

## Natural abundance solid-state $^{67}\text{Zn}$ NMR characterization of MOF-5 at ultrahigh magnetic field

Andre Sutrisno,<sup>a</sup> Sanyuan Ding,<sup>b</sup> Wei Wang,<sup>b</sup> and Yining Huang<sup>a</sup>

(a) Department of Chemistry, University of Western Ontario, London, Ontario, Canada

(b) State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu, 730000, P. R. China

[yhuang@uwo.ca](mailto:yhuang@uwo.ca)

In recent years, a new class of porous materials namely metal-organic framework (MOF) has been developed [1, 2]. MOFs are crystalline hybrid inorganic-organic solids prepared via self-assembly of metal cations with organic linkers to form three-dimensional networks with novel topologies. The materials have high thermal stability, permanent porosity, flexible framework and exceptionally high surface areas. They have shown tremendous potentials for applications in catalysis, ion-exchange, in particular, gas storage and separation. The metal center in several important series of MOFs is zinc. In the present work, we report the first natural abundance  $^{67}\text{Zn}$  SSNMR study of Zn environment in a representative MOF, namely MOF-5. Specifically, we have measured natural abundance  $^{67}\text{Zn}$  spectra of MOF-5 samples with different degree of solvation at ultrahigh field of 21.1 T.

MOF-5 is one of the most widely studied MOF compounds. It possesses large cubic cavities with oxygen-centred  $\text{Zn}_4\text{O}$  tetrahedral at each of the cube's corners connected by an organic linker 1,4-benzendicarboxylate (BDC). It is thermally stable up to 350°C and has a very large surface area of ca. 4,000  $\text{m}^2/\text{g}$ . Previous studies showed that the solvent molecules can be completely removed from the framework by either solvent extraction or heat treatment while the framework still maintains its integrity and crystallinity.

Figure 1 shows the  $^{67}\text{Zn}$  static NMR spectra of MOF-5 with different degree of  $\text{CHCl}_3$  solvation. The solvated MOF-5 sample used in this study contains 14.9 % (by weight) of chloroform in its voids. Its spectrum is very sharp. Upon desolvation, the spectra of partially desolvated MOF-5 with ca. 8.2 wt.% guest molecules becomes

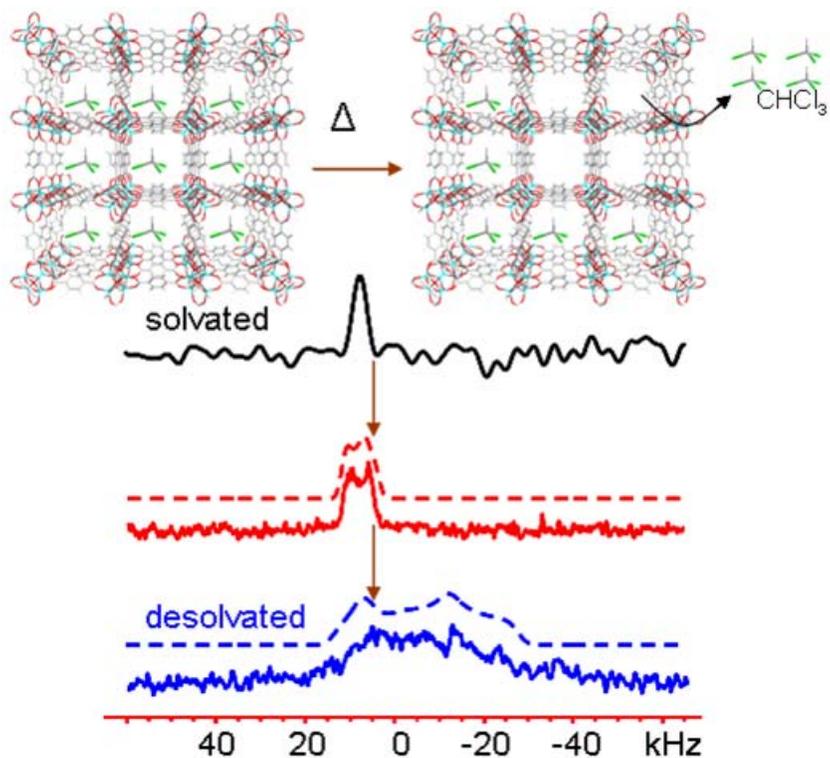
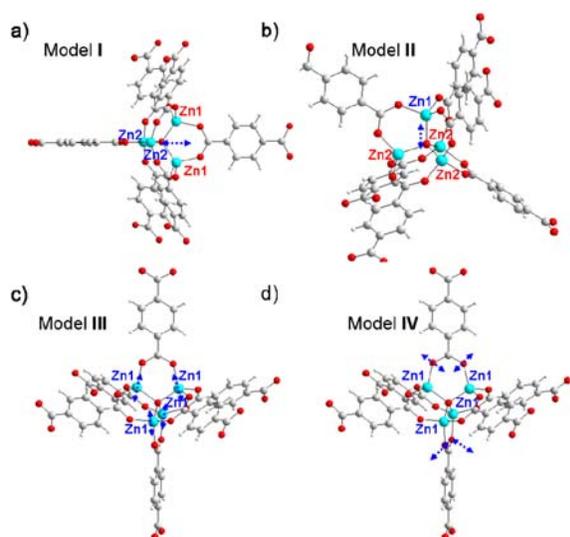


