

Investigation of the CO₂ Adsorption on Cu-BTC by Combining Vibrational Spectroscopy and Molecular Dynamics

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Metal-Organic Frameworks (MOFs) are a novel class of materials with promising performances in the field of gas adsorption due to their high specific area and stable nanoporous network. It has been demonstrated that by tailoring the nanocavities size and the nature of specific chemical interaction sites, it is possible to obtain high selectivity for low molecular weight compounds. The adsorption capability is highly affected by the presence of water, which can directly influence both the structure of the material and the amount of available interaction sites. In particular, Cu-BTC MOF is widely adopted for CO₂ capture. In this work, we provide information at molecular level on the mechanism of CO₂ adsorption in Cu-BTC, through “in situ” quantitative spectroscopic investigation at various temperature, and CO₂ pressure. The experimental results have been integrated with molecular dynamics simulations, based on a force field already available in literature, to shed light on the role of interaction sites and of induced structural modifications.

1. Introduction

Carbon dioxide emissions have dramatic consequences for humans and environment. Extensive efforts are focused on its capture and adsorption (Duren et al., 2009) by selecting or designing of novel materials which exhibits a good compromise between adsorption capability and selectivity. In this regards, Metal-Organic Frameworks (MOFs) are very promising materials (Hamon et al., 2010; Babarao and Jiang, 2008) for applications in gas separation, gas capture and catalysis. MOFs consist of metal ions coordinated to ligands (organic groups) which form stable three-dimensional structures (Yang et al., 2008), characterized by very high surface area (about five times higher than zeolites). Process efficiency depends on MOFs structures and on the specific pair metal/ligands. The major advance of MOFs over zeolites or activated carbons is related to the higher possibility of tailoring their structures and chemistry in order to meet the requirements for specific applications by using feasible and modular synthesis (Garcia-Péres et al., 2009). In the context of CO₂ adsorption, several authors investigated the effect of organic ligands and metal ions, of pore size and topology on the adsorption properties in MOFs (Duren et al., 2009). For instance, Aprea et al. (2010) evaluated the CO₂ adsorption isotherms on copper benzene tri-carboxylate (Cu-BTC) varying temperature by means of a volumetric technique, confirming its noticeable CO₂ adsorption capacity. Further, the effect of water removal on the adsorption mechanism is investigated by Valenzano et al. (2010) by combining Raman spectroscopy and gravimetric measurements.

In this work we analyse the adsorption of CO₂ in Cu-BTC through the synergistic use of *in situ* vibrational spectroscopy (FTIR) and Molecular Dynamics (MD). Both approaches represent, in fact, powerful tools to get insights on the interaction at molecular level. The Cu-BTC has been selected among MOFs since it is one of the most simple in terms of structure; it can be synthesized from non-expensive primary compounds and it is also commercially available. It is worth noting that, in the literature, are available several papers dealing with Grand Canonical Monte Carlo (GCMC) simulations (Yang et al., 2008). One of the limits of the GCMC derives

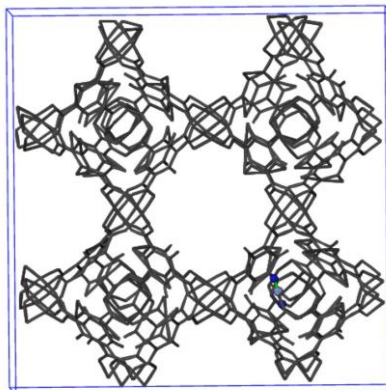


Figure 1. Snapshot of the simulation box with eight cells of Cu-BTC and one CO₂ molecule (placed inside the tetrahedral pocket).

from the assumption of rigid structure of the MOF. With MD simulations, this drawback can be overcome. The novelty of our work is the use of the combination of atomistic MD simulations and quantitative *in situ* spectroscopy. As a result, we show that in the diluted regime, three CO₂ populations can be identified in the system, due to the presence of Cu-BTC specific interaction sites which we found to play a different role varying temperature.

