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Probing polymorphism and stimuli induced structural changes in Metal-Organic Frameworks with THz Raman Spectroscopy

THz (low frequency) Raman spectroscopy extends the capabilities of conventional Raman spectroscopy, probing the range below 200 cm^{-1} . [1] Signals in this region are mainly attributed to intermolecular vibrations of higher mass and phonon modes that are strongly correlated to the crystal structure of a material. They give information about the degree of crystallinity, molecular orientation and can be used to classify different allotropes and polymorphs. [1,2,3] Therefore, THz Raman Spectroscopy is a powerful technique for obtaining both chemical and structural information in one measurement. [1,2,3] Herein, we first introduce THz Raman spectroscopy as a fast and reliable technique for MOF-polymorph distinction, as shown with Fe-terephthalic acid based MOF examples. In addition, THz Raman can be used for in-situ phase transition analysis. Here, we probe the solvent-induced phase transitions in MOF systems and investigate the swelling behavior of MIL88 by THz Raman spectroscopy. [4] Furthermore, we demonstrate the non-linear evolution of lattice modes as a function of temperature via low-frequency vibrational spectroscopy. We delve into the balance between conventional positive thermal expansion and phonon-driven negative thermal expansion in a mixed-linker solid solution of a frustrated metal-organic framework.

References

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Figures

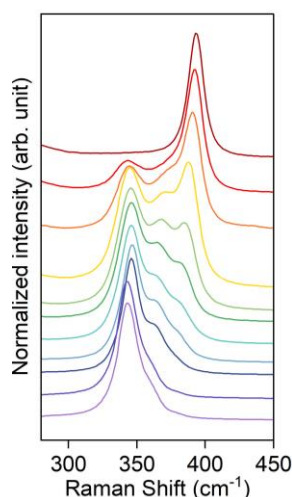


Figure 1: Raman Spectra of a solid solution series