Unfolding the terahertz spectrum of soft porous crystals:
rigid unit modes and their impact on phonon properties

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Soft porous crystals form a subclass of metal-organic frameworks (MOFs) and exhibit framework dynamics as response to external stimuli such as temperature, pressure, light, and the presence of guest molecules. [1] Controlling the framework dynamics is crucial with an eye toward application in new functional materials. This requires insight in the low-frequency phonon modes, situated in the terahertz range, which mediate it. [2] These involve displacements of all atoms, in which complete structural units may move in their entirety. Therefore, they are also referred to as rigid unit modes (RUMs) [3]. The collective behavior of the RUMs in combination with their dependence on long-range interactions between the building blocks, urges the use of computational techniques to characterize them. [4,5]

In this contribution, we present a new theoretical approach, supported by experimental Raman measurements, to identify RUMs in a set of MIL-53-type materials *i.e.* soft porous crystals with a winerack topology. [6] The MIL-53 family is known for its large-scale breathing between a closed and a large pore phase. [7] The phase transition is characterized by a significant change in its terahertz spectrum. [8,9] By reducing the phonon modes to merely translations and rotations of the building blocks, we can now predict and compare the RUMs between MIL-53-type materials consisting of different building blocks. This reveals the existence of a group of universal RUMs, typical for the winerack topology, for which only the vibrational frequency changes after building block substitution. We can pinpoint the effect of specific building block substitutions on the vibrational entropy, providing mechanistic insight in the phase transition.

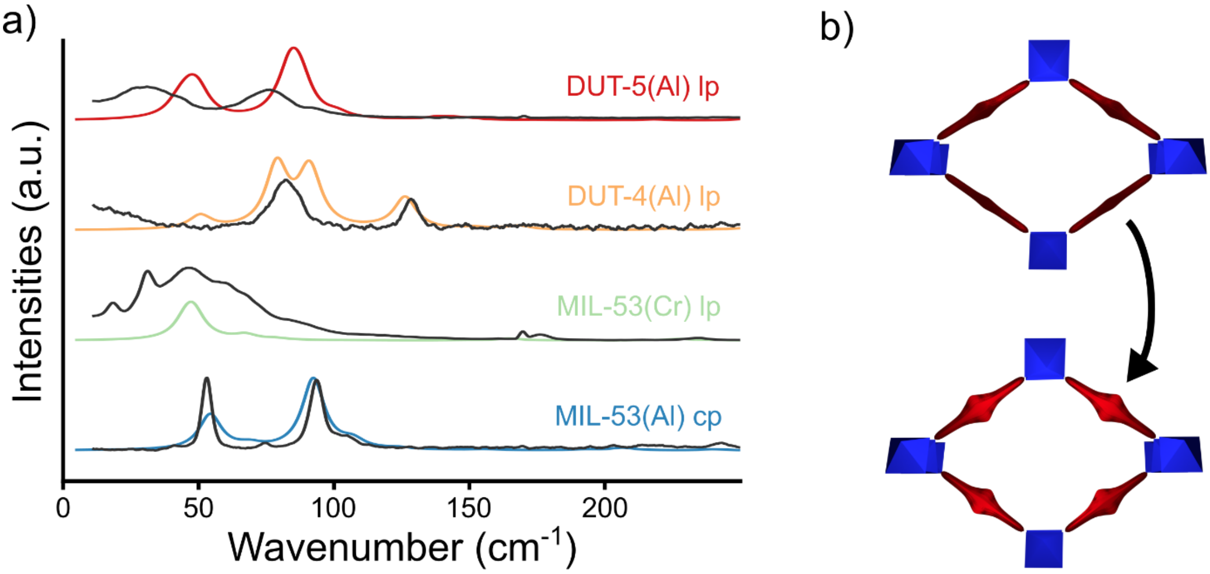

Figure: (a) Experimental (gray) and theoretical (color) Raman spectra in the range 0-250 cm^{-1}. (b) Schematic visualization of the Raman active RUM inducing rotations of the linker.

References

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