

“Good vibrations”: Terahertz modes and lattice dynamics in metal-organic frameworks

Ryder, M. R., Civalleri, B., Bennett, T. D., Henke, S., Rudic, S., Cinque, G., Fernandez-Alonso, F. & Tan, J.-C. Identifying the Role of Terahertz Vibrations in Metal–Organic Frameworks: From Gate-Opening Phenomenon to Shear-Driven Structural Destabilization. *Physical Review Letters* **113**, doi:10.1103/PhysRevLett.113.215502 (2014).

Metal-organic frameworks (MOFs) are a rather new class of micro-engineered materials, possessing flexible frameworks, large surface areas and tuneable pore size. Interest in these materials has grown quickly in the past decade due to their capacity to adsorb gases or solvents, suggesting there is the potential for a wider range of applications than similar microporous structures such as zeolites and molecular sieves. Whilst the current focus for MOFs remains in gas separation and carbon dioxide sequestration for carbon capture, the future looks promising for their usage in fields such as microelectronics and biomedicine, amongst others.

Developing a better understanding of MOFs should enable more control over the ‘breathing’ behaviours exhibited, whereby the frameworks distort significantly in a reversible manner for release and readsorption of molecules. The results presented establish information about the lattice dynamics, particularly the low energy vibrations of the framework. The Multimode InfraRed Imaging and Microspectroscopy (MIRIAM) beamline B22 at Diamond Light Source offers full infrared (IR) capabilities both in diffraction limited IR microanalysis and Terahertz (THz) spectroscopy. 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 in the THz range are linked to the structural elasticity that allows the pore breathing mechanism to operate. This opens up opportunities to pinpoint possible deformation methods and to develop new materials that are less prone to detrimental distortions, which could result in the collapse of the framework.

Metal-organic frameworks¹ 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 units comprising metal ions connected together by organic molecules acting as bridging linkers. These building blocks are self-assembled at the molecular level, generating highly-ordered crystalline frameworks with vast physico-chemical properties. Over the last decade, MOFs have drawn considerable interest from cognate science and engineering disciplines due to their structural and functional flexibility, promising a myriad of technological applications. The applications being envisaged vary from smart sensors and CO₂ sequestration, to drug delivery and water desalination².

One of the major selling points of MOFs, as an advanced next-generation material, is the exceptionally large internal surface area that some of the frameworks can possess, with certain MOFs having an internal surface area as

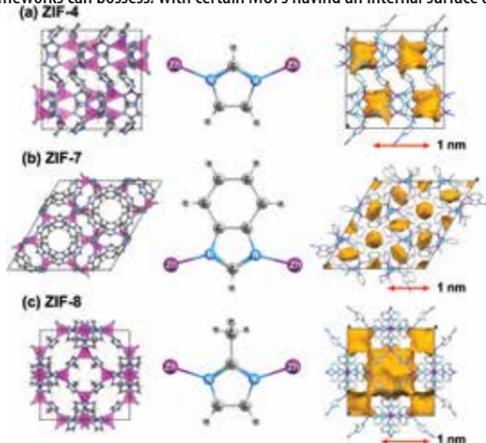


Figure 1: Open framework structures of (a) ZIF-4, (b) ZIF-7, and (c) ZIF-8. The inorganic building units are ZnN₄ tetrahedra (purple), the imidazole-based organic building units are shown in middle panel. Yellow surfaces depict the pore accessible volume. Hydrogen is omitted for clarity.

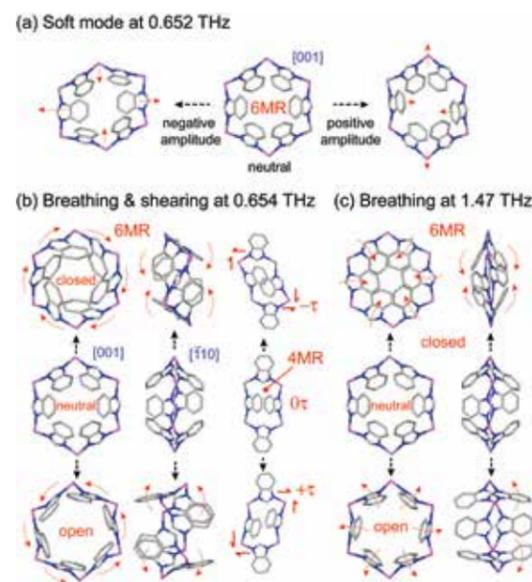


Figure 2: Low-energy lattice dynamics in ZIF-7. (a) Soft mode that could trigger phase transition; (b) breathing mode accommodated by collective 6-membered ring (MR) spiral motion and 4MR shearing; (c) breathing mode via synchronous flapping of organic linkages.

