Diffuse scattering contains information about static and dynamic correlations within a crystal. The dynamic contribution (thermal diffuse scattering, TDS) is dominated by low-energy vibrational modes and/or modes that involve translations of strongly-scattering elements (i.e. heavy atoms in X-ray studies). These same vibrational modes are often key to the mechanical flexibility of solids, and so understanding their nature and microscopic origin is an important step in functional materials design.

This contribution will describe the development of an automated coarse-graining approach, which aims to capture the key low-energy dynamics of framework materials and allow validation of this interpretation in terms of the TDS component of single-crystal X-ray diffraction measurements. For framework materials, the low-energy modes tend to be associated with parallel motions of atoms at the nodes. This is true for inorganic solids (Zn(CN)$_2$, H$_2$O) [1,2] and metal–organic frameworks [3] alike. The proposed coarse-graining is straightforward: we keep the atoms at the nodes and replace the linkers with springs of fixed stiffness. Assigning a smaller energy penalty to framework hinging, one can calculate the coarse-grained phonon dispersion of the framework structure, and thus the form of the thermal diffuse scattering. An example of the comparison between experiment and calculation is shown in the Figure. The method, that only requires a structure as an input, allows a straightforward approach for approximating TDS and for its interpretation in terms of whole-framework breathing and/or flexing modes. Its effectiveness will be discussed for a variety of chemically-different framework materials.

Figure 1. Measured and calculated (overlayed) thermal diffuse scattering for NH$_4$[Zn(HCOO)$_3$].