

X-ray absorption spectroscopy as a useful tool for revealing the structural details associated to the ZIF-8 flexibility upon gas adsorption.

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Among the different families of metal organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs)¹ have received a great deal of attention due to their thermal and chemical stability.² However, unlike zeolites with relatively rigid frameworks and apertures, the structure of ZIFs is rather flexible.^{3,4} Indeed, in the case of the prototypical ZIF-8 (Zn(MeIM)₂; MeIM = 2-methylimidazole), a change in the structure can be triggered by either mechanical pressure,⁵ or gas adsorption.⁶ This so called “gate opening” transition involves the swing of the MeIM linkers increasing the pore window size which induces a sudden increase in the gas uptake.⁶ We have studied the local structural changes associated with the ZIF-8 framework flexibility upon nitrogen gas adsorption by in situ X-ray absorption spectroscopy (XAS) and high energy resolution fluorescence detected X-ray absorption near edge structure (HERFD-XANES) spectroscopy.⁷ To elucidate the source of the spectral changes in the XANES region of the absorption spectra observed along the gas adsorption and through the transition from the closed to the open pore configuration, *ab-initio* calculations have been performed. Our results demonstrate that the transition from the closed to the open pore configurations not only involves the rotation of the MeIM ligand, but a further bend of the Me group away from the plane defined by the IM ring. Additionally, the contribution of the N₂ molecules adsorbed in the centre of the 4-ring window has been included in the scattering model to fully reproduce the main features of the X-ray absorption spectra in the open pore configuration.

References:

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