

**Reviewer report of the Ph.D. thesis of Mikuláš Peksa “Ordering, transport and rotational dynamics of adsorbed carbon dioxide in metal-organic framework  $Zn_2(BDC)_2(DABCO)$ ”**

The Thesis summarises the research of Mikuláš Peksa focussed on dynamics of carbon dioxide in a metal-organic framework (DMOF-1). Two approaches were used: the analysis of molecular dynamics (MD) simulations and NMR experiments.

The Thesis follows the traditional layout: Introduction – Experimental details – Results – Conclusions. The introductory chapters are devoted to microporous host systems and to the theory of NMR. I appreciate very concise and meticulous explanation of the theory of NMR. The experimental and computational methods used in the work are summarised in the following chapter, which is then followed by the results. The experimental findings, such as chemical shift anisotropies and diffusion anisotropies of adsorbed  $CO_2$  at variable temperatures, are systematically compared with the MD simulations. New mathematical tools for this experiment-theory comparisons are derived in several places of the Thesis. Another important part of the Thesis is the NMR relaxation experiment and its analysis and interpretation in terms of the relaxation mechanisms.

The thesis is well written with only a few mistakes/inaccuracies and with a reasonable number of typos. The studied problematics is interesting, important and timely. The obtained results are original and deepen our understanding of  $CO_2$  adsorption in porous materials.

Most of the work presented in the Thesis has been published in two publications in a good scientific journal (*Microporous and Mesoporous Materials*, IF = 4.2); Mikuláš Peksa is the main author of both publications. These publications confirm very good quality of the conducted research and undoubtedly qualify the applicant for the Ph.D. degree.

In conclusion, I am convinced that the research done by the applicant is of high quality. Therefore, it is my pleasure to recommend the Thesis for approval and acceptance.

Prague, October 10, 2019

doc. RNDr. Martin Dračínský, Ph.D.

Questions that might be discussed during the defence:

- 1) You assume that the chemical shift tensor of the carbon nucleus in  $CO_2$  is independent of molecular deformation. Is this a reasonable assumption? Do you have, for example, DFT

calculated chemical shift tensors for snapshots from the MD simulation supporting this assumption?

- 2) Page 25: You claim: "The inter-molecular chemical shift interaction can be neglected because of the small CO<sub>2</sub> adsorption heat." Is there a relation between interaction energy and intermolecular shielding? Can a weakly bound compound be strongly affected by intermolecular shielding (e.g. by aromatic rings)?
- 3) Page 56: You claim: "The value of  $E_{\parallel/\perp}$  decreases with CO<sub>2</sub> loading. This is a consequence of higher population of adsorption site II due to occupation of adsorption site I." You also assume that for perpendicular diffusion, the molecule has to pass this trajectory: site I → site II → site II (neighbouring channel) → site I. Can you make a conclusion based on the loading dependence of the  $E_{\parallel/\perp}$  value that the barrier for the site I → site II jump is higher than for the site II → site II (neighbouring channel) process?
- 4) Page 59: You discuss a discrepancy between the MD simulation and NMR experiments in the loading dependence of  $E_{\parallel}$ . You speculate that a reason for this discrepancy might be a cooperativity of CO<sub>2</sub> binding not captured by the simulations. Have you tried/considered some DFT calculations that could relatively easily confirm or disprove this speculation?
- 5) Do you think that measurement of <sup>17</sup>O spectra of labelled carbon dioxide would be beneficial for the investigation of CO<sub>2</sub> dynamics?

A few randomly selected formal errors or minor mistakes:

Page 4: "Classical molecular dynamics simulation was used in this work since it is **unprecedented** method for theoretical calculations for systems with large number of atoms."

Page 7: "Because of the interaction between carboxylate oxygen and hydrogen of the benzene ring the BDC is stabilized in the plane of the paddle." I think more correct would be: Because of the conjugation of  $\pi$  electrons of the carboxylate group and the benzene ring, the BDC is planar.

Page 8: "... the inner surface of this MOF was estimated to be 1450 m<sup>2</sup> s<sup>-1</sup>." The units should probably be m<sup>2</sup>g<sup>-1</sup> or m<sup>2</sup>cm<sup>-3</sup>.

Page 13: "While Ni and Co MOFs show significant -effect upon adsorption..." What is -effect?