Experimental report

30/09/2025

Proposal: 7-05-624 **Council:** 10/2024

Title: Unraveling the Distorted Local Structure in Metal- and RRE-Doped Zeolitic Imidazole Framework 8 (ZIF-8) by Inelastic Neutron Scattering

Research area: Materials

This proposal is a resubmission of 7-05-613

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Samples: Nd-C8H10N4Zn
Cu-C8H10N4Zn
Pd-C8H10N4Zn
Ru-C8H10N4Zn
Sm-C8H10N4Zn
Fe-C8H10N4Zn
Same sample as original proposal but with other gaz added: N2, 1 bar

Instrument	Requested days	Allocated days	From	To
IN1	4	4	12/05/2025	14/05/2025
			09/10/2025	11/10/2025

Abstract:

ZIF-8 is a metal-organic framework known for its high surface area, porosity, selective gas adsorption capacities, and a gate-opening effect. Imidazole (Im) molecules in ZIF-8 link to two ZnII ions forming Metal-Linker-Metal bridges with an angle of ~ 120 º. In parallel, each metal has a tetrahedral coordination containing four nitrogen atoms belonging to four Im. The overall connectivity gives rise to a M12Im24 cages with a small pore window showing stimuli induced the gate-opening effect. Nevertheless, the relatively uncommon tetrahedral four-nitrogen coordination of Zn ions in ZIF-8 imply that the framework only accepts the integration of other metals as dopants. Doping ZIF-8 with transition metals and rare-earth elements could introduce structural distortions that potentially enhance gas adsorption properties, particularly for CO2. The aim of this INS experiment is to reveal how doping alters the local structure, impacting the adsorption capacity and gate-opening effects of ZIFs.

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In this experiment was measured 3 different Metal-Organic Frameworks (MOFs) based on the ZIF-8. It was obtained the INS spectrum for the pristine ZIF-8 and also the spectra for this MOF doped with Cu^{2+} and Fe^{3+} (see Fig. 1). Subsequently, it was injected 1 bar of CO_2 in the three systems and the spectra for gas-sorbed MOFs were also obtained in order to identify changes after the CO_2 adsorption and those ones produce by the doping as is shown in Fig. 1. It was utilized the monochromator with crystals of Cu(220) to capture energy transfers of E_i = 26-223 meV (k_i = 210-1800 cm^{-1}), with an energy resolution of $\Delta E/E$ = 2%, the monochromator with crystals of Si(311) to collect energy transfers of E_i = 16.5-60 meV (k_i = 133-484 cm^{-1}), and that one with crystals of Si(111) to measure energy transfers of E_i = 4.5-20 meV (k_i = 36-161 cm^{-1}), both with $\Delta E/E$ = 0.8%. All measurements were done at 10 K for both empty and gassed MOFs, using aluminum sample holders, which were also measured empty. Density Functional Theory and Molecular Dynamics calculations have been also performed aiming to interpret the experimental results.

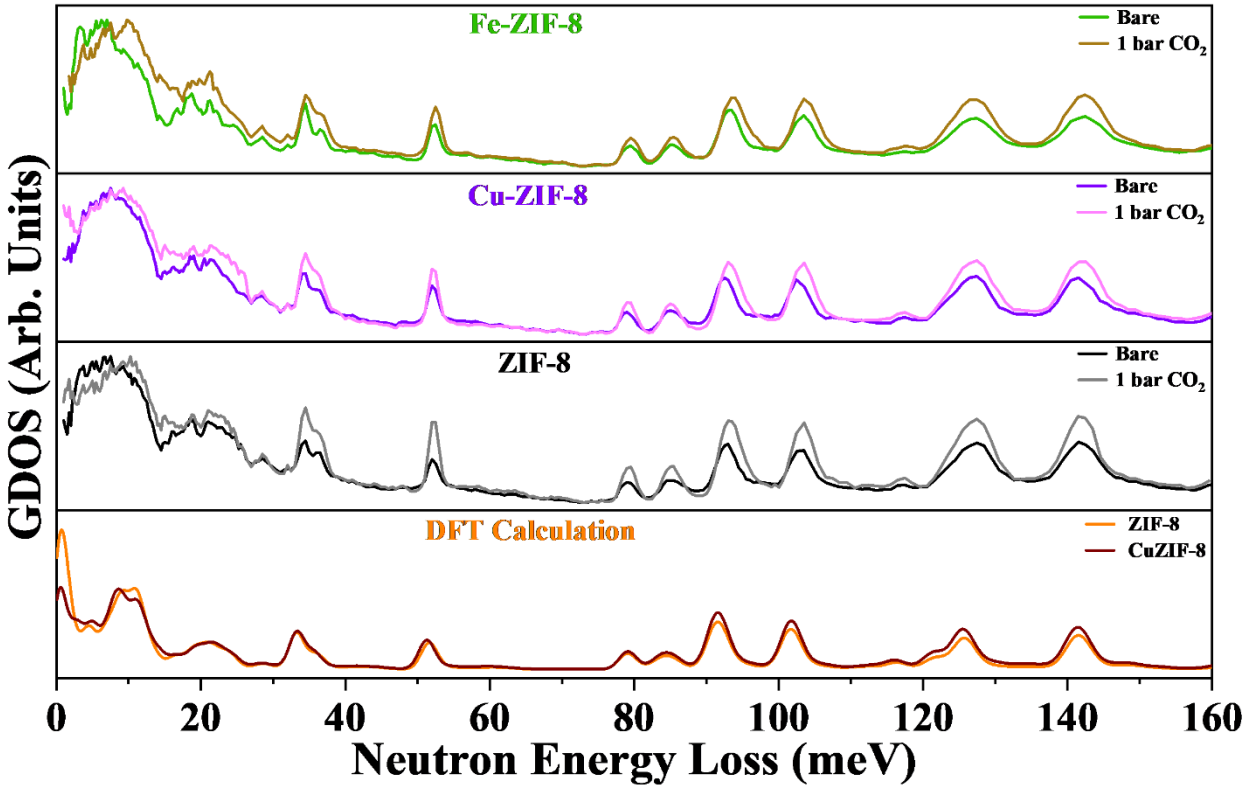


Figure 1: INS spectra for the ZIF-8, Cu- and Fe-ZIF-8; and DFT-calculated INS spectra for ZIF-8 and CuZIF-8.