Beyond Static Profiles: Stretched NMF for Phase-Resolved Analysis of MOFs via Variable-Temperature and Pressure PXRD

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Stretched Non-negative Matrix Factorization (sNMF) offers a promising approach for analyzing non ambient condition powder X-ray diffraction (PXRD) data of metal-organic frameworks (MOFs) which exhibit temperature- (VT-PXRD) or pressure- (VP-PXRD) driven phase transitions. Conventional NMF struggles to disentangle components when signals undergo thermal expansion or contraction, as it assumes fixed component profiles. sNMF addresses this by introducing a stretching factor matrix to model differential expansion rates across components, enabling precise decomposition even when structural changes occur due to phase transitions.[1] This approach is particularly valuable for *in situ* studies, where dynamic structural changes require algorithms robust to both peak shifts and intensity variations and accurate phase identification informs mechanistic understanding of transition pathways. This methodological advancement could be particularly significant in the context of MOFs, which are known for their structural flexibility and responsiveness to external stimuli. In these systems, phase transitions often involve continuous or discontinuous peak shifts, changes in relative intensity, and the appearance of intermediate or transient states that are difficult to resolve using conventional analytical methods. So, we want to show the novelty and the power of this approach in the field of MOFs advanced structural characterization by applying it to a series of VT- and VP-PXRD of model compounds, such as MIL-53 [2], M(bdp) (M=Co, Ni, Fe; H_2bdp = 1,4-bis(1H-pyrazol-4-yl)benzene) [3], M(btca) (M=Zn, Co; H_2btca=benzotriazole-5-carboxylic acid) [4], to highlight the pronounced phase transitions and to identify physically meaningful components, such as transient coordination states in Co(btca) or intermediate breathing states in MIL-53, which are often obscured by overlapping diffraction patterns. Our goal is to prove that sNMF provides a robust tool for dynamic structural analysis in functional materials research by resolving overlapping signals induced by both thermal/pressure effects and phase changes. In this work, we present sNMF not just as an extension of NMF, but as a useful method for tackling the challenges of complex and evolving diffraction data, offering a valuable instrument available to the crystallographic community.

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