected at 2260 cm$^{-1}$, while the weak combination band appeared around 2304 cm$^{-1}$. Another band is well distinguished at ca. 2254 cm$^{-1}$ and has no analogue in the spectrum of adsorbed $^{12}$CO$_2$. We attribute this band to small amounts of $^{13}$CO$_2$ contaminants usually present in $^{12}$CO$_2$. Finally, a weak satellite $\nu_3$(^{12}CO$_2$) band was detected at 2337.0 cm$^{-1}$. In this case again the band appears at a slightly higher wavenumber as compared to the same band detected after adsorption of pure $^{12}$CO$_2$ and the band contour indicates the absence of a lower-frequency shoulder.

Very similar results were obtained with the NH$_2$-MIL-53(Al) sample. The $\nu_2$ band of adsorbed $^{13}$CO$_2$ (asymmetric from the low-frequency side) was registered at 2336.9 cm$^{-1}$ and shifted to 2271.5 cm$^{-1}$ upon $^{13}$CO$_2$ adsorption (Figure 1A, spectra c,d). Here again, the satellite bands were more symmetric and detected at slightly higher frequencies (2337.0 and 2271.7 cm$^{-1}$) but the effect was definitely less pronounced as compared to the MIL-53(Al) sample.

The spectra of the deformation CO$_2$ modes are noisier because of the presence of strong background bands in the region (Figure 1B). An intense band at 663 cm$^{-1}$ and a weaker one at 650 cm$^{-1}$ are recorded with the MIL-53(Al) sample. The two bands were shifted to 645 and 635 cm$^{-1}$ when $^{13}$CO$_2$ was adsorbed. With the NH$_2$-MIL-53(Al) sample the bands were detected at slightly lower wavenumbers: 661 and 647 cm$^{-1}$ ($^{12}$CO$_2$ adsorption) and 643 and 629 cm$^{-1}$ ($^{13}$CO$_2$ adsorption). Note that additional heterogeneity of the adsorption forms is not excluded from the contour of the bands. A slight modulation around 668 cm$^{-1}$ is observed in the spectra of adsorbed $^{13}$CO$_2$ (around 648 cm$^{-1}$ for $^{12}$CO$_2$). This is attributed to the not efficient subtraction of the gas-phase likely due to a slight effect of the solid on a part of the gaseous CO$_2$ in vicinity. In all cases the isotopic shift factor for the $\nu_2$ band (1.028–1.025) is consistent with the theoretical expectations. We have also found that the intensities of the lower-frequency bands do not decrease with temperature, which excludes their assignment to “hot” bands.

Analysis of the region of the combination modes of CO$_2$ is more difficult because of the superposition with some OH and NH stretching bands. Relatively intense bands at 3613 cm$^{-1}$ are detected in the spectra of $^{13}$CO$_2$ adsorbed on both samples (Figure 1C). These bands are absent from the spectra of adsorbed $^{12}$CO$_2$ and are attributed to the $\nu_1 + \nu_3$ combination modes. Taking into account the isotopic shift factor, the respective band for adsorbed $^{12}$CO$_2$ is expected around 3693 cm$^{-1}$. A careful inspection of the spectra indicated that indeed such features are observed but superimposed to the negative OH bands (see the inset in Figure 1C). The other combination band, $2\nu_2 + \nu_3$, is of very low intensity and is distinguished in the spectra of adsorbed $^{12}$CO$_2$ around 3582 cm$^{-1}$.

In the 1400–1300 cm$^{-1}$ region, where the $\nu_1$ band is expected, some small deviations of the spectra, due to small changes in the intense background bands in this region, were detected (Figure S3). However, comparison between the spectra of the two adsorbed isotopologues ($^{12}$CO$_2$ and $^{13}$CO$_2$) indicated the lack of any bands assignable to the $\nu_1$ and/or $2\nu_2$ modes. These results suggest that CO$_2$ is not bonded through its C atom.

