ESRF	**Experiment title:** Spectroscopic investigations on the small-molecule adsorption mechanism in a perfluorinated Ce-based MOF	**Experiment number**: CH-5953
Beamline: BM23	**Date of experiment**: from: 24/07/2021 to: 27/07/2021	**Date of report**: 29/03/2023
Shifts: 9	**Local contact(s)**: Cesare Atzori	*Received at ESRF:*

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Report:

Proposal summary:

We propose to perform combined in situ DRIFTS/XAS/MS experiment at the Ce K-edge during evacuation and gas/vapour adsorption of a perfluorinated Ce(IV)-based metal-organic framework (MOF) with MIL-140 topology at beamline BM23. The aim of the experiment is to gain detailed insight into the changes in the local environment of Ce when removing H2O from the as-synthesised, hydrated material and when the MOF is exposed to adsorptives such as CO2 and CD3CN. This is motivated by the interest in further understanding the unique adsorption behaviour of this MOF, which involves a combination of interaction of the guests with both open coordination sites on the metal atoms and fluorine atoms from the organic linkers, accompanied by concerted rotation of the aromatic rings upon insertion of the guest species, as suggested by in situ infrared (IR) spectroscopy, in situ powder X-ray diffraction (PXRD) and density functional theory (DFT) calculations.

Experimental description:

Combined DRIFTS/XAS/MS experiments were performed at the Ce K-edge (40.443 keV) in transmission geometry, using the combined DRIFTS/XAS/MS setup available at BM23. Ce K-edge is chosen instead of Ce LIII-edge, because the EXAFS k-range at the latter is limited by Ce LII edge. The sample was hosted in the DRIFTS cell in the powder form, and its mass was optimized to obtain the best S/N ratio for XAS measurements. Sample was desolvated in He flow in situ, heating from RT to 423 K, cool back to RT and then dose the adsorptives (CO2 and CD3CN, separately in two different experiments) gradually increasing the partial pressure of the adsorptive in the gas feed. Acetonitrile, being strongly adsorbed, was desorbed by means of a programmed heating ramp. Long EXAFS were at each pressure point during the adsorption experiments (around 15 points for each adsorptive). Water desorption and the uptake of the adsorptives were monitored by mass spectrometer connected to the gas outlet of the cell.

Results and discussion:

XAS data allowed us to refine the position of the atoms neighbouring Ce: water or carbon dioxide. Their distances were refind by the means of EXAFS fitting (see Figure 1 and [1])

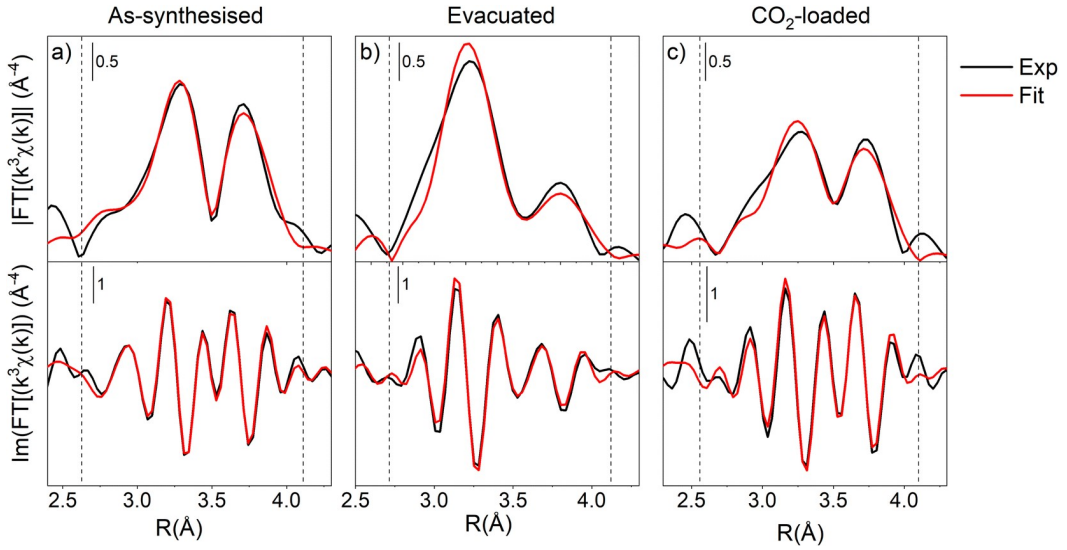

Figure 1 – Comparison between experimental (black lines) and fitted values (red lines) of magnitude (top) and imaginary part (bottom) of phase-uncorrected Fourier transform of k3-weighted Ce K-edge EXAFS spectra for the as-synthesised (a), evacuated (b) and CO2-loaded (c) states. Dashed lines delimit the fitting range.

FTIR spectra were measured while desorbing CD3CN, showing a desorptiom mechanism characterized by two different steps, as shown in Figure 3. The band at 2285 cm^{-1} is most likely due to an interaction of CD_3CN with Ce centers within the porous system of the MOF.

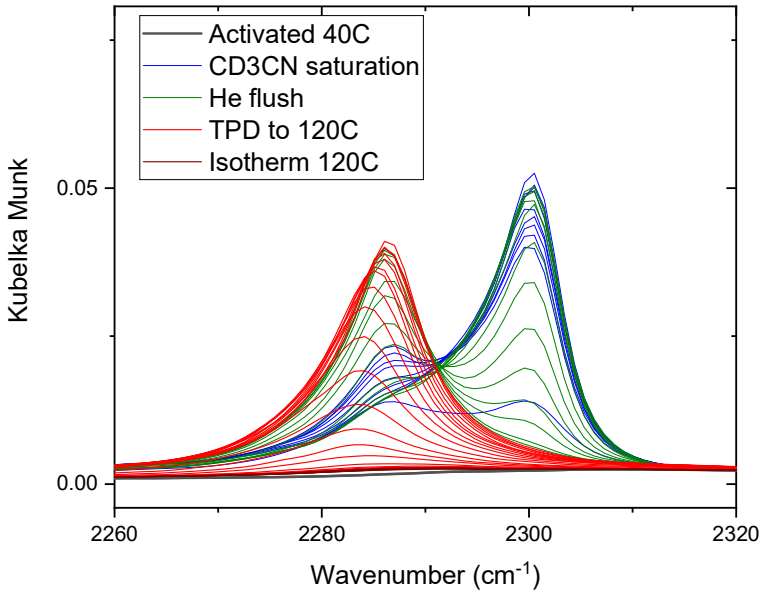

Figure 2 – Background subtracted Kubelka-Munk transformed DRIFTS spectra on Ce-MIL-140-F4 upon desorption of deuterated acetonitrile. Bands at 2300 and 2285 cm^{-1} are due to the stretching of the CN bond of adsorbed molecules.

Conclusions:

The experiment gave us sensible information: XAS data were fitted to complement the structural model developed from PXRD data which was involving a concerted rotation of the perfluorinated aromatic rings. Data was published in [1].

References

[1] M. Cavallo, C. Atzori, M. Signorile, F. Costantino, D. M. Venturi, A. Koutsianos, K. A. Lomachenko, L. Calucci, F. Martini, A. Giovanelli, M. Geppi, V. Crocellà, M. Taddei, J. Mater. Chem. A 2023, 11, 5568–5583.