Figure 1:  $^{67}\text{Zn}$  static NMR spectra at 21.1 T of MOF-5 with different degree of solvation.

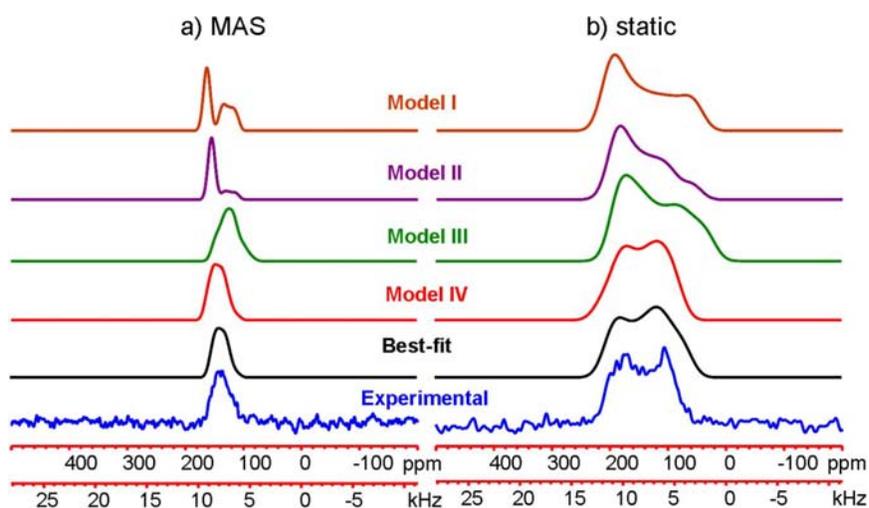


**Figure 2:** Four possible distortion models in  $\text{Zn}_4\text{O}(\text{BDC})_6^{6-}$  cluster in MOF-5.

broader due to the change in the Zn coordination environment. To gain insight into the relation between the observed  $^{67}\text{Zn}$  NMR spectra and the possible structural distortions in MOF-5 upon desolvation, the approach of computational modeling was employed.

Figure 2 shows four possible models of distortion on a series of  $\text{Zn}_4\text{O}(\text{BDC})_6^{6-}$  clusters with slightly modified geometries. For each model, a series of theoretical MAS and static spectra were calculated by using the computed NMR parameters, which then were compared with the overall profiles of the experimental spectra.

Figure 3 illustrates the best-matching MAS and static spectra for each type of distortion in a partially desolvated MOF-5 sample. It appears that the best-matching MAS and static spectra corresponding to a change in O–C–O angle by 4 degrees (model IV) have the overall line-shapes more resembling experimental than those obtained from other models. We have also examined  $^{67}\text{Zn}$  NMR spectra in a completely desolvated MOF-5 sample. The breadth of the central transition pattern in the static spectrum of this sample is about 45 kHz. Using the same computational approach, we suggest that a change of O–C–O angle (model IV) from  $125^\circ$  in solvated to  $137^\circ$  in a fully desolvated sample (corresponding to an increase in the Zn–O<sub>BDC</sub> distance by 0.11 Å) occurs upon removal of all the guest species.



**Figure 3:** Comparison of  $^{67}\text{Zn}$  experimental MAS (a) and static (b) NMR spectra recorded at 21.1 T in partially desolvated MOF-5 together with representative theoretical spectra from four distortion models.

#### References

- [1] M. O'Keeffe, M.A. Peskov, S.J. Ramsden, O.M. Yaghi, *Acc. Chem. Res.* **41** (2008) 1782.
- [2] "Metal-Organic Frameworks", *Chemical Society Reviews*, volume **38**, issue 5, (2009).