Consider now the coverage effect. Here we will discuss mainly the $\nu_3$ band because the deformation modes cannot be followed accurately due to their low intensities and the background changes. The spectra recorded with the MIL-53(Al) sample during the decrease of the CO$_2$ equilibrium pressure (initially adsorbed at 100 mbar) are shown in Figure 2A. It is seen that the $\nu_3$ band decreases in intensity with the equilibrium pressure. At pressures of 10 mbar or lower the band maximum is practically coverage independent and is located at 2336.7 cm$^{-1}$. With the pressure increase the band maximum is
3.1.3. \( \text{CO}_2 \)-Induced Changes in the Background Spectra.

Adsorption of \( \text{CO}_2 \) or \( ^{13}\text{CO}_2 \) on the MIL-53(Al) sample causes a red shift of the 3708 cm\(^{-1} \) band to 3681 cm\(^{-1} \) (Figures 1 and 2 and Figure S5). In this case it is preferable to analyze the changes caused by \( ^{13}\text{CO}_2 \) adsorption in order to avoid the superimposition with the \( \nu_1 + \nu_2 \) combination band of \( ^{12}\text{CO}_2 \). A careful analysis indicates that at lower coverages the shoulder at 3702 cm\(^{-1} \) is preferentially affected, followed by the band at 3708 cm\(^{-1} \), but only one shifted band appears. The shifted band is more intense than the negative bands, which indicates formation of an H-bond. The \( \text{CO}_2 \) induced shift of the \( \nu_1 \) modes is between \( -21 \) and \(-28 \) cm\(^{-1} \). This value is intermediate between the shifts caused by low-temperature adsorption of \( \text{N}_2 \) and \( \text{CO} \) (ca. \(-12 \) and \(-45 \) cm\(^{-1} \), respectively)\(^{37} \) and is consistent with the proton affinities of the three molecules.

Concerning the \( \text{NH}_2\)-MIL-53(Al) sample, the \( \nu_1 \) modes are also affected and the shifted band consists of two components: a main one at 3674 cm\(^{-1} \) and a shoulder at 3668 cm\(^{-1} \). A careful analysis indicates that \( \text{CO}_2 \) affects mainly the original \( \nu_1 \) (OH) band at 3702 cm\(^{-1} \) and to a minor extent the band at 3681 cm\(^{-1} \). However, it is not possible to relate the two shifted components to the two original OH bands. A more detailed interpretation will be offered below.

With the MIL-53(Al) sample a band at 977 cm\(^{-1} \) (OH deformation modes) is shifted to higher frequencies, but the shift (around \(+40 \) cm\(^{-1} \)) cannot be exactly determined because of the superimposition (Figure 2D). In any case, such a shift is expected to occur when an H-bond is formed. With the \( \text{NH}_2\)-MIL-53(Al) sample the shifted \( \delta_1 \) (OH) band is well detected at 1017 cm\(^{-1} \) (Figure 1D). A careful inspection of the spectra indicates some fine structure of the negative band which could suggest some heterogeneity of the affected hydroxyls. However, similar conclusions should be taken with care because false negative bands can be obtained when the principal band is out of scale.

The spectra presented in Figure 2 also indicate that a correlation exists between the intensities of the \( \nu_1 \) (CO\(_2\)) band and the shifted \( \nu_1 \) (OH) and \( \delta_1 \) (OH) bands. All these results, coupled with the absence of any IR active \( \nu_3 \) mode, imply formation of \( \text{OH}...\text{OCO} \) complexes.

It is seen that the NH modes are also affected by \( \text{CO}_2 \) adsorption. However, compared to the OH groups, only a small fraction of the NH groups are involved in the process (see the intensities of the original bands, Figure S1). Analysis of the spectra indicates that the bands are rather broadened than shifted. Therefore, we have no evidence of direct bonding of \( \text{CO}_2 \) to the amino groups at these experimental conditions.

