# ZIF metalo organinių karkasų ligandų dinamikos tyrimas dielektrinės spektroskopijos metodu

# Investigation of linker rotation dynamics in ZIF family metal-organic frameworks using broadband dielectric spectroscopy

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MOFS or metal-organic frameworks are clusters of polytopic organic ligands, which connect metal ions through coordination bonds. Choosing specific metal centers and design of organic linkers allows relatively simple tuning of properties of these materials towards enhancement of their capabilities. Recent studies have shown, that often organic linkers possess some type of flexibility or rotational mobility, which is a contrasting characteristic in respect to other porous materials like zeolites and might be responsible for unique properties of MOFs [1].

Zeolitic imidazolate frameworks (ZIFs) are subclass of metal-organic frameworks consisting of tetrahedrally-coordinated transition metal ions binded by imidazolate linkers. ZIFs are promising compounds due to their thermal, chemical stability and high porosity. ZIFs are used for gas adsorption and separation, catalyzation, chemical sensors- electronic devices, drug delivery

One of the most attractive MOFs among the ZIF family for gas separation is ZIF-8, which has $Zn^{2+}$ core connected by 2-methylimidazole linkers. This zeolitic framework has narrow size 3.4 Å- diameter 6-ring windows which interconnect larger cavities of 11.6 Å in diameter. It was found, that despite ZIF-8 should separate smaller molecules than its 6-ring windows size, some larger molecules (methane, nitrogen) are also adsorbed by this framework. Such adsorption was clarified by 2-methylimidazole linker gate- opening (breathing) principle.

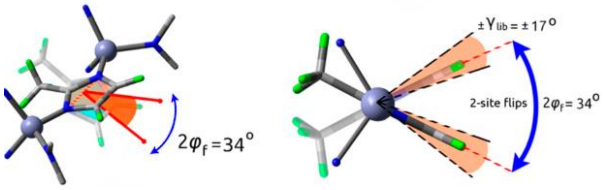


Fig. 1 ZIF-8 linkers motional model [2]. Upon heating, the fast twosite flips are followed by fast librations on the equilibrium positions sites. At high temperatures the librations amplitude is comparable with flips amplitude, thus increasing considerably the ZIF-8 windows aperture.

Our investigations of dielectric properties of ZIF-90 MOFs showed, that broadband dielectric spectroscopy can be used to probe linker rotation dynamics and the influence of adsorbed molecules [3] in FOFs. In order to investigate the influence of interexchange of different metal centers and organic linkers we further investigated dielectric properties of ZIF-8, ZIF-67 and ZIF-90 in the 1 Hz – 1MHz frequency and 200 K – 500 K temperature ranges. Investigated ZIFs were synthesized following a novel environmentally friendly synthesis method using water as a solvent. Analysis of measured complicated dielectric spectra allowed us to distinguish several relaxation processes caused by lattice and adsorbed polar molecule dynamics. Temperature evolution of these relaxation processes and influence of surrounding gas atmosphere was analysed in order to identify and characterise linker rotations in these MOFs.

*Keywords: MOF, ZIF, linker rotation, dielectric spectroscopy.*

## Literatūra

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