2. Materials and Methods

2.1 Experimental methods

The FTIR measurements were performed under gas flowing using a modified Linkam cell (THMS350V) equipped with temperature control (83 – 623 K) and a vacuum system. The cell was connected through service lines to a mass-flow-controller to set the CO₂ flux, while a solenoid valve controlled the downstream pressure. The flux was 20 SCCM with a concentration of 0.0078 mol/L at 150 Torr. The system was equipped with a Pirani vacuumeter and a MKS Baratron 121 pressure transducer (full scale 1000 Torr, resolution 0.01 Torr and accuracy $\pm 0.5\%$ of the reading). The equipment allowed the *in-situ* activation of the sample and the collection of isothermal data at different temperatures. The diffusion cell was accommodated in the sample compartment of a modified FTIR spectrometer (Spectrum 100 from Perkin_Elmer, Norwalk, CT), equipped with a Ge/KBr beam splitter and a wide-band DTGS detector. Spectra were acquired in the single-beam mode and the instrumental parameters were set as follows: resolution = 2 cm⁻¹; data interval = 0.250 cm⁻¹; Optical Path Difference (OPD) velocity = 0.20 cm/s; spectral range 450-4000 cm⁻¹. The absorbance spectra were obtained using a background collected on the cell with KBr window, at the test conditions.

2.2 Molecular Dynamics

Molecular dynamics can be used to obtain some useful insight about the most probable positions of carbon dioxide inside the Cu-BTC and hence to connect those results with spectroscopic data. Since the most expected positions are probably connected to long-range interactions between specific atoms in MOF and atoms of CO₂ molecules, we choose to adopt an all-atoms level of detail. This implies high computational costs, which heavily limit the choice of the size of the system. To cope with this drawback it is possible to adopt a multi-scale simulation approach which benefits, in terms of computational efficiency, both of coarse descriptions (e.g. Brasiello et al., 2010) and of the level of detail of an all-atoms simulation (e.g. Brasiello et al., 2012; Pizzirusso et al., 2015).

The system consists of a set of material points (beads) which interact each other through suitable potentials (e.g. Brasiello et al., 2011). Each bead represents an atom, while the system represents a suitable portion of the solid, placed in the bulk of the material together with the carbon dioxide molecules. The equations applied to the system are the following:

$$m_i \ddot{\mathbf{r}}_i = - \frac{\partial U}{\partial \mathbf{r}_i} \quad (1)$$

In which the right-hand side is the force-field given by:

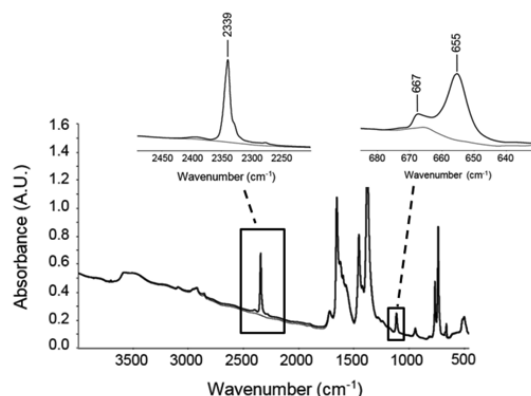


Figure 2. Absorbance spectra of fully dried Cu-BTC (thin line) and of Cu-BTC equilibrated at 150 Torr (thick line), at 308 K. The insets highlight the antisymmetric stretching and the bending ranges.

$$U = \underbrace{\frac{1}{2} \sum_{\text{bonds}} U_{\text{bonds}}(r_{ij}, r_{eq}) + \frac{1}{2} \sum_{\text{angles}} U_{\text{angles}}(\theta_{ijk}, \theta_{eq}) + \frac{1}{2} \sum_{\text{dihedrals}} U_{\text{dihedrals}}(\phi_{ijk}, \phi_{eq})}_{U_{\text{intermolecular}}} + \underbrace{4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{Q_i Q_j}{4\pi\epsilon_0 r_{ij}}}_{U_{\text{intramolecular}}} \quad (2)$$

