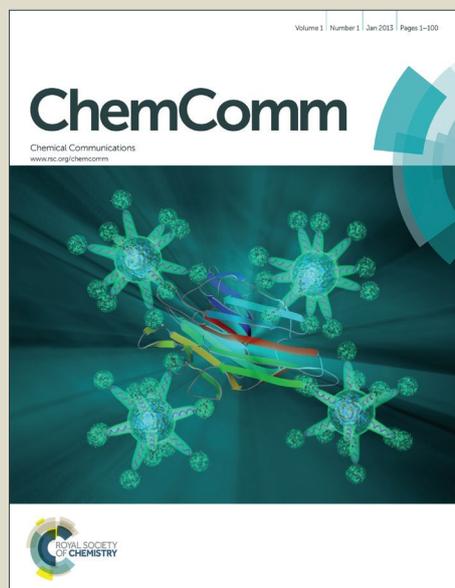


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Received 00th January 20xx,
 20xx,

Adsorption of CO₂ on MIL-53(Al): FTIR evidence of formation of dimeric CO₂ species

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

FTIR spectra of ¹²CO₂ and ¹²CO₂ + ¹³CO₂ mixtures adsorbed on MIL-53(Al) reveal formation of highly symmetric dimeric (CO₂)₂ species connected to two structural OH groups.

The interest in different metal organic framework (MOF) materials is continuously increasing due to their unique adsorption properties. In particular, various MOFs are considered as advanced materials for CO₂ capture.^{1–6} Therefore, gaining knowledge into the nature of the CO₂ adsorption sites and the adsorption geometry is of great interest. Accordingly, many researchers have utilized different techniques to study in detail the CO₂ adsorption process.^{3–12}

In this communication we report new IR spectral observations on CO₂ adsorption on MIL-53(Al) (aluminum hydroxylterephthalate), namely the vibrational interaction between two CO₂ molecules forming a dimeric structure and the role of the OH groups in the process.

The experimental and computational details and the background spectra of the sample at ambient and low temperature are described in the ESI[†] (Sections 1–3 and Figure S1). Particular attention is paid on the signatures of the OH groups^{13–17} and the narrow and large pore forms of the MOF structure.^{11,13,15}

Adsorption of CO₂ on the sample at 100 K leads initially to the development of a broad band centred at 2339 cm⁻¹ characterizing the IR active antisymmetric stretching modes of

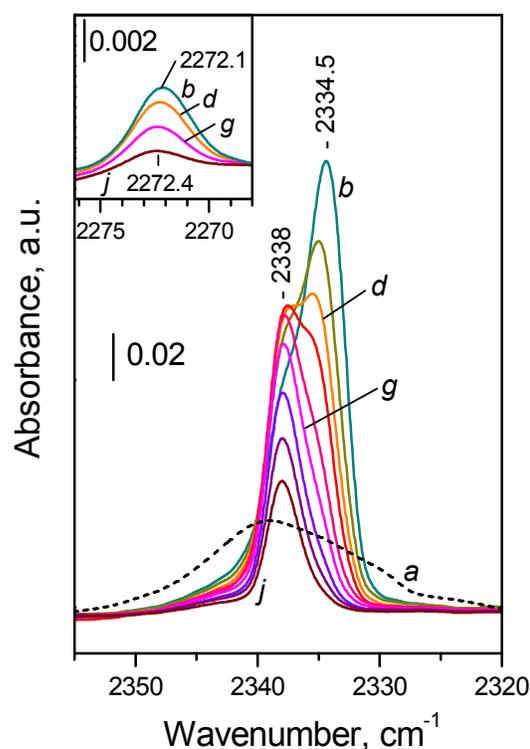


Fig. 1. FTIR spectra of ¹²CO₂ adsorbed at 100 K on MIL-53(Al). Initial ¹²CO₂ equilibrium pressure of 5 mbar (a) and evolution of the spectra during evacuation at 100 K (b–j). The spectra are background and gas-phase corrected. The inset shows selected spectra in the region of ν_{as}(¹³CO₂) modes.

the ¹²CO₂ molecule^{12,18} (Figure 1, spectrum a). At this stage the OH groups remained unaffected and we therefore assign this feature to weakly adsorbed ¹²CO₂, likely located on the external MOF surface thus blocking the access to the MOF pores. At the same time the pressure dropped due to CO₂ condensation on the sample and on the coldest parts of the system.