Finally, we tried to analyze the region around 1020 cm\(^{-1} \) modes indicative of NP and LP forms of the MIL-53(Al) material. However, because of the superimposition with the intense shifted \( \delta_1 \) (OH) bands, we were not able to draw definite conclusions from this set of experiments. However, analysis of another sensitive pair of bands (NP at 766 cm\(^{-1} \) and LP at 755 cm\(^{-1} \))\(^{40} \) suggests that at high \( \text{CO}_2 \) equilibrium pressure a partial transformation of the material to the NP form occurs. These results are consistent with similar findings with a MIL-53-Cr sample.\(^{26} \)

3.2. Low-Temperature Adsorption of \( \text{CO}_2 \)

3.2.1. Background Spectra.

Some background bands of many MOF materials are very sensitive to the temperature. In the low-temperature experiments, the actual temperature of the pellet depends on the pressure and the nature of the gas because...
these parameters determine the thermal conductivity of the media. Therefore, during the low-temperature adsorption experiments, both temperature and adsorbate-induced effects are registered. In order to distinguish between them, the temperature effect should be well-known.

As seen from Figure S1, at low temperature (and in the presence of He) the bands due to isolated hydroxyls are shifted to higher frequencies and become narrower while the δ(OH) bands slightly shift to lower frequencies. This indicates that at room temperature these OH groups have been involved in weak H-bonds and the strength of this bond decreases at low temperature. Small deviations are observed with the MIL-53(Al) sample in the region of the δ(CH) modes of the terephthalate ligand around 1020 cm\(^{-1}\). At low temperature the relative intensity of the band at 1024 cm\(^{-1}\) increases at the expense of the band at 1019 cm\(^{-1}\), indicating increase of the fraction of the LP form.

### 3.2.2. Spectral Signatures of Adsorbed CO\(_2\)

Immediately after introduction of CO\(_2\) at 100 K to the MIL-53(Al) sample, a broad band at 2338.8 cm\(^{-1}\) develops (Figure 3, spectra a,b).

The band has lower frequency shoulders located at 2334, 2329, and 2325 cm\(^{-1}\). The background spectra are only slightly affected. We assign the broad band to the \(\nu_3\) modes of weakly adsorbed CO\(_2\). The relatively high wavenumber of this band indicates the lack of pore effects. This, coupled with the fact that the OH groups remain practically unaffected, indicates the band is due to CO\(_2\) adsorbed on the external MOF surface.

These conclusions are supported by analysis of the region of deformation modes: two bands at 661 and 655 cm\(^{-1}\), typical of solid CO\(_2\), were observed (not shown). Subsequent evacuation at 100 K leads to fast disappearance of the broad feature around 2339 cm\(^{-1}\) and development of a sharp \(\nu_3\) band at 2333.9 cm\(^{-1}\) (Figure 3, spectra c–e). Additional evacuation (Figure 3, spectra f–n) causes decrease in intensity of the band at 2333.9 cm\(^{-1}\) and development, at its expense, of another band at 2338.0 cm\(^{-1}\). The latter one further decreases in intensity without changing its position. These spectral changes are typical of conversion between monomeric and dimeric surface species.\(^{41,42}\)

Consider now the changes of the satellite \(^{13}\)CO\(_2\) band. Normally, it is expected that this band should demonstrate the same behavior as the respective \(^{12}\)CO\(_2\) band if no vibrational interaction occurs. However, at the initial stages of adsorption the position of the satellite band was at 2272.8 cm\(^{-1}\) (broad band due to weakly adsorbed molecules on the external surface) and then shifted to 2272.1 cm\(^{-1}\). Further evacuation led to a decrease in intensity of the band and a negligible shift of its maximum to 2272.4 cm\(^{-1}\). These results demonstrate that the two bands, around 2338 cm\(^{-1}\) (higher frequency, or HF) and 2334 cm\(^{-1}\) (lower frequency, or LF), are characterized by only one \(^{13}\)CO\(_2\) satellite band around 2272.4–2272.1 cm\(^{-1}\).

Very similar results were obtained with the NH\(_2\)-MIL-53 sample (Figure 4). At the initial stages of adsorption a broad
band at 2339 cm\(^{-1}\) with shoulders at 2336 and 2335 cm\(^{-1}\) developed. Here again, the background spectrum was hardly affected. Evacuation leads first to development of a LF band at 2334.8 cm\(^{-1}\) which then decreases in intensity and is converted to another, HF band at 2388.0 cm\(^{-1}\). Note that in this case the difference between the HF and LF bands is slightly smaller. In the \(^{13}\)C satellite region initially a band at 2281 cm\(^{-1}\) with a lower frequency shoulder at 2274 cm\(^{-1}\) appeared immediately after CO\(_2\) adsorption. During evacuation a band at 2272.5 cm\(^{-1}\) developed and then declined, slightly shifting to 2272.8 cm\(^{-1}\). Here again, the HF and LF bands (2234.8 and 2238 cm\(^{-1}\)) had only one \(^{13}\)CO\(_2\) satellite band.

