Metal-organic frameworks (MOFs) are a relatively new, yet already extremely promising class of hybrid multifunctional materials that feature nanoscale open-framework architectures. MOFs are constructed from basic building blocks that are self-assembled at the molecular level, generating highly ordered crystalline frameworks with vast physical and chemical properties. Over the last decade, MOFs have drawn considerable interest from both academic science and industry due to their structural and functional flexibility, promising a myriad of technological applications. MOFs offer advantages over other sorbents and separations methods, such as zeolites and molecular sieves. Whilst the current focus for MOFs remains in gas separation and carbon dioxide sequestration for energy applications, an improved knowledge of the fundamental physical properties of framework materials is important, particularly a detailed understanding of the lattice dynamics underlying the elasticity, crystal structure and thermo-mechanical behaviour.

The practical functionalities of specific MOF materials are intrinsically controlled by their elastic properties, which are governed by collective lattice dynamics prevalent at the molecular length scale. This study has demonstrated a new methodology to gain crucial insights into the complex lattice dynamics underlying MOFs. Importantly, this new approach can be used to decipher a wide range of basic physical phenomena that could exist for MOFs and indeed exists in many other related framework materials. Interrogation mechanisms include cooperative ‘gate-opening’ and ‘breathing’ of the nanoropes of MOFs, crucial for the understanding of gas separation and storage functions. The latter technique enabled the study of low energy molecular vibrations in MOFs. Experimental results showed that low-energy dynamics are important in determining physical properties of the frameworks. New evidence demonstrates that molecular modes such as zeolites and molecular sieves. Whilst the current focus for MOFs remains in gas separation and carbon dioxide sequestration for energy applications, an improved knowledge of the fundamental physical properties of framework materials is important, particularly a detailed understanding of the lattice dynamics underlying the elasticity, crystal structure and thermo-mechanical behaviour.

This work focuses on a topical subclass of MOF materials, termed Zeolithic Imidazolate Frameworks (ZIFs), whose framework architecture and topologies closely resemble those of inorganic zeolites. We have investigated the vibrational properties and low-frequency conformational dynamics of three prototypical ZIF materials: ZIF-4, ZIF-7, and ZIF-8 (Fig. 1). To take full advantage of the vast number of possible applications, an improved knowledge of the fundamental physical properties of framework materials is important, particularly a detailed understanding of the lattice dynamics underlying the elasticity, crystal structure and thermo-mechanical behaviour.

The high-resolution IR absorption spectra of each ZIF material were recorded at Diamond Light Source beamlines B22. The comparison between the experimental and calculated IR spectra for each framework can be seen in Fig. 3, which confirmed the excellent agreement between the two approaches. From comparing the spectra of each of the three ZIF structures, it was demonstrated that the peaks resulting from the ring deformations of the imidazole–linked rings are present around 600–700 cm⁻¹, and that the Zn–N bond stretching contributed to the flexible Zn4-n tetrahedra located at 325–350 cm⁻¹. It has been identified that all framework-specific modes are located in the terahertz (THz) region of the vibrational spectra, notably under 3 THz (100 cm⁻¹), thus confirming the theoretical predictions. Computational studies performed using high-performance supercomputing nodes have been performed.

In summary, the research showed that high-resolution synchrotron and neutron vibrational spectroscopy, in conjunction with ab initio density-functional theory, can shed light on complex lattice dynamics of nonporous MOF materials. In addition, it was demonstrated that the correlation between theoretical predictions and experiments was remarkable across the whole vibrational spectra (0–4000 cm⁻¹), and that the most interesting vibrational behaviour was located in the low-energy THz region. The results showed for the first time that the ZIFs materials only show the framework vibrations, but also reveal unique physical phenomena of specific framework structures, for example those driven instabilities, gate-opening, and pore breathing. Specifically, this research has highlighted interesting information relating to the mechanical properties of ZIFs, including possible phase transitions associated to soft modes. By studying the THz vibrations of framework materials, therefore, the possible deformation mechanisms that could hinder their ability to reach full commercial potential can be pinpointed and overcome.

References: