COMBINING SOLID-STATE NMR METHODS & COMPUTATION TO STUDY CONFINED CO_2 CHEMISTRY IN POROUS MATERIALS

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Porous CO_2-chemisorbent materials are critical for addressing rising atmospheric CO_2 levels, enabling applications such as direct air capture and industrial flue gas separation. However, understanding their reactivity and the atomic-level details of CO_2 adsorption at the gas-solid interface remains a significant challenge, hindering the design of improved materials. This talk highlights our group's recent advancements in elucidating CO_2 speciation in confined spaces under both dry and humid conditions, combining surface-enhanced solid-state NMR spectroscopy with computational modelling.

We demonstrate the power of NMR-assisted adsorption methods, NMR relaxation, and chemical shift anisotropy to quantitatively discriminate between six distinct CO_2 species—ranging from physisorbed CO_2 to chemisorbed carbamic acid, carbamate ion pairs, and moisture-induced bicarbonate. Unlike conventional volumetric or gravimetric techniques, NMR uniquely resolves these species, enabling the generation of individual CO_2 isotherms for each adsorbed component. This approach provides unprecedented insights into their molecular dynamics and adsorption mechanisms. A key breakthrough presented in this talk is the first successful application of Magic-Angle Spinning (MAS) – Dynamic Nuclear Polarization (DNP) NMR to study CO_2 adsorption in real-world scenarios. This innovative approach overcomes the sensitivity limitations imposed by the low natural abundance of ^{13}C in atmospheric CO_2 (~ 1 %), achieving unprecedented signal enhancement while maintaining speciation integrity. We demonstrate its success in resolving chemi- and physisorbed CO_2 species in amine-modified SBA-15 exposed to ambient air, marking a significant step towards the detection of CO_2 surface species.

The versatility of our methodology is demonstrated across diverse porous systems, including amine-modified mesoporous silicas and covalent organic frameworks (COFs). Additionally, we highlight the potential of the Calgary Framework 20 (CALF-20) MOF, which exhibits exceptional CO_2 uptake, selectivity, and durability under humid conditions. This work offers a unified framework for understanding CO_2 adsorption and guiding the design of next-generation adsorbents.

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