Probing the adsorption in microporous materials by hyphenated NMR and physorption

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Abstract: Porosimetry is an important and recurrent analysis in material chemistry characterization. Materials such as metal-organic frameworks (MOFs), mesoporous silicas, and zeolites are typically characterized using gas/vapor adsorption and desorption isotherms.[1,2] Through the controlled partial pressure loading of an evacuated sample volume, this technique determines indirectly qualitative and quantitative properties of the pore environment, like BET surface area and pore volume, with limited insight into the quantifiable nature of guest/host interactions. Low-field Nuclear Magnetic Resonance relaxometry (LFNMR) is an experimental technique applied commonly to porous media analysis, able to directly measure the content and physicochemical properties of the porous environment through nuclear spin relaxation of the contained liquid.[3,4] In this work, we present a first account of simultaneous online physisorption and LFNMR for the study of microporous MOFs, with vapors of methanol, ethanol and water at 35°C. A low cost homemade permanent magnet was designed to be integrated with a commercial physisorption analyzer, without interference. Results show the complementarity of LFNMR to the sorption isotherms by the $T_1$ and $T_2$ relaxation time distributions, which scope the nature and specificity of the interactions between different guest molecules and adsorbents. This low-field hyphenated NMR instrumentation demonstrates generality, practicality and versatility without the use of superconducting magnets, hyperpolarization techniques, isotopic labeling, nor high-pressure gas intrusion.

Figure 1 – a) NMR and physisorption hyphenated system. b) Superposition of the simultaneously acquired isotherms with both modalities. c) Different guest molecules present distinct relaxation time distributions when adsorbed by same material.