NMR Studies of Adsorption and Diffusion in New Materials for CO_2 Capture

Alexander C. Forse

College of Chemistry, U.C. Berkeley, Berkeley, 94720, CA

Carbon capture and storage is one of several technologies that must be rapidly deployed to reduce greenhouse gas emissions. Recent research has shown that amine-appended metal-organic framework (MOF) materials can capture CO_2 from target gas mixtures in a more energy efficient manner than traditional amine solvents.[1] The commercialization (ongoing at a start-up company) and deployment of these materials could be facilitated if the molecular mechanisms of CO_2 uptake and transport could be understood and optimized.

We have developed *in situ* NMR methods to study the adsorption of CO_2 in amine-appended MOF materials. In particular we use solid-state NMR experiments of gas-dosed samples combined with density functional theory calculations to probe different states of adsorption in what is termed "NMR isotherms." The measurements reveal a rich chemistry with the chemisorption mechanism dependent on the MOF composition.[2,3] Crucially, we link our results to the CO_2 capture performance of MOF materials, and discover a new material for capturing CO_2 from power station flue gases.

We further show how the residual chemical shift anisotropies of pore-confined CO_2 can be used to study the extremely anisotropic diffusion of CO_2 in MOF materials featuring 1-dimensional pores.[4] By combining our pulsed field gradient NMR experiments with spectral simulations we obtain accurate diffusion anisotropy values.[5] Our measurements are complemented by single-crystal diffraction experiments and molecular dynamics simulations to unravel the structural basis of the observed diffusion behaviour. Finally we show how the MOF structure can be systematically tuned to optimize gas transport in MOF materials, something that is vital for their practical implementation.

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