# Understanding phase transformations in flexible metal-organic frameworks using computational vibrational spectroscopy

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Metal-organic frameworks (MOFs) are porous, crystalline materials consisting of inorganic moieties connected through organic linkers [1]. Their chemical and physical versatility and the ability to tune their properties turn them into ideal candidates for specific industrial applications such as gas storage, gas separation, and catalysis. Some MOFs exhibit a large degree of flexibility, sometimes even undergoing phase transformations upon external stimuli. This behavior is called breathing if the phase transformation induces a drastic change in unit cell volume [2]. Over the last decade, an enormous endeavor has been undertaken to understand this phenomenon [3, 4]. Various experts indicate that terahertz vibrations may trigger the observed flexibility [5]. However, the understanding of this part of the frequency region is not well developed so far due to the experimental difficulties in measuring in the terahertz region on the one hand and computational hurdles to obtain accurate vibrational spectra for such low wavenumbers on the other hand.

We have now characterized the complete vibrational spectrum of the prototypical example of a breathing MOF, MIL-53(Al), following a combined experimental/computational approach [6]. High-quality IR and Raman spectra of the different phases of MIL-53(Al) were measured experimentally and predicted using both static and dynamic density functional theory (DFT) calculations. The excellent correspondence between experiment and theory allowed us to propose several terahertz vibrations that are crucial for the occurrence of a phase transformation. Starting from the structure of MIL-53(Al), we have also investigated topologically similar structures with different metal atoms, different organic linkers, and/or different compensating anions, predicting their vibrational fingerprints via static DFT calculations using the Vienna Ab Initio Simulation Package (VASP) [7]. The simulated results have been compared with experimental reference data to validate the accuracy of our calculations. In this way, valuable insights have been obtained into the framework dynamics responsible for phase transformations in flexible MOFs..

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