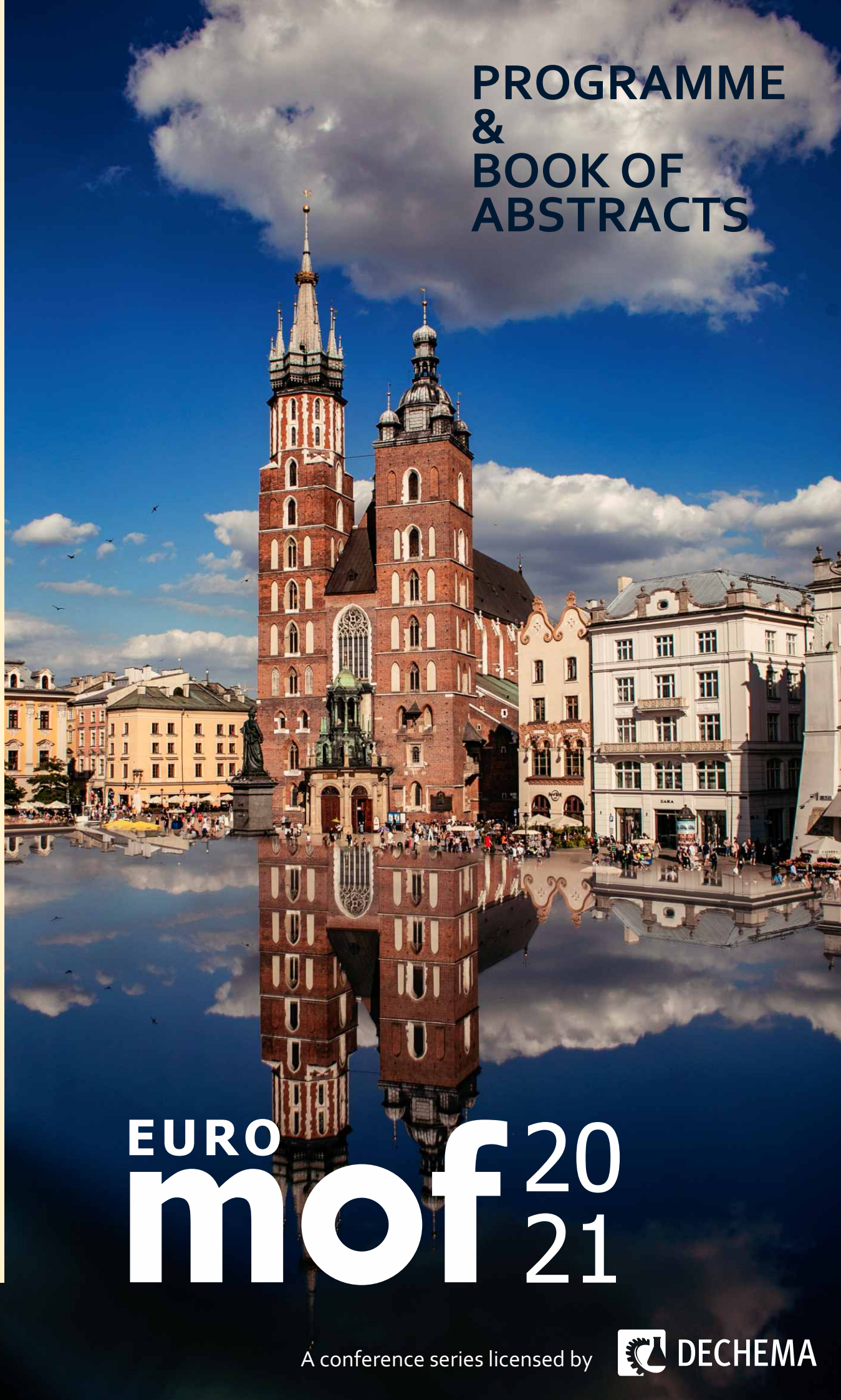
4th European Conference on Metal Organic Frameworks and Porous Polymers

13-15 September 2021, Jagiellonian University in Kraków, Poland

PROGRAMME & BOOK OF ABSTRACTS



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ABSTRACTS

POSTER PRESENTATIONS

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S3P15 (YIS)	**Tuning terahertz vibrations to control flexibility in soft porous crystals**

Alexander E. J. Hoffman*, Jelle Wieme*, Irena Senkovska**, Alexander Krylov***, Sven M. J. Rogge*, Stefan Kaskel**, Veronique Van Speybroeck*

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Soft porous crystals are promising materials for gas adsorption/separation, drug delivery, and sensing applications [1]. A particular type of flexibility is framework breathing, in which the material undergoes a transition between a large pore (LP) phase and a closed pore (CP) phase. Design criteria leading to breathing were proposed [2] and macroscopic insight in the conditions giving rise to this phenomenon was provided via a thermodynamic approach [3]. Despite these scientific advances, a microscopic understanding of breathing is lacking. The missing link may be found in the lattice dynamics as terahertz vibrations trigger flexible behavior [4]. Low-frequency phonon modes in DUT-8(Ni) have been shown to strongly depend on the phase [5]. Furthermore in MIL-53(Al), the lattice vibrations of the CP and the LP phases have been fully characterized [6] and the normal modes contributing to the breathing transition have been identified [7].
In this study, the terahertz vibrations of different soft porous crystals with a winerack-type framework, such as DUT-8(Ni) and MIL-53(Al), have been investigated via a combination of solid-state density functional theory calculations and experimental Raman spectroscopy. In this way, universal terahertz vibrations have been discovered that could be seen as rigid unit modes (RUMs). These RUMs typically combine translations and rotations of the linkers and metal clusters. By substituting building blocks, such as the linkers, metal ions, and compensating anions, it is possible to tune the vibrational frequencies of these RUMs, which has a large impact on the observed flexibility. It is demonstrated that changing the linker type has the biggest influence on the vibrational frequencies, whereas changes in the metal ion yield more subtle effects. These insights will aid experimentalists in the design of tailor-made breathing soft porous crystals.