Subsequent evacuation at 100 K leads to fast disappearance of the broad feature at 2339 cm⁻¹ and

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‡ Electronic Supplementary Information (ESI) available: Electronic supplementary information (ESI) available: Experimental and computational details, Figures S1–S5 and corresponding text. See DOI: 10.1039/x0xx00000x

development of a sharp $\nu_{\text{as}}(^{12}\text{CO}_2)$ band at 2334.5 cm^{-1} with a shoulder at 2338 cm^{-1} (Figure 1, spectrum b). Simultaneously the OH groups become affected: shifted bands due to $\nu(\text{OH})$ at $3682\text{--}80\text{ cm}^{-1}$ and $\delta(\text{OH})$ at 1015 cm^{-1} developed (see Figure S2 from the ESI). This evidences entering of CO_2 in the MOF pores and allows assigning the 2334.5 cm^{-1} band to CO_2 H-bonded to hydroxyl groups.

Additional evacuation (Figure 1, spectra c-f) causes a decrease in intensity of the band at 2334.5 cm^{-1} and development, at its expense, of the band at 2338 cm^{-1} . The latter one further decreases in intensity without changing its position (Figure 1, spectra g-j). Analysis of the $\nu(\text{OH})$ and $\delta(\text{OH})$ modes (Figure S2 from the ESI) indicates this band is also due to H-bonded CO_2 . Because the band at 2338 cm^{-1} is the only $\nu_{\text{as}}(\text{CO}_2)$ band detected at low coverage, it is assigned to $\text{OH}\cdots\text{O}^{12}\text{CO}$ adducts. The frequency is similar to that reported for CO_2 adsorbed on various MOFs and coincides with the value used as reference.¹⁹

The spectra presented in Figure 1 clearly demonstrate conversion between two adsorption forms (characterized by bands at 2338 and 2334.5 cm^{-1}). Note that the maximal integral intensity of the 2338 cm^{-1} band is roughly two times lower than that of the band 2334.5 cm^{-1} which suggests that the species formed at high coverage can be associated with structures involving two CO_2 molecules. The appearance of only one ν_{as} band for these species indicates that the CO_2 molecules are equivalent, i.e. the complex formed is highly symmetric.

The picture resembles numerous published spectra²⁰⁻²² showing the conversion of geminal to mono-ligand species, according to the reaction:



where S is a surface site (in our case, an OH group).

However, adsorption of a second CO_2 molecule to the same OH group should lead to an additional shift of the $\nu(\text{OH})$ and $\delta(\text{OH})$ modes, which was not observed (see Figure S2 from the ESI). Another important drawback from the geminal model comes from analysis of the $\nu_{\text{as}}(^{13}\text{CO}_2)$ band arising from the natural ^{13}C abundance. Normally, one could expect that this band will demonstrate the same behavior as the respective $^{12}\text{CO}_2$ band. Surprisingly, as seen from the inset in Figure 1, the maximum of the $\nu_{\text{as}}(^{13}\text{CO}_2)$ band at 2272 cm^{-1} is practically coverage independent. Because the natural abundance of ^{13}C is very low, ca. 1 %, the probability of having two $^{13}\text{CO}_2$ molecules in a dimeric structure is close to zero. Therefore, the results strongly suggest that the position of the 2334.5 cm^{-1} band is determined from some kind of vibrational interaction between two $^{12}\text{CO}_2$ molecules in dimeric structures.

