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Effect of low frequency phonons on structural properties of ZIFs with SOD topology.

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Abstract

The structural transformations of periodic structures are very often initiated by the dynamical fluctuation of the equilibrium structure. The natural mechanical excitations in crystals are called phonons. If the energy of these fluctuations is low, they can easily be transformed into static deformations which define new structural properties of the materials. This is the case in so called gate opening transformations which modify the structure and the adsorptive properties of porous solids. Using the example of three SOD-type zeolitic imidazolate frameworks (ZIFs) containing linker molecules with different substituents, we show that analysis of low-frequency phonons obtained from density-functional theory (DFT) calculations allows one to model the observed gate opening and to understand the microscopic mechanism of this structural transformation.

1. Introduction

Any structural variations observed in the nature can be understood on the basis of direct relations between solid structure and its dynamical properties. The structural transformations are usually initiated by dynamical structural fluctuations which can be expressed in terms of

mechanical excitations called phonons (or normal modes) [1]. This name, originally attributed to purely harmonic collective translational vibrations of atomic periodic solids, has been also used in the context of orientational vibrations (librations) and anharmonic vibrations [2,3]. The total phonon spectrum is very rich and contains $3N_{tot}$ values, where N_{tot} is the total number of atoms in the material. The structural properties are mostly defined by the low frequency vibrations which may exhibit a frequency reduction when a structural transformation is approached. These specific vibrations are called *soft phonons* [4]. The structural analysis of solid deformations and in particular the role of soft modes is an important part of the studies of structural transformation mechanisms.

Metal-organic framework (MOFs) are hybrid structures, with mixed inorganic and organic composition, i.e. metallic centers coordinated by oxygen or nitrogen atoms, and connected by linkers with (very often) aromatic rings [5]. They have recently attracted a lot of attention due to large spectra of possible applications and in particular, structural transformations which potentially allow one to modulate the framework adsorptive properties [5-7]. A possible role of the soft modes in the structural transformations of the MIL-53 metal-organic framework (MOF) structure has been proposed as the mechanism provoking the lattice instabilities in this structure. However, no specific soft phonons were indicated [8-12]. It was also reported that the soft acoustic phonons also contribute to the negative thermal expansion in MOFs [13,14].

Recently, it has been shown [15,16] that collective low frequency THz vibrational modes contribute to physical mechanism of pore gate-opening and breathing phenomena in a subclass of MOFs, zeolitic imidazolate framework (ZIF) structures. In this paper we show that the numerical analysis of phonon spectrum provides detailed insight into the mechanism of gate opening. This information is not accessible from the experimental data.

In the next chapter we review the concept of phonons, normal modes and their relation to the soft modes. Then, we discuss an example of the MOF structures, based on the sodalite-type ZIF-8, and show that the soft modes are the important part of the deformation mechanism. We emphasize that the phonon numerical analysis is a new methodology which can correctly identify collective low energy vibrations responsible for lattice deformations.

2. Phonon formalism: a short review.

Let us consider a solid structure composed of N_{tot} atoms (where N_{tot} is on the order of the Avogadro number). If the material is ordered and periodic, its structure can be characterized by a unit cells composed of n ($\ll N_{tot}$) atoms. Thermal fluctuations displace atoms from its equilibrium position \mathbf{r} by an amount \mathbf{u} . The total potential energy U of any periodic structure is a function of the instantaneous positions of all atoms (index i) $\mathbf{u}(l, i)$ and *the equations of motion* of the lattice follow the formula:

$$m_i \ddot{u}_\alpha(l, i) = - \frac{\partial U}{\partial r_\alpha(l, i)} = - \sum_{\beta, j} V_{\alpha\beta}(li, l'j) u_\beta(l', j)$$

The $\alpha, \beta = x, y, z$ are the Cartesian coordinates. The l, l' and i, j are the indices of lattice unit cells and the atoms in any unit cell, respectively. The coefficients $V_{\alpha\beta}(li, l'j)$ are the second derivatives of the potential energy U and are called *atomic force constants*.

The equations of motion form a set of simultaneous linear differential equations. Their solution is simplified by the periodicity of the lattice:

$$u_{\alpha}(l, i) = \frac{1}{\sqrt{m_i}} u_{\alpha}(i) e^{-i\omega t + i\mathbf{k}\mathbf{R}(l)}$$

where $u_{\alpha}(i)$ is independent of l and represent the atomic position in any unit cell. $\mathbf{R}(l)$ is the position vector of the l -th unit cell, m_i is the atom mass. The substitution of the solution into the equation of motion gives [1]:

$$\omega^2 u_{\alpha}(i) = \sum_{\beta, j} D_{\alpha, \beta}(i, j; \mathbf{k}) u_{\beta}(j)$$

where the elements of the matrix $D(\mathbf{k})$ are given by:

$$D_{\alpha, \beta}(i, j; \mathbf{k}) = \frac{1}{\sqrt{m_i m_j}} \sum_{l'} V_{\alpha\beta}(li, l'j) e^{-i\mathbf{k}(\mathbf{R}(l) - \mathbf{R}(l'))}$$

Therefore, as a consequence of the periodicity of the lattice, the problem reduces to $3n$ linear equations (n – number of atoms in the unit cell). The coefficients $D_{\alpha\beta}(i, j, \mathbf{k})$ do not depend on the choice of l . The vector \mathbf{k} in the exponent is called the wave vector and defines a modulation of the phonon amplitude along the periodic lattice.

This set of linear equations have a solution if the determinant of the coefficients vanishes:

$$|D_{\alpha, \beta}(i, j; \mathbf{k}) - \omega^2 \delta_{\alpha, \beta} \delta_{i, j}| = 0$$

The solutions of this equation are $3n$ values of $\omega_m^2(\mathbf{k})$ where $m = 1, \dots, 3n$. As the matrix $D(\mathbf{k})$ is Hermitian [1], the solutions are always real, so $\omega_m(\mathbf{k})$ are either real or purely imaginary. Consequently, the microscopic condition for the stability of the lattice is that each $\omega_m^2(\mathbf{k})$ should be positive. The relation expressed by the equation

$$\omega = \omega_m(\mathbf{k})$$

Is known as the *dispersion relation*.

For each of the $3n$ values of $\omega_m^2(\mathbf{k})$ corresponding to a given value of \mathbf{k} there exists a vector $\mathbf{e}(i, \mathbf{k}, m)$ whose components are the solutions to the set of linear equations:

$$\omega_m^2(\mathbