



# Conformational analysis of 1,2-dichloroethane adsorbed in metal-organic frameworks

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## ABSTRACT

This paper describes the conformational analysis of 1,2-dichloroethane adsorbed into three different metal-organic frameworks, MIL-53(Al), MIL-68(In), MIL-53-NH<sub>2</sub>(Al), by using FT-Raman spectroscopy in combination with powder XRD and TGA. For non-polar frameworks, the main guest-host interactions are van der Waal interactions between the C–H bonds of 1,2-dichloroethane (DCE) and the  $\pi$  system of terephthalate ligands. The polar framework of MIL-53-NH<sub>2</sub> is able to stabilize the *gauche* conformation of DCE at room temperature. The conformational enthalpy of each system was determined through variable temperature FT-Raman spectroscopy. Furthermore, the line-width of the Raman bands provides information regarding the molecular motion of the halocarbons at various temperatures inside the framework.

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## 1. Introduction

Metal-organic frameworks (MOFs) are a class of microporous materials. Porous and thermally stable novel MOFs were first reported in 1999 by Yaghi et al. [1] MOFs are more versatile than other microporous materials such as zeolites, due to their ability to functionalize organic linkers, which facilitates rational design. Different organic linkers can be used to form different frameworks with the same metal to change the properties of the resulting MOF [2–4]. Due to the porous nature of MOFs, their most common applications involve the adsorption of different guest molecules [5–8]. In order to understand the adsorption process, it is important to know how the guest molecule interacts with the framework of the MOF.

Halocarbons are highly toxic to the environment and humans. They are known to cause cancer, brain damage, birth defects, liver failure, and an assortment of other diseases [9,10]. 1,2-Dichloroethane (DCE) (Fig. 1) is a widely used organic solvent, of which over 100 tons is consumed on an annual basis in Canada. DCE's toxicological properties include being a possible carcinogen, causing chronic liver and kidney problems. It also has moderate to acute toxicity levels from oral exposure or inhalation. Disposal of halocarbon waste is problematic as incineration can lead to poisons and corrosive acids being released. Long-term storage may

present a solution to the current problem. MOFs are a potentially viable candidate for adsorption and removal of DCE from solvated systems.

In this paper, the results of the conformational analysis of DCE in a series of MOFs by FT-Raman spectroscopy, thermal gravimetric analysis, and powder X-ray diffraction will be presented. The purpose of this study is to examine how different MOF properties affect the adsorption of DCE.

The conformation of DCE has been the target of investigation since the 1930s [11]. Multiple techniques such as NMR, vibrational spectroscopy, photoelectric spectroscopy, and theoretical calculations have been used to determine the conformations of different halocarbons [12–15]. DCE can exist in both the *trans* and *gauche* conformations (Fig. 1). Vibrational spectroscopy has been used to study the conformation of halocarbons as the C–Cl stretch for both the *trans* and *gauche* conformers can be easily resolved. To investigate the conformational behavior of halocarbons, variable-temperature vibrational spectroscopy was often employed [11]. It was determined that for DCE in the liquid and gas phase, a mixture of both the *trans* and *gauche* conformer co-exist, whereas in the crystalline solid only the *trans* conformer exists. The conformational mixture of DCE in the liquid and gas phases does not exist as a 50/50 mixture as the energy difference between the *trans* and *gauche* conformers is 5.02 kJ/mol. In the gas phase the *trans* population of DCE is favored and its population is 77%, whereas in the liquid phase the *trans* population of DCE is 35% [16]. The phenomenon that stabilizes the *gauche* conformer in the liquid phase is polar interactions that exist between DCE molecules. DCE

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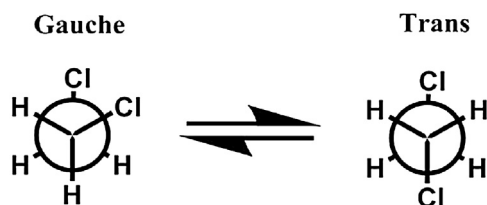


Fig. 1. (left) DCE *gauche* conformation, (right) DCE *trans* conformation.

has a net dipole moment of 3.12 D in the *gauche* conformation, and the *trans* conformer has no permanent dipole moment [17]. It has previously shown that the *gauche* conformer is stabilized in polar solvents by solvent-solute effect [18]. Hydrogen bonding has also been shown to be an important interaction with guest molecules and MOFs [19].

In non-polar solvents such as  $\text{CCl}_4$ , it has been proven by theoretical calculations that there is still a preference for the *gauche* conformer. The solvent can be seen as a dielectric medium that can have an induced dipole. This induced dipole allows DCE to favour the *gauche* conformer to a larger extent than seen in the gas phase [20]. Previous studies have shown that guest-host interactions between chlorinated hydrocarbons and porous materials, such as zeolites, exist [17,21]. Zeolites with either cations or small cages allow DCE to have a higher percentage of the *gauche* isomer [17,22]. Siliceous zeolites that have neutral frameworks showed a preference for the *trans* isomer [17,22]. A previous Raman spectroscopic study determined the volume difference between the two conformers, showing that the *gauche* conformer's volume is  $2.7 \text{ cm}^3/\text{mol}$  smaller than that of the *trans* isomer [13]. Studies also show vibrational spectroscopy having a strong temperature dependency on host-guest interactions [23,24]. This study will present the relative proportion of DCE in the *trans* conformation and *gauche* conformation when loaded into different MOFs (MIL-53(Al), MIL-68(In), MIL-53-NH<sub>2</sub>(Al)) (Fig. 2).