In order to verify that the behavior of the $\nu_{\text{as}}(^{13}\text{CO}_2)$ band is due to surrounding of $^{13}\text{CO}_2$ by $^{12}\text{CO}_2$ molecules, we studied the adsorption of $^{13}\text{CO}_2$ alone as well as of a 1 : 1 $^{12}\text{CO}_2 + ^{13}\text{CO}_2$ isotopic mixture. These experiments were performed at higher temperature, ca. 200 K, in order to avoid the formation of CO_2 condensed on the external surface.

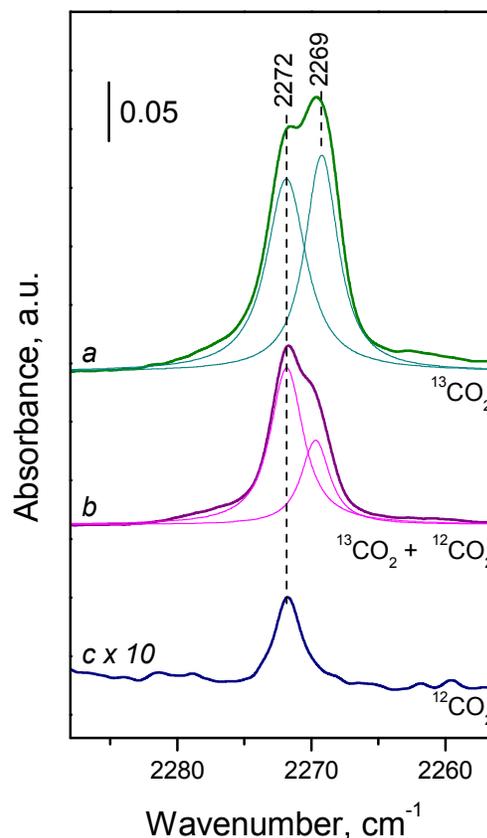


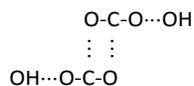
Fig. 2 FTIR spectra in the $\nu_{\text{as}}(^{13}\text{CO}_2)$ region of: $^{13}\text{CO}_2$ (a), $^{12}\text{CO}_2 + ^{13}\text{CO}_2$ (1 : 1 molar ratio) (b) and $^{12}\text{CO}_2$ (c) adsorbed at ca. 200 K on MIL-53(Al) (initial equilibrium pressure of 1 mbar). The spectra are background and gas-phase corrected.

Figure 2, spectrum a, demonstrates that adsorption of $^{13}\text{CO}_2$, as in the case of ^{12}CO adsorption, results in the formation of two $\nu_{\text{as}}(^{13}\text{CO}_2)$ bands. This unambiguously proves that the lower frequency component is associated with some kind of vibrational interaction between the adsorbed molecules. This conclusion is further supported by the spectrum of an adsorbed $^{12}\text{CO}_2 + ^{13}\text{CO}_2$ isotopic mixture (Figure 2, spectrum b). In agreement with the fact that only 50 % of the CO_2 molecules are ^{13}C -labelled, the overall intensity of the $\nu_{\text{as}}(^{13}\text{CO}_2)$ bands is ca. $\frac{1}{2}$ of the intensity of the bands shown in spectrum "a". However, in this case the relative intensity of the lower frequency band is significantly reduced. This is consistent with the statistic expectation that only one half of the $^{13}\text{CO}_2$ molecules participate in the vibrational interaction. Further decrease of the $^{13}\text{CO}_2$ concentration down to the ^{13}C natural abundance results in practical disappearance of the lower frequency band (Figure 2, spectrum c).

It is well known that the dipole-dipole coupling between the adsorbed molecules leads to increase in the stretching frequency (the so-called dynamic shift).²³ For this interaction to occur, the adsorbed molecules should be in close proximity, the dipoles oriented in the same direction and parallel to each other and should vibrate with the same frequency. Therefore, dynamic interaction is enhanced with coverage increase which should lead to a blue shift of the vibration frequency. In our

case we have the opposite shift which suggests that the interacting dipoles are oriented in opposite direction.