in which r_{ij} is the distance between atoms i and j . In Eq. (2), we distinguish intermolecular and intramolecular potentials. Intermolecular potentials take into account bonds, angles and torsional interactions between consecutive linked atoms, while intramolecular potentials represent Lennard-Jones and Coulombic interactions. Periodic boundary conditions are applied on each edge of the simulation box. Several force field parameters are available in literature (Duren et al., 2009; Rappe et al., 1992). Here, Universal Force Field (UFF) is adopted since it is well-established that it provides better results in terms of properties predictions and transferability. The adopted simulation box of Cu-BTC with a carbon dioxide molecule is shown in Fig. 1; only a portion of a Cu-BTC crystal can be taken into account. More precisely, as can be seen easily in Fig. 1, the considered portion includes eight tetrahedral pockets and eight central cavities, which corresponds to eight elementary cells of the Cu-BTC. It is worth noting that each tetrahedral pocket is connected to the central cavities through four triangular shape channels, each one located at a vertex.

3. Results and discussions

The FTIR spectra were collected at 308 K and 173 K on the Cu-BTC fully dried and on Cu-BTC equilibrated at different pressures, from 40 to 150 Torr, after the activation of the sample under vacuum at 423 K. In Fig. 2 were compared the spectra of fully dried Cu-BTC (thin line) and the same sample equilibrated at 150 Torr (thick line).

The bands characteristic of the guest molecule are immediately apparent at 2339 cm^{-1} [O=C=O antisymmetric stretching, ν_3] and at 655 cm^{-1} [O=C=O bending, ν_2]. The spectra of CO_2 adsorbed at each pressure can be isolated after suppression of the polymer interference by difference spectroscopy, i.e. by subtracting the spectrum of the activated sample from that of the sample equilibrated at a specific CO_2 pressure.

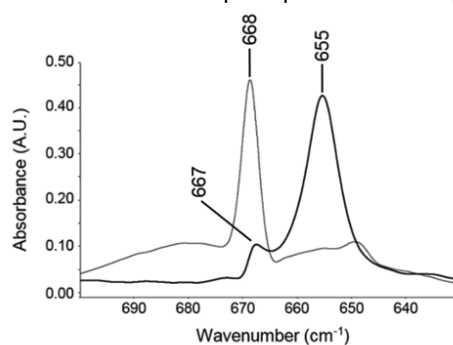


Figure 3. Absorbance spectra in the bending region of CO_2 gas-phase (thin line) and of Cu-BTC/ CO_2 (thick line).

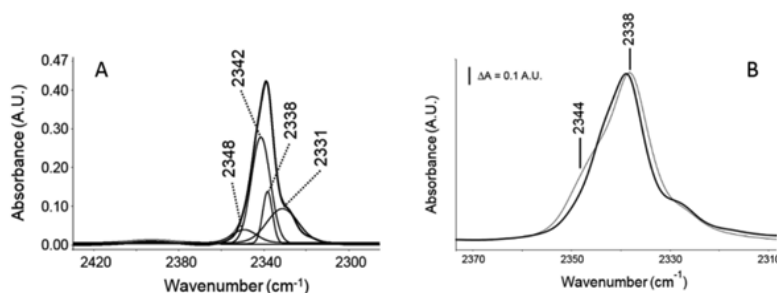


Figure 4. A) LSCF analysis of the spectrum of CO₂ adsorbed in the Cu-BTC stretching region, at 308 K and 150 Torr. B) Comparison of the spectra of CO₂ adsorbed in Cu-BTC at 308 K (thick line) and 173 K (thin line).

The comparison between the spectra of CO₂ adsorbed in Cu-BTC and in the gas phase is in line with previous literature reports (Nijem et al., 2011): the ν_3 mode is *red-shifted* by -10 cm^{-1} , the ν_2 vibration by -13 cm^{-1} . These shifts are due to a molecular interaction between the nucleophilic oxygen of CO₂ and the Cu cation (Valenzano et al., 2010). In the bending region a fully resolved, low intensity component is also detected at 667 cm^{-1} , a frequency essentially coincident with that of gas-phase CO₂ (668 cm^{-1}), see Fig. 3.