It is clearly seen that for the two samples conversion between two adsorption forms occurs and the phenomenon is due to interaction between adsorbed CO\(_2\) molecules. The maximal integral intensities of the HF bands are roughly 2 times lower than those of the LF bands, which suggests that the species formed at high coverage can be associated with structures involving two CO\(_2\) molecules. The appearance of only one \(\nu_1\) band for these dimeric species shows that the CO\(_2\) molecules are equivalent; i.e., the complex formed is symmetric.

In dimeric structures practically all \(^{13}\)CO\(_2\) molecules due to \(^{13}\)C natural abundance should have \(^{12}\)CO\(_2\) neighbors. The fact that after the removal of solid-like CO\(_2\) the \(\nu_1^{(13)}\) frequency remains coverage independent indicates that the \(\nu_1^{(13)}\) frequency change is due to some kind of vibrational interaction. This interaction is more pronounced with the MIL-53(Al) sample.

### 3.3. Adsorption of CO\(_2\) at Intermediate Temperature.

#### 3.3.1. Sample MIL-53(Al)

In order to verify that the LF–HF band conversion and the behavior of the \(\nu_1^{(13)}\) band are due to vibrational interaction, we comparatively studied the adsorption of \(^{13}\)CO\(_2\) alone as well as that of a 1:1 \(^{12}\)CO\(_2\) + \(^{13}\)CO\(_2\) isotopic mixture. These experiments were performed at higher temperature, ca. 200 K, in order to avoid the formation of solid-like CO\(_2\). Another aim of these studies is to reach higher CO\(_2\) coverages that were not possible to attain at ambient temperature (due to thermodynamic reasons) and at low temperature (attributed to blocking of the pores).

Consider first the spectra at relatively low coverages. If a 1:1 \(^{12}\)CO\(_2\) + \(^{13}\)CO\(_2\) mixture is adsorbed, statistically the isotopic composition of the dimers formed should be 25\% \(^{12}\)CO\(_2\)\(^2\), 50\% \(^{12}\)CO\(_2\)(\(^{13}\)CO\(_2\)) and 25\% \(^{13}\)CO\(_2\)\(^2\). Therefore, if our conclusions were true, the LF band should be related only to \(^{13}\)CO\(_2\) species and thus should appear with strongly reduced relative intensity in the spectra of the isotopic mixture. In contrast, monomeric and \(^{12}\)CO\(_2\)(\(^{13}\)CO\(_2\)) dimeric species should be responsible for the development of the HF band.

The spectra presented in Figure S5A,B fully support this statement. Indeed, it is seen that the LF band is much more pronounced when pure \(^{13}\)CO\(_2\) was adsorbed. Surprisingly, the LF band was additionally red-shifted with coverage increase (Figure S5A, spectrum f). In order to follow more precisely these changes, we analyzed the second derivatives of the spectra (Figure S5C,D). Consider first the HF band. It is practically coverage independent in the spectra of adsorbed \(^{13}\)CO\(_2\). A slight red shift is observed in the spectra of adsorbed isotopic mixture which is associated with the contribution of mixed dimers to this band and indicates that the vibrational interaction between \(^{12}\)CO\(_2\) and \(^{13}\)CO\(_2\)\(^2\), although negligible, is not absent. Note that this is the reason for the already noted very slight red shift of the satellite bands.

The LF band only slightly shifts with coverage increase when the isotopic mixture is adsorbed. However, the shift is more essential in the spectra of adsorbed \(^{13}\)CO\(_2\) (1.6 cm\(^{-1}\)). Analysis of the \(\nu_1\) (OH), \(\delta_1\) (OH), and \(\nu_2\) (CO\(_2\)) regions did not show any additional peculiarities. These results imply that with coverage increase additional vibrational interaction occurs and indicate formation of some kind of oligomeric species.

