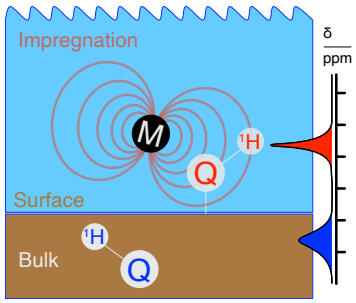
ÚOCHB AV ČR
IOCB PRAGUE

Ph.D. Project

PARAMAGNETIC NMR ON PHASE INTERFACE AS A TOOL FOR SURFACE ANALYSIS

SUPERVISOR: JAN BLAHUT
(jan.blahut@uochb.cas.cz)

Solid-state NMR considers as an essential tool for analysis and **characterization of material.** Multiple studies appear characterizing silicates, boron-oxide materials, porous organic polymers, surface organometallic catalysts and microporous metal-organic frameworks (MOFs) including our contributions focused on paramagnetic MOFs.[1] This task is especially relevant when **diffraction methods fail** due to the absence of long-range periodical arrangement and in characterization of defects which appear to be of high importance for advanced material functionality.[2] Apart from that, solid-state NMR also finds important application for small organic molecules where solid-pharmaceutical formulation can be studied directly including *de-novo* polymorphs characterization.[3]



For material samples, where surface functionalities are of the main interest, the signal of **the bulk must be separated from the signal of atoms localized on the material surface.**

In the porous material, the need for **separation of the signals** located in the pores is particularly emphasised, because catalytic activity and exceptional adsorption selectivity are associated with pore structure and defects. Several approaches were reported, including dynamic nuclear polarisation selective isotope labelling, comparison of the NMR shift between the experiment and the theoretical model and NMR-active molecular probes.

Similar problem of functional group resolution is often addressed in the NMR of biomolecules, where tremendous success was achieved by the application of **paramagnetic probe molecules**,[4] which either modify relaxation and linewidth of target groups or, more favourably, change their NMR shift. The question that comes is how to efficiently introduce paramagnetic centre in the vicinity of material surface. The target structures, especially in zeolitic and organo-porous materials, typically feature polar and Lewis-base character. Therefore, they are well suited for interaction with a coordination-unsaturated metal centre introduced by material impregnation. Currently quite overlooked family of lanthanide-based NMR shifting agents were intentionally designed for coordination to polar groups[5] and are, therefore, perfectly suited for material surface tracking. Various ligand structures with different bulkiness are available, complexing lanthanide atoms inducing various strengths and signs of paramagnetic-induced shift.

We therefore propose to utilise paramagnetic shifting agents for characterisation of functional surface in materials.

This project includes **systematic testing** of paramagnetic-impregnation technique on series materials as well as **development and implementation** of solid-state NMR pulse **sequences** tailored for analysis of paramagnetic materials[6] as well.

Flemingovo nám. 2
166 10 Praha 6
Czech Republic
+420 220 183 333
uochb@uochb.cas.cz
www.uochb.cz
IČ: 61388963
DIČ: CZ61388963

REFERENCE

(1) Blahut, J.; Lejeune, A. L.; Ehrling, S.; Senkovska, I.; Kaskel, S.; Wisser, F. M.; Pintacuda, G. Monitoring Dynamics, Structure, and Magnetism of Switchable Metal–Organic Frameworks via 1 H-Detected MAS NMR. *Angew. Chemie Int. Ed.* **2021**, *60* (40), 21778–21783. https://doi.org/10.1002/anie.202107032.

(2) Yin, J.; Kang, Z.; Fu, Y.; Cao, W.; Wang, Y.; Guan, H.; Yin, Y.; Chen, B.; Yi, X.; Chen, W.; Shao, W.; Zhu, Y.; Zheng, A.; Wang, Q.; Kong, X. Molecular Identification and Quantification of Defect Sites in Metal-Organic Frameworks with NMR Probe Molecules. *Nat. Commun.* **2022**, *13* (1), 5112. https://doi.org/10.1038/s41467-022-32809-9.

(3) Li, M.; Xu, W.; Su, Y. Solid-State NMR Spectroscopy in Pharmaceutical Sciences. *TrAC Trends Anal. Chem.* **2021**, *135*, 116152. https://doi.org/10.1016/j.trac.2020.116152.

(4) Miao, Q.; Nitsche, C.; Orton, H.; Overhand, M.; Otting, G.; Ubbink, M. Paramagnetic Chemical Probes for Studying Biological Macromolecules. *Chem. Rev.* **2022**, acs.chemrev.1c00708. https://doi.org/10.1021/acs.chemrev.1c00708.

(5) Cockerill, A. F.; Davies, G. L. O.; Harden, R. C.; Rackham, D. M. Lanthanide Shift Reagents for Nuclear Magnetic Resonance Spectroscopy. *Chem. Rev.* **1973**, *73* (6), 553–588. https://doi.org/10.1021/cr60286a001.

(6) Blahut, J.; Benda, L.; Lejeune, A. L.; Sanders, K. J.; Burcher, B.; Jeanneau, E.; Proriol, D.; Catita, L.; Breuil, P.-A. R.; Quoineaud, A.-A.; Pell, A. J.; Pintacuda, G. Proton-Detected Fast-Magic-Angle Spinning NMR of Paramagnetic Inorganic Solids. *RSC Adv.* **2021**, *11* (47), 29870–29876. https://doi.org/10.1039/D1RA04110J.

Flemingovo nám. 2
166 10 Praha 6
Czech Republic

+420 220 183 333
uochb@uochb.cas.cz
www.uochb.cz

IČ: 61388963
DIČ: CZ61388963