The results can be rationalized considering the following interaction:



According to this scheme, if the two CO₂ molecules are ¹²CO₂, they will interact vibrationally and the frequency will increase. However, if one of the molecules is ¹³CO₂, the interaction will be negligible due to the difference in the vibrational frequencies. Note that, based on our spectroscopic results, we cannot give a definite answer whether the adsorbed CO₂ molecules are tilted (O–H⋯O angle ≠ 180°) or not.

It was also found that the formation of the dimeric structures is connected with a CO₂-induced partial conversion of the material to a narrow-pore form as indicated by analysis of the region around 1020 cm⁻¹ and is in agreement with literature reports.¹¹ Figure S3 from the ESI shows the deformation C-H (ν_{18a}) modes of the terephthalate ligands. The position of this band is indicative of the large pore (1024 cm⁻¹) and narrow pore (1019 cm⁻¹) forms of the MOF structure.¹⁵ It is seen that before CO₂ adsorption the large pore form is predominant. Formation of dimeric structures upon CO₂ adsorption (band at 2334.5 cm⁻¹) provokes a substantial conversion to a narrow pore form. However, when the principal part of the dimeric structures is converted into monomeric ones, a tendency to a back conversion to the large pore form is seen. Note that the difference in the energy of narrow and large pore forms of MIL-53(Al) is very small.⁶ Evidently, the energy gained as a result of the formation of the dimeric complex is high enough to cause a conversion of the MOF structure to a narrow pore form.

The above assumption is fully confirmed by the CO₂ adsorption-desorption isotherms measured at 195 K (Fig. S4 form ESI) clearly showing the breathing behavior of our MIL-53(Al) sample.

We further employed periodic density functional theory calculations (for details see ESI) to get an insight into the geometry of the CO₂ adsorption complexes. The optimised structure of the CO₂ dimer formed in the narrow pore form of MIL-53(Al) is shown in Fig. 3, while the structure of the CO₂ monomer (large pore MIL-53(Al)) is presented in Fig. S5 in the

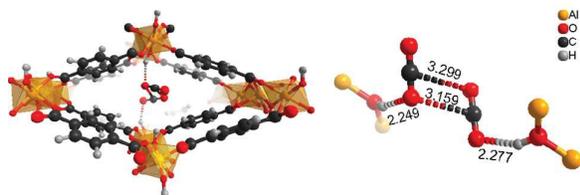


Fig. 3. Optimised structure of a CO₂ dimer in the narrow-pore structure of MIL-53(Al). Right panel depicts the location of the adsorption complex in the pore and the left panel shows a local structure of the dimer interacting with the lattice hydroxyls. Optimized interatomic distances are given in angstroms (for the colours the reader is referred to the WEB version of the article).