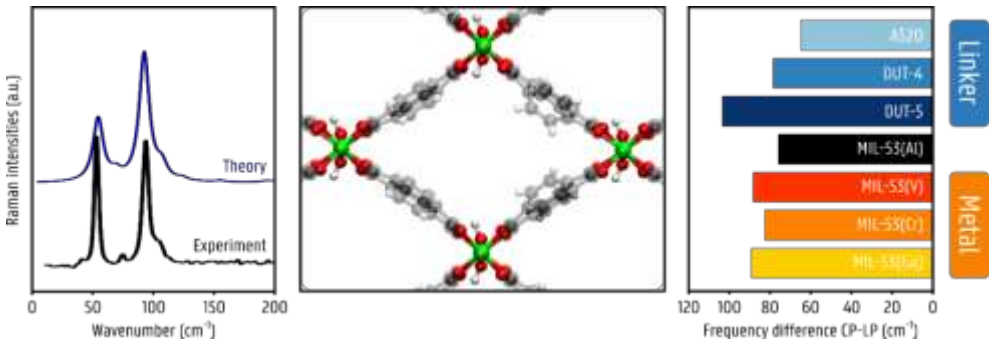

Figure 1. (Left) Experimental and theoretical Raman spectrum of MIL-53(Al) in the range 0-200 cm^{-1} (Center) Visualization of RUM inducing translation of the linkers (Right) Vibrational frequency differences of this mode between the CP and LP phase for different structures.

[1] S. Horike, Nat. Chem. 1 (2009) 695; [2] G. Ferey, Chem. Soc. Rev. 38 (2009) 1380; [3] L. Vanduyfhuys, Nat. Commun. 9 (2018) 204; [4] M.R. Ryder, Phys. Rev. Lett. 113 (2014) 215502; [5] A. Krylov, Phys. Chem. Chem. Phys. 19 (2017) 32099; [6] A.E.J. Hoffman, J. Phys. Chem. C 122 (2018) 2734; [7] A.E.J. Hoffman, Z. Kristallogr. Cryst. Mater. 234 (2019) 529

S4P06	**Raman spectroscopy study of the switchable phases of metal-organic frameworks DUT-8**

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We report the results of a Raman scattering study of a switchable Metal-Organic Framework DUT-8 belonging to the class of pillared layer MOFs [1]. Several samples of DUT-8 series were studied. The Raman spectra comparison showed a significant difference in the low-wavenumber region for open 23 cm^{-1} (op) and closed 59 and 46 cm^{-1} (cp) pore phase of DUT-8 [2,3] (Figure 1). This characteristic spectral feature could be a basis for rapid and routinely applicable Raman based technique for characterization of different switchable MOF's phases and for in situ evaluation and analysis of them by the spectral profile.

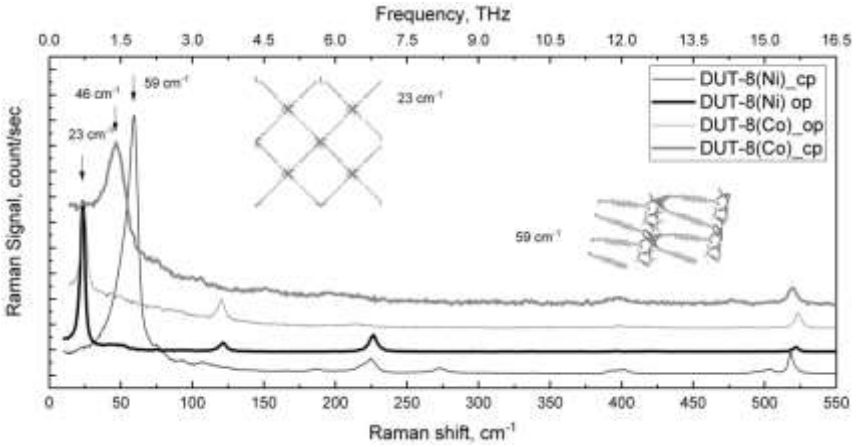

Figure 1. Comparison Raman spectra of DUT-8(Ni) and DUT-8(Co) in the op and cp phases.

Raman spectroscopy in situ investigations on DUT-8(Ni) under hydrostatic pressure provide meaningful insights into the phase transformation mechanism of dynamic MOFs due to the distinct differences in the characteristic lattice vibration frequencies of the op and cp phases. The comparison with results of DFT simulations of vibrational spectra at atmospheric pressure is performed.

Acknowledgments
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References
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