## MS19-O5

# Investigating $CO_2$ uptake in $Sc_2BDC_3$ using XRD, *ab initio* DFT and GCMC methods

Jonathan Richardson[1], Jorge Sotelo[1], Stephen Moggach[1], Jamie McHardy[1], Carole Morrison[1], Tina Düren[2], Paul Wright[3]

1. School of Chemistry, University of Edinburgh, Edinburgh, United Kingdom
2. Centre for Advanced Separations Engineering, University of Bath, Bath, United Kingdom
3. School of Chemistry, University of St Andrews, St Andrews, United Kingdom

email: J.G.Richardson@ed.ac.uk

Despite the large number of MOFs that have been synthesised and are present in the Cambridge Structural Database, 84,185 as of Nov. 2017, very few have been studied for both their gas adsorption and mechanical properties.[1] Most investigations concerning the former are based upon adsorption isotherms and hence there is a lack of understanding concerning the location of adsorbed guest molecules within the pores and the nature of specific interactions between the guest molecules and the framework. Up to 2014, 120 crystallographic studies on frameworks containing adsorbed gas molecules had been reported, with only 47 frameworks investigated in all.[2] A more detailed understanding of these interactions will help us develop more insightful structure-property relationships, thereby aiding chemists in designing MOFs with enhanced or specific guest uptake.

The small-pore MOF $Sc_2BDC_3$ (where BDC = benzenedicarboxylate) was initially observed to undergo an orthorhombic-to-monoclinic phase transition, via rotation of one pair of BDC linkers, under $CO_2$ uptake at p = 1 bar and 235 K.[3] Here, we have used a combination of capillary gas cell XRD experimental and *ab initio* DFT and GCMC computational methods to show that the framework also undergoes the same phase transition, gradually, at 298 K at higher $CO_2$ pressures (complete at 3 bar). Additionally, a third adsorption site, which was not seen in the original investigation at 235 K, was observed; this discovery verified the expected maximum uptake of $CO_2$.

*Ab initio* DFT calculations determined that the monoclinic form of $Sc_2BDC_3$ is the lower energy geometry-optimised structure (by 13.3 kJ mol$^{-1}$); the orthorhombic phase however is present at 298 K due to the entropic term having greater weighting at this temperature. Therefore, the formation of the monoclinic phase at room temperature upon $CO_2$ uptake is a result of $CO_2$-framework interactions exceeding the energy barrier to linker rotation. This was shown using GCMC to model $CO_2$ uptake in the experimental framework structures, with stronger $CO_2$-framework interactions in the monoclinic phase. Additionally, there was good agreement between the binding site hierarchies observed by the three different methods, with a clear switching of the site hierarchy between the two phases. When a $CO_2/CH_4$ gas mixture was applied to this material, the XRD and computational methods showed that $Sc_2BDC_3$ has selectivity for $CO_2$ over $CH_4$; this was a result of weaker $CH_4$-framework interactions and specific $CH_4$ adsorption site locations which allowed $CO_2$ to occupy its strongest adsorption site unhindered.

References:

[1] Moghadam, P. Z. et al. (2017). Chem. Mater. 29, 2618-2635
[2] Carrington, E. J. et al. (2014). Acta. Cryst. B70, 404-422
[3] Miller, S. R. et al. (2009). Langmuir. 25, 3618-3626

**Keywords: MOF, XRD, computation**

## MS20 Rating and improving data quality: instrumentation, analysis and postprocessing

**Chairs: Dr. Karine Röwer, Dr. Loes Kroon-Batenburg**

### MS20-O1

## Experimental charge density studies: improvements in data processing

Regine Herbst-Irmer[1]

1. Institute of Inorganic Chemistry, University of Göttingen, Göttingen, Germany

**email: rherbst@chemie.uni-goettingen.de**

In experimental charge density investigation, it is indispensable to use the highest possible quality of data. Systematic errors should be avoided.

One systematic error is the low-energy contamination caused by focusing multilayer optics. To eliminate this problem filtering by interposition of a low-density material foil into the beam was proposed. However, filtering lowers the intensity, which might be crucial, especially for charge density data collection, and is of course not possible for already measured data. The low-energy contamination mainly affects the reflections with indices 3h 3k 3l. In the program SADABS [1], a $3\lambda$ correction in analogy to the earlier $2/\lambda$ correction is now implemented. [2]

In several charge density studies, we noticed that the residual density improved significantly after ten resolution dependent scale factors were refined. The dependency of the scale factors against resolution showed a typical pattern for all data sets, but the variation was much smaller for data collected at 15 K instead of 100 K. Therefore, this procedure seems to cure errors that are resolution and temperature dependent such as thermal diffuse scattering (TDS). Similar results could be obtained by processing data with relatively small integration boxes instead of refined box sizes. This procedure seems to emulate a rough TDS correction. However, to find the best integration box is very time consuming. In a nested interval approach, a correction factor $\{\alpha = a[\sin(\vartheta)/\lambda]^2 + b[\sin(\vartheta)/\lambda]^3\}$ is determined that minimizes these errors and improves the model quality. [3]

References:

[1] Krause, L. et al. (2015). J. Appl. Cryst. 28, 3-10.
[2] Krause, L. et al. (2015). J. Appl. Cryst. 48, 1907–1913.
[3] Niepötter, B. et al. (2015). J. Appl. Cryst. 48, 1485–1497.

**Keywords: data quality, low-energy contamination, thermal diffuse scattering**