This component demonstrates the presence of a *gas-like* fraction of adsorbed CO₂, i.e., non-interacting guest molecules in the framework cavities. According to the intensity ratio between the respective components, it is concluded that the fraction of freely rotating CO₂ molecules is minor with respect to the interacting fraction. Work is in progress to develop a methodology to quantify the respective populations.

A closer analysis in the stretching range has been performed on difference spectra, by Least Squares Curve Fitting (LSCF). Four components were identified, whose position is indicated in Fig. 4 (A).

The 2331 cm^{-1} component corresponds to a non-fundamental mode [a *hot-band* combination ($\nu_2' - \nu_2 + \nu_3$)] and is not to be interpreted as a perturbation of the fundamental mode. The two components at 2338 and 2342 cm^{-1} identify two interacting CO₂ populations, whereby the interaction strength decreases in going from the high to the low frequency component. Finally, a last feature is found at 2348 cm^{-1} , very close to the ν_3 frequency of the CO₂ gas-phase (2349 cm^{-1}). The presence of this feature, in accord with the results in the bending range, confirms the occurrence of a *gas-like* fraction in the Cu-BTC nanocavities.

Experimental results give specific information about CO₂ populations in Cu-BTC, each corresponding to interactions with specific MOF's sites. In order to find a correspondence between FTIR data and CO₂ populations, we perform Molecular Dynamics simulations at constant temperature (NVT) of a box formed by eight fundamental cells of Cu-BTC with a single CO₂ molecule inside. It can be easily demonstrated that experimental conditions correspond to a numerical concentration of CO₂ molecules inside the box of less than one (diluted regime) which implies that no self CO₂ interactions can be considered in a statistical sense. Assuming that ergodic approach holds, we have preliminarily verified that for the purposes of this work, a simulation time of 12 ns is enough to attain significant statistics. On the basis of spectroscopic investigation, it is reasonable to assume that the identified interactional sites should correspond to different spatial positions within the system. From a statistical point of view, we expect that such spatial positions are the most explored during the simulation time.

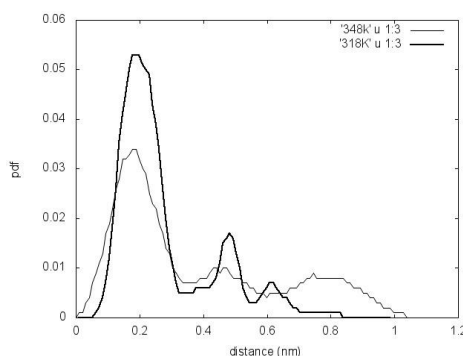


Figure 5. Probability density function of distance of the centre of mass of the CO₂ molecule referred to the centre of the tetrahedral pocket provided by NVT simulations at 348K (thin line) and 318K (thick line).

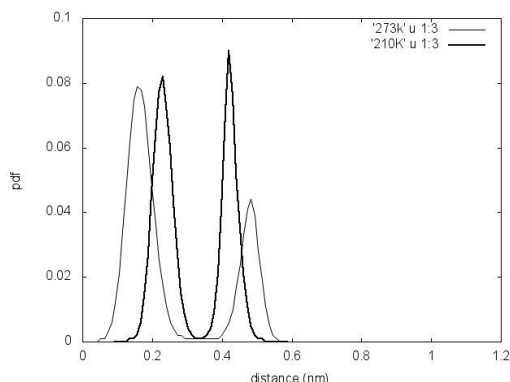


Figure 6. Probability density function of distance of the centre of mass of the CO₂ molecule referred to the centre of the tetrahedral pocket provided by NVT simulations at 273K (thin line) and 210K (thick line).