large as 10,000 m² g⁻¹ reported¹. When you couple this extreme level of accessible pore surface area with the tuneability and control of the nanopore volumes, it starts to become obvious why this new class of hybrid material is of such high scientific interest.

This work focuses on a topical subclass of MOF materials, termed Zeolitic Imidazolate Frameworks (ZIFs), whose framework architectures 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 underpinning the elasticity central to structural stability and thermo-mechanical behaviour.

The practical functionalities of specific MOF materials are intrinsically controlled by their elastic responses, 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 underpinning MOFs. Importantly, this new approach can be utilised to decipher a wide range of basic physical phenomena that could exist for MOFs and indeed in many other related framework materials. Intriguing mechanisms include co-operative ‘gate-opening’ and ‘breathing’ of the nanopores of MOFs, crucial for the understanding of gas separation and storage functions (Fig. 2). This new method involves the use of *ab initio* Density Functional Theory (DFT) to unravel the complete vibrational nature of the framework, elucidating the detailed underlying physical phenomena. These first-principles DFT calculations are computationally demanding and thereby performed using high-performance supercomputing facilities. To confirm the theory, high-accuracy spectroscopic experiments at both Diamond and the ISIS Pulsed Neutron & Muon Source have been performed.

The high-resolution IR absorption spectra of each ZIF material were recorded at Diamond’s MIRIAM beamline (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-derived linkers are present around 600–700 cm⁻¹, and the Zn–N bond stretching attributed to the flexible ZnN₄ tetrahedra are located at 265–325 cm⁻¹. It has been identified that all framework-specific modes are located in the terahertz (THz) region of the vibrational spectra, notably under 10 THz (333 cm⁻¹), with primary signatures associated with the lattice dynamics

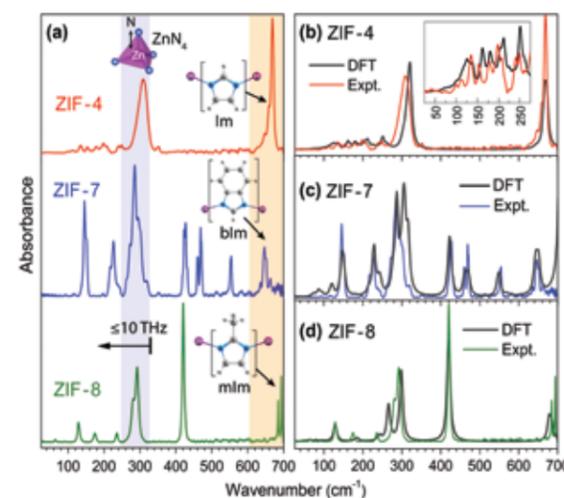


Figure 3: Infrared absorption spectra in the 25–700 cm⁻¹ region. (a) synchrotron-based experimental THz spectra. Comparison of experimental IR and theoretical DFT spectra for (b) ZIF-4, (c) ZIF-7 and (d) ZIF-8.

observed below 3 THz (100 cm⁻¹). The terahertz vibrational signatures are described as *collective*, meaning they encompass contributions from the entire crystalline lattice. However, the THz modes of greatest interest are the ones associated with framework shearing (cage distortion)³, pore-breathing, gate-opening effects and soft modes, as depicted in Fig. 2 for the example of ZIF-7.

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 nanoporous MOF materials. In addition, it was discovered that the correlation between theoretical predictions and experiments were remarkable across the whole vibrational spectra (0–4000 cm⁻¹), and that the most exciting vibrational behaviour was located in the low-energy THz region. The results showed for the first time that the THz modes not only show the framework vibrations, but also reveal unique physical phenomena of specific frameworks in question, for example shear driven instabilities, gate-opening, and pore breathing. Specifically, this research also highlighted interesting information relating to the mechanical properties of ZIFs, including possible phase transitions ascribed 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:

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