We discuss now the changes occurring at higher coverage. In these cases the \(\nu_1\) \(^{13}\)CO\(_2\) band was of very high intensity and out of scale (Figure 6A). Second derivatives (see Figure 6A, inset) indicate development of a high frequency component located at 2275.0 cm\(^{-1}\) (2340.3 cm\(^{-1}\) for adsorbed \(^{12}\)CO\(_2\)).
Although, due to superimposition, the band attributed to 13C18O16O at ca. 2254 cm\(^{-1}\) cannot be precisely followed, it is clearly seen that it is hardly affected by coverage. A high-frequency component of the \(\nu_1 + \nu_3\) combination band also develops at 3614.2 cm\(^{-1}\).

In the low-frequency region a new \(\nu_2(13\text{CO}_2)\) band appeared at 640 cm\(^{-1}\). Although superimposed to the \(\nu_2\) bands produced at lower coverage, the band is well seen in the difference spectrum (Figure 6B, inset). When 12\text{CO}_2 was adsorbed, the band was registered at 658 cm\(^{-1}\).

Consider now the hydroxyl bands. At the highest coverage practically all OH groups are affected by adsorbed CO\(_2\). However, in this case the CO\(_2\)-induced shift of \(\nu(\text{OH})\) is smaller. The difference spectrum (inset in Figure 6C) clearly shows the consumption of a component at 3715 cm\(^{-1}\) and development of a broader band at 3691 cm\(^{-1}\) (\(\Delta\nu(\text{OH}) = -23\) cm\(^{-1}\)). A negative band at 3680 cm\(^{-1}\) is also seen, confirming the decrease in concentration of the dimeric species at high coverage. In agreement with these changes, the shift of the \(\delta(\text{OH})\) modes is also reduced; \(\Delta\delta(\text{OH}) = -30\) cm\(^{-1}\) (see the inset in Figure 6D).

Similar results, although with different shift values, were earlier reported with MIL-53(Gr) sample (in this case the hydroxyls are of lower acidity as compared to the hydroxyls in MIL-53(Al)).\(^{26}\) A careful analysis of our spectra reveals additional small bands (at ca. 3674 and 1030 cm\(^{-1}\)) representing decreasing shifts of both \(\nu(\text{OH})\) and \(\delta(\text{OH})\) modes (\(-40\) and \(-65\) cm\(^{-1}\), respectively). All these findings indicate that at high coverage new polymeric species are formed. It seems that these species interact strongly with one (or a few) OH group while the interaction with the other hydroxyls is weakened. Although the polymers are produced at the expense of the dimers and/or oligomers, the latter species have not fully disappeared even after all OH groups were affected by CO\(_2\). Finally, we note that the relative intensity of the 13\text{CO}_2 combination band at 3615 cm\(^{-1}\) is relatively high, which suggests that not all of the 13\text{CO}_2 molecules from the polymeric species are bonded to OH groups.

### 3.3.2. Sample NH\(_2\)-MIL-53(Al)

The conversion between monomeric and dimeric CO\(_2\) species on NH\(_2\)-MIL-53(Al) was confirmed in a set of experiments, as already observed with MIL-53(Al) (see Figure S7).

Figure 7 shows the spectral changes occurring after CO\(_2\) adsorption at 200 K on NH\(_2\)-MIL-53(Al) at increasing coverages up to the coverage when almost all "free" OH groups are affected. It is clear that no polymers are formed in this case. This is seen by the absence of both a new \(\nu(\text{CO}_2)\) band (Figure 7B) and a low-frequency component of the shifted \(\nu(\text{OH})\) band (Figure 7B). A careful analysis of the spectra shows that, at high coverage, the 3684 cm\(^{-1}\) hydroxyls...
are also affected by CO₂. Normally, one could expect that the formation of a new H-bond should lead to the breaking of the preexisting H-bond with the amino group. However, the results demonstrate that this is not the case. The difference spectra shown in the insets in Figure 7C,D show that the shifted ν(OH) band is at 3660 cm⁻¹, i.e. at position lower by 10 cm⁻¹ than the band of the shifted "free" hydroxyls. This is attributed to the formation of bifurcated complexes, i.e., the proton of the OH group is bonded to two additional atoms. The conclusion is confirmed by the spectra in the δ(OH) region where a component of the shifted band at 1028 cm⁻¹ is clearly observed. However, in any case the preexisting H-bond is considerably weakened which is consistent with the low stability of the complexes formed.