In order to get better insights from the statistical investigation, we introduce, at each time, the distance d measured between the centre of mass of CO₂ molecule and the centre of the fundamental cell in which is located. In Fig. 5, are reported the corresponding probability density functions (pdf) of such variable for two NVT simulations at 348K and 318K, respectively. At both temperatures, three peaks appear which represent three different CO₂ populations. From the comparison with the snapshot of Cu-BTC reported in Fig. 1 (the length of the simulation box is 2.49 nm), it is possible to interpret the position of these peaks as follows: the peak with maximum at about 0.2 nm is related to a position within the tetrahedral pocket; the peak with maximum at about 0.45 nm corresponds to a position which could be ascribed to the triangular channels; the peak with the maximum at about 0.8 nm is referred to a position within the central cavities. We observe that at 348K, the dispersion of the population located within the tetrahedral pocket is significantly lower compared to the case of the other two populations. Highest dispersion is observed for the peak at 0.8 nm. This means that the CO₂ molecule is able to explore the whole space of both the triangular channels and of the central cavities. At 318K, we observe that the positions inside the tetrahedral pocket exhibits higher probability with respect to the case at 348K with lower dispersion around the corresponding maximum. Moreover, the most probable positions within the central cavities are those close to Cu ions and, in particular, positions at distance higher than 0.8 nm are not allowed.

By progressive temperature reduction, it is evident that the positions within the central cavities become less and less available to CO₂ molecule, as can be seen by comparison of Fig. 5 and Fig. 6. In particular, from 273K down we observe only two CO₂ populations: the one associated with the triangular channels and the one located within the tetrahedral pockets. Moreover, the dispersion around the correspondent maximum for both populations declines by decreasing temperature. It is worth noting that at 210K the positions related to the triangular channels become more probable than the ones within the tetrahedral pockets.

The simulation results can be correlated to those of FTIR analysis. We can infer that the gas-like fraction (which experimentally represents the lower fraction) corresponds to the CO₂ displaying the peak with the maximum at about 0.8 nm at 348K, which at lower temperature tends to disappear. This is consistent with the trend, as a function of temperature, evident in the spectra reported in Fig. 4 (B). With similar argumentation, the other two pdf peaks can be assigned to the other two CO₂ populations identified through FTIR measurements. In particular, we observe that both the value of the maximum associated to position related to the triangular channels and the value of the absorbance peak at 2342 cm⁻¹ increase by lowering the temperature. Consequently, we can argue that the interactions corresponding to this absorbance peak is related to CO₂ confined in the region of the triangular channels which is the region close to Cu ions. This confirms literature results (Valenzano et al., 2010). Similarly, the absorbance peak at 2338 cm⁻¹ should correspond to the population located within the tetrahedral pockets.

In Fig. 7, we further report the pdf related to a NVT simulation performed at 73K. In agreement with the trend observed, at significant low temperature, only the CO₂ population, located in correspondence of the triangular channels, appears. Further experimental investigations and topological analysis are required to verify the proposed picture and will be the object of future work.

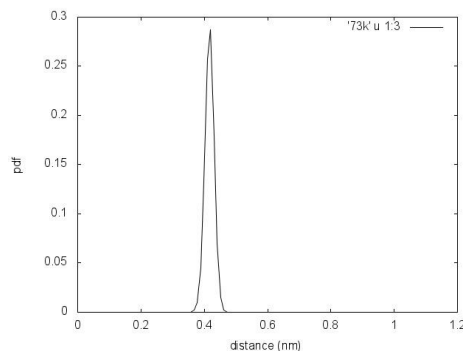


Figure 7. Probability density function of distance of the centre of mass of the CO_2 molecule referred to the centre of the tetrahedral pocket provided by NVT simulations at 73K.

4. Conclusions

In this work a system of eight elementary cells of Cu-BTC MOF with one CO_2 molecule has been analysed through all-atoms MD simulations combined with investigation by *in situ* FTIR techniques. The selected CO_2 concentration corresponds, in particular, to the dilute regime, experimentally investigated. Spectroscopic analysis showed the presence of three populations of carbon dioxide in the MOF. Among them, a gas-like fraction has been found. MD simulations have been used to infer the identified CO_2 populations to the topology of the system. In particular, the gas-like fraction is coherently identified with the CO_2 in the central cavity, while, at low temperature, we argue the possibility that the steric hindered position in the triangular channels (close to Cu ions) is most favourable. Further experiments need to strength this picture.

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