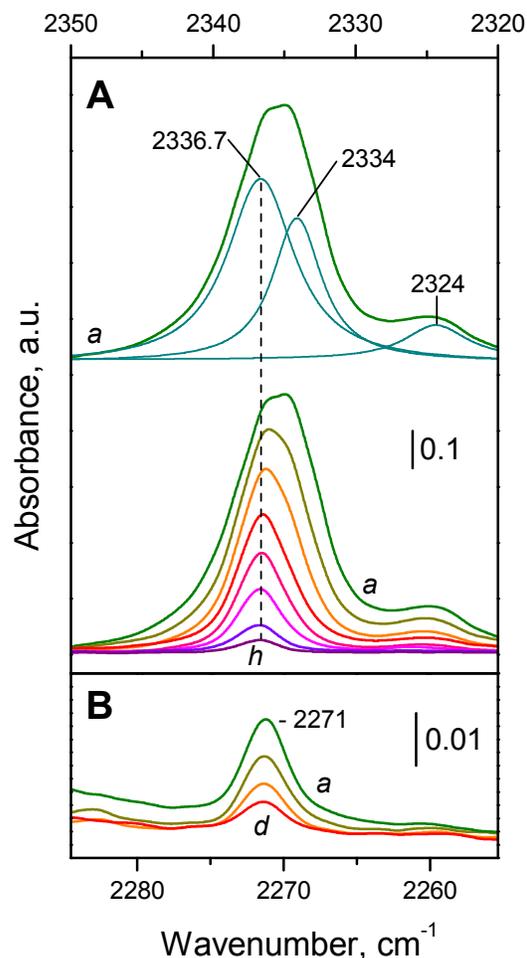


Fig. 4. FTIR spectra of ¹²CO₂ adsorbed at ambient temperature on MIL-53(Al). Equilibrium pressure of 100 (a), 50 (b), 30 (c), 15 (d), 10 (e), 5 (f), 1 (g) and ca. 0.1 mbar CO₂ (h). The spectra are background and gas-phase corrected. Panel A, region of ν_{as}(¹²CO₂). Panel B, selected spectra in the ν_{as}(¹³CO₂) region.

ESI. In both structures, adsorbed CO₂ molecules form weak bonds with the bridging hydroxyl groups of MIL-53(Al) framework. The dimer adsorption complex is characterized by a slipped parallel configurations of the CO₂ molecules closely resembling the van der Waals complexes reported for the condensed phase carbon dioxide.²⁴ In line with the experimental observations, the IR active symmetric with respect to the bimolecular [CO₂]₂ ensemble ν₃ mode in the dimer complex is red-shifted by ca. 4 cm⁻¹.

The results obtained at low temperature, although having a fundamental significance, are not closely related to the practical application. Therefore, we studied CO₂ adsorption at ambient temperature. Briefly, CO₂ adsorption at low pressures (Figure 4A, spectra d-h) leads to appearance of a band at 2337 cm⁻¹. The band is slightly shifted as compared to the low temperature experiments, which is likely due to a temperature effect. At increase of the equilibrium pressure above 15 mbar (Figure 4A, spectra a-c), two more bands, at 2334 and 2324

cm⁻¹ develop. The latter is usually assigned to a "hot" CO₂ band and will be not discussed here.

The band at 2334 cm⁻¹ is assigned to dimeric ¹²CO₂ structures and the conclusion is supported by analysis of the ν_{as}(¹³CO₂) band (Figure 4B). Thus, the results demonstrate that even at room temperature dimeric species are produced after CO₂ adsorption on MIL-53(Al) when the equilibrium CO₂ pressure is high enough. For instance, it was estimated that ca. 20 % of the adsorbed CO₂ is in dimeric form at 30 mbar equilibrium pressure.

It is worth discussing how the formation of CO₂ dimers affects the adsorption characteristics. We imply that this should not seriously affect the adsorption isotherms because the energy gained in the formation of the dimer is consumed for the phase transition to the narrow pore form. It was earlier shown⁶ that CO₂ interacting simultaneously with two OH groups is a stable structure in the narrow pore form of the MOF and in this case the maximal number of adsorbed molecules is ½ of the number of OH groups. However, the formation of the dimeric structures shown in Fig. 4 indicates that all of the OH groups can attach one CO₂ molecule each.

In conclusion, adsorption of CO₂ on MIL-53(Al) leads, at low coverages, to formation of OH...OCO adducts. At high coverages dimeric CO₂ species are produced where each CO₂ molecule interacts via one of its oxygens with the proton from an OH group. The two CO₂ molecules interact vibrationally which leads to decrease of the ν₃ frequency. Upon formation of these dimers, transition from the large pore to the narrow pore form occurs.

Acknowledgments: The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 608490, project M4CO2. The authors thank Prof. M. Daturi for some helpful suggestions as well as Dr. G. Li and Dr. I. A. W. Filot for computational support. NWO is acknowledged for providing access to supercomputer resources.

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