4. DISCUSSION

4.1. Monomeric Species. The experiments described in this work, as well as analysis of the literature data, show that, at low CO₂ uptake, complexes between CO₂ and the structural OH groups of the investigated MOFs are formed. The spectral performance of these species is summarized in Table 2.

The shift of ν(OH) depends on the proton affinity (PA) of the guest molecule. The PA of CO₂ (540 kJ mol⁻¹) is intermediate between the PAs of N₂ (494 kJ mol⁻¹) and CO (594 kJ mol⁻¹), which means that the CO₂-induced shift should be intermediate between the N₂- and CO-induced shifts. Note that coordination of an electron acceptor to the O atom from a hydroxyl group should also lead to a red shift of the ν(OH) modes. However, this shift is much smaller as compared to the shift caused by the formation of H-bond. Indeed, it is considered that formation of a very strong bond with a metal cation (passing from I to II and III type hydroxyls) leads to a decrease in the OH stretching frequency by ca. 50 cm⁻¹. Therefore, weak interaction with guest molecules should result in a much smaller shift.

Not only with our samples, but also with other MOFs, CO₂ adsorption causes a red shift of the ν₃(CO₂) mode with respect to the gas-phase CO₂ frequency (see Table 1). However, the value is close to the reference value proposed for CO₂ sorbed in porous materials and we can stress that this mode is negligibly blue-shifted upon adsorption. This conclusion is consistent with the low adsorption enthalpy of CO₂.

Note also that no IR active ν₁ mode was observed with CO₂ on the two samples, which strongly indicates that the CO₂ molecule is not bonded through the C atom. However, two ν₂ bands were detected in each case. Usually, the split of ν₂ is considered as strong evidence of formation of C-bonded CO₂ due to the lowering of the symmetry and removal of the degeneracy of the deformation modes. We discuss now the possible reasons for this contradiction.

![Figure 7. FTIR spectra recorded after adsorption of ¹³CO₂ on NH₂-MIL-53(Al) at 200 K. The spectra are obtained after introduction of ¹³CO₂ (2 mbar) at 200 K to the sample (a) followed by progressive evacuation at the same temperature (b–e). Panel A, ν₃(¹³CO₂) region; panel B, ν₂(¹³CO₂) region; panel C, ν(OH) region; and panel D, δ(OH) region. The insets in panels C and D show difference "a−b" spectra in the respective regions. All spectra are background and gas-phase corrected. The asterisks in panel B show peaks due to nonefficient ¹³CO₂ gas-phase subtraction.](image)

Table 2. Spectral Signatures of the Different CO₂ Adsorption Complexes Observed in This Study

<table>
<thead>
<tr>
<th>sample</th>
<th>ν₃(¹₂CO₂), cm⁻¹</th>
<th>ν₂(¹₂CO₂), cm⁻¹</th>
<th>ν(OH), cm⁻¹</th>
<th>δ(OH), cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-53(Al)</td>
<td>2337.0 (298 K)</td>
<td>663, 650</td>
<td>3680</td>
<td>ca. 1014</td>
</tr>
<tr>
<td></td>
<td>2337.4 (200 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2338.0 (100 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₂-MIL-53(Al)</td>
<td>2337.0 (298 K)</td>
<td>661, 643</td>
<td>3674–3668</td>
<td>1018–1011</td>
</tr>
<tr>
<td></td>
<td>2338.0 (100 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MIL-53(Al)</td>
<td>2334.7 (298 K)</td>
<td>663, 650</td>
<td>3683</td>
<td>ca. 1014</td>
</tr>
<tr>
<td></td>
<td>2334.1 (200 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2333.9 (100 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₂-MIL-53(Al)</td>
<td>2334.5 (298 K)</td>
<td>661, 643</td>
<td>3674–3668</td>
<td>1018–1011</td>
</tr>
<tr>
<td></td>
<td>2334.8 (100 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MIL-53(Al)</td>
<td>2340.3 + (?) (200 K)</td>
<td>658</td>
<td>3691 + 3668 (w)</td>
<td>1004 + 1030 (w)</td>
</tr>
</tbody>
</table>
A bent triatomic molecule (e.g., H₂O) has only three vibration modes. Therefore, the appearance of two deformation modes for adsorbed CO₂ cannot be simply related to the symmetry lowering. Evidently, the symmetry of the entire adsorption complex should be taken into account.

