EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title: Characterization of the adsorption sites in MFU-4L and ZIF-8 Metal-Organic Frameworks using high-resolution X-ray powder diffraction**	**Experiment number**: ch3737
Beamline: ID31	**Date of experiment**: from: 25.02.2013 to: 01.03.2013	**Date of report**: 16.04.2013
Shifts: 9	**Local contact(s)**: Christina DRATHEN	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Dr. Robert E. Dinnebier, Max Planck Institute for Solid State Research, Stuttgart, Germany
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Report:

The adsorption of inert gases Kr and Xe in MFU-4L was investigated and it was shown that both Kr and Xe atoms exclusively occupy the Wyckoff position 32f at approximately (1/3, 1/3, 1/3). This means that both inert gases occupy the four large pores of the unit cell, where the chlorine atom are pointing away from each other. Adsorbed atoms coordinate the 1,2,3-triazole ring. The nearest neighbors of intercalated atoms are nitrogen atoms at distances of ~ 3.71 Å. The atoms of the adsorbed inert gases in both cases form a cube of edge length ~ 10.24 Å. Increasing the pressure increased the occupancy of the only located gas position. At 160 K the maximal occupancy of the position by Kr atoms was ~ 42%. Further increasing of the pressure caused inhomogeneous adsorption and separation of the material into two phases: one part of sample continued to adsorb gas molecules, another desorbed almost all gas molecules. This phase separation was not visible from laboratory powder diffraction experiments due to the broad instrumental function. Analysis of this inhomogeneous adsorption by both MFU-4L and ZIF-8 requires further structural investigations.

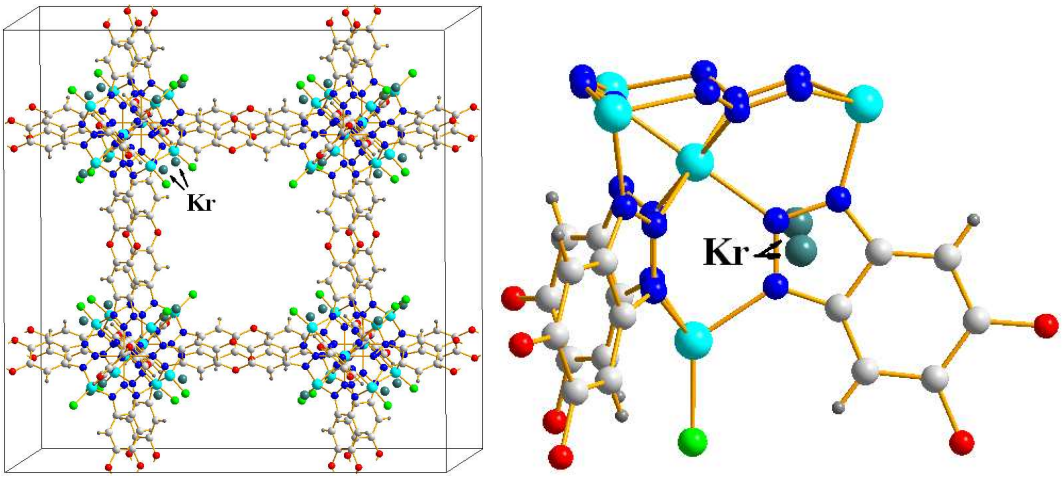

Fig. 1. Adsorption sites of Kr atoms by MFU-4L.

In ZIF-8 at 185 K 4 different positions of adsorbed Xe atoms were found. Xe1 at position (*x*,*x*,*z*), coordinated to the immidazole organic ligand and was the major position of Xe adsorption. Xe2 at position (*x*,0,0), coordinated to the CH_3 group, and Xe3 at position (*x*,*x*,*x*), coordinated to the opening window of the large pore, have a fractional occupancy of 5-25% up to a pressure of 100 mbar. Increasing pressure up to 400 mbar decreased the occupancies of Xe2(*x*,0,0) and Xe3(*x*,*x*,*x*) to values close to 0 and increased the occupancy of Xe1(*x*,*x*,*z*) to 70% which did not change with further increasing of the pressure, and also the new position Xe4 at (0,0,0) was occupied with a fractional occupancy of 45%. Further increasing of the pressure at 185 K did not cause any changing in the occupancies of the adsorption sites.

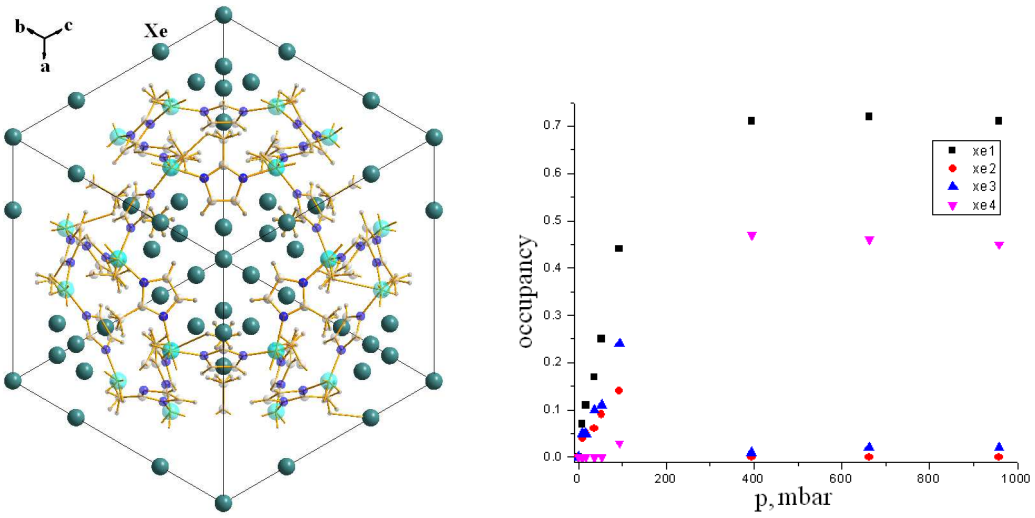

Fig. 1. Right: location of all Xe position in ZIF-8 Left: occupancies of adsorption sites of Xe atoms in ZIF-8.

The adsorption of CO_2 molecules by both ZIF-8 and MFU-4L is very different from the adsorption of noble gases: the change of the lattice parameter of MOFs during CO_2 adsorption is comparable with the changes of the lattice parameters of these MOFs during noble gas adsorption, but the determination of the

exact localization of the CO_2 molecules in the cavities is complicated by the strong disorder of the CO_2 units. MEM calculations to resolve this issue are in progress.