

# Ligand-assisted enhancement of CO<sub>2</sub> capture in metal-organic frameworks

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Capturing and sequestering CO<sub>2</sub> is a route to partial mitigation of climate change associated with anthropogenic carbon dioxide emissions. Conventional CO<sub>2</sub> capture processes require a large heat of regeneration, resulting in losses of 25-40%. Among candidate alternative methods for CO<sub>2</sub> separation, physisorption via metal-organic frameworks (MOFs) is one of the most promising. These materials are three-dimensional nanoporous extended solids composed of metal centers connected by organic molecules (called bridging ligands or linkers).

In this work, we use first-principles van der Waals (vdW)-corrected calculations to identify and understand how CO<sub>2</sub> binds to two novel MOFs: BTT-type and MOF-74, both featuring open metal centers. We analyze the interaction mechanism and identify the key aspects which allow to tune the binding energy in a manner optimal for CO<sub>2</sub> capture.

Our study indicates that CO<sub>2</sub> binds to the open metal cation sites, but with an adsorption energy that can be enhanced by more than a factor of two depending on the choice of the bridging ligand. In all cases, the binding can be attributed to a combination of electrostatics and dispersion, both critically sensitive to the local environment, and contributing nearly equally to the overall binding strength.

The possibility to independently tailor these energetics to obtain new materials that efficiently capture CO<sub>2</sub> is discussed in the context of recent experiments.