Consider first the situation of C-bonded CO₂ (Scheme 1, left). Even if the linearity of the molecule is hardly affected, the deformation modes could be split into two components, in-plane and out-of-plane vibrations (visualized by differently colored arrows). However, a nonlinear O-bonded complex should also demonstrate similar in-plane and out-of-plane deformation modes (Scheme 1, right). Therefore, taking into account the above discussion, we conclude that at low coverage deformation modes (Scheme 1, right). Therefore, taking into account the above discussion, we conclude that at low coverage deformation modes (Scheme 1, right).

Consider now the polymers formed in MIL-53(Al) at high CO₂ coverage. They have several pronounced peculiarities. First, they are characterized by a ν₁(CO₂) band at higher wavenumbers (2340.3 cm⁻¹ for 12CO₂). Unfortunately, due to the very high intensities and superimposition, we are not able to determine all bands characteristic of the polymeric species. However, difference spectra suggested the existence of low-frequency features which indicates a split of the ν₁(CO₂) band into two or more components.

The change of the values of the CO₂-induced shifts of the ν(OH) and δ(OH) modes at high CO₂ coverages is an interesting phenomenon. At first sight (and discarding the weak OH band at 3669 cm⁻¹ demonstrating an enhanced shift) the phenomenon can easily be attributed to heterogeneity of the hydroxyl groups: initially the most acidic hydroxyls are affected followed by the less acidic ones. However, this explanation is not consistent with the experimental observation for several reasons: (i) only one type of structural hydroxyls is expected for MIL-53(Al), (ii) the hydroxyl band at ca. 3680 cm⁻¹ is formed with the different hydroxyl bands in the 3720–3708 cm⁻¹ region (expected to be involved in different H-bonds with the framework before CO₂ adsorption), and (iii) no similar heterogeneity has been seen using CO and N₂ as molecular probes. In addition, the partial destruction of the dimeric species indicates formation of a new type of bonding with the hydroxyls.

Our result can be rationalized by the assumption that the polymeric structures formed interact simultaneously with several OH groups. However, the interaction with one (or a few) hydroxyl is enhanced leading to a relatively large shift of the OH band. Consequently, the interaction with the rest of the OH groups is weakened.

Similar results were previously reported with a MIL-53(Cr) sample where a decreased shift of the OH modes and a new ν(CO₂) band were associated with a new adsorption form and reopening of the MOF structure. In our case we are not able to make definite conclusions on the pore structure, especially at high CO₂ coverages, because of the band superimposition. Indeed, due to the higher acidity of the hydroxyls in the aluminum-containing MIL-53 (compared to MIL-53-Cr), the shifted δ(OH) band masks the pore-diagnostic bands around 1020 cm⁻¹. However, the very similar frequencies of adsorbed CO₂ strongly support the idea that at high CO₂ pressure MIL-53(Al) is also converted in a LP form. These results are in full agreement with the absence of polymeric species in the NH₂-MIL-53(Al) sample, which is consistent with the relatively stable narrow-pore form of this material.

In conclusion, the present work clarifies a row of questions on the spectral performance of CO₂ adsorbed in porous materials. We also provide an easy IR tool for distinguishing between monomeric and dimeric CO₂ species in MOFs. Although here we report on two samples, MIL-53(Al) and NH₂-MIL-53(Al), we have observed similar phenomena with other MOF materials, which suggests that the reported dimerization and polymerization of adsorbed CO₂ are not
isolated phenomena. Finally, our results throw light upon the
mechanism of adsorbate-induced phase transition of MOFs.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b07492.

Background IR spectra and IR spectra of adsorbed $^{13}$CO$_2$
and $^{13}$COO$_2$ (PDF)

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