## 2. Experimental

MOF MIL-53(Al), MIL-68(In), and MIL-53-NH<sub>2</sub>(Al) were all synthesized using previously published syntheses [2–4]. The exact quantities of materials, solvent, temperature and synthesis time can be found in Table 1.

To perform the loading, each sample was evacuated in a glass tube under vacuum for 6 h at 300 °C. The sample was then sealed

using Teflon tape under vacuum, and DCE was loaded using a micro-syringe, followed by flame sealing the glass tube. The glass tube was then heated to 95 °C overnight to allow DCE to enter the pores.

The PXRD experiments were carried out by using a Rigaku diffractometer with Co K $\alpha$  radiation ( $\lambda = 1.7902 \text{ \AA}$ ). All the samples were scanned between 5 and 45° at a scan rate of 10°/min, with a 0.02° increment rate.

In order to determine the maximum loading of each sample thermal gravimetric analysis (TGA) was performed. TGA experiments were conducted by using a Mettler Toledo TGA/SDTA 851e with a flow rate of N<sub>2</sub> of 60 mL/min. Each sample was heated from 298 to 673 K at a rate of 10 K/min. The derivative of each TGA curve (DTG) was used to determine the total loading of each MOF.

FT-Raman experiments were carried out on a Bruker RFS 100/S FT-Raman spectrometer equipped with a Nd<sup>3+</sup>/YAG laser operating at the wavelength of 1064 nm and a liquid nitrogen-cooled Ge detector. The maximum laser power of the spectrometer was 500 mW. The power of the laser at the sample varied with each system in order to maximize the signal, while minimizing the fluorescence of the sample. The laser power ranged from 50 to 150 mW at the sample during the experiments. The resolution used for a majority of samples was  $4 \text{ cm}^{-1}$  with the exception of the DCE/MIL-53-NH<sub>2</sub> system where a resolution of  $2 \text{ cm}^{-1}$  was used. To conduct the VT experiments, a Bruker Eurotherm 800 series temperature control unit with an accuracy of  $\pm 1 \text{ }^\circ\text{C}$  was used.

## 3. Results and discussion

### 3.1. Dichloroethane/MIL-53

MIL-53, which stands for Matériaux de l'Institut Lavoisier 53, is a metal-organic framework that contains benzene dicarboxylate (BDC) ligands as organic linkers that connect to metal centers (aluminum for this study) to form a stable and flexible framework [2]. Depending on the absorbed molecule, MIL-53(Al) will slightly alter its framework by changing its pore size, which is so-called the breathing effect [2]. Depending on the nature of guest molecule, the pore size of this flexible framework will change differently. For example, the as-made (AM), the high-temperature (HT) and the low-temperature (LT) phases all have a different pore size [2]. In addition to the change in pore diameter, crystallographic space groups and unit cell dimensions also change upon adsorption. For example, MIL-53(AM) belongs to a monoclinic crystal system and

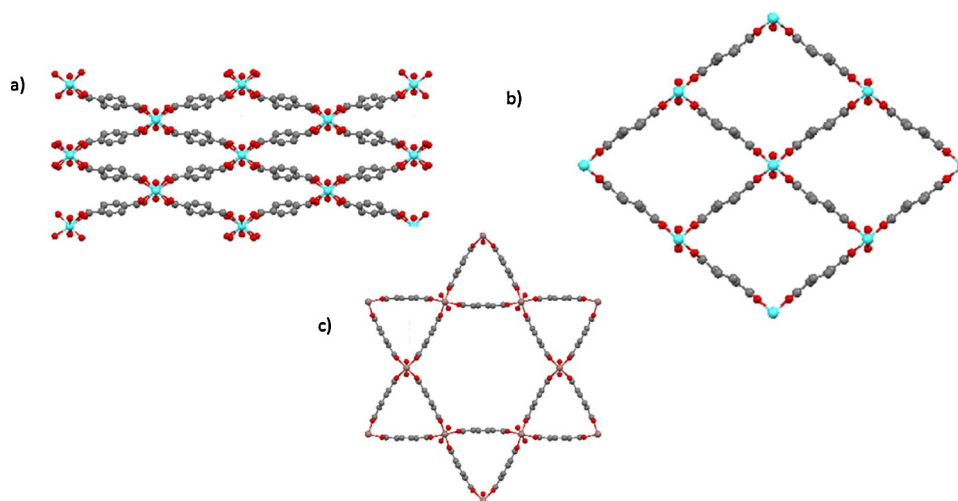


Fig. 2. a) MIL-53(As-Made) (red = oxygen, blue = aluminum, grey = carbon), b) MIL-53(High Temperature) (red = oxygen, blue = aluminum, grey = carbon), c) MIL-68 (As-Made) (red = oxygen, mauve = indium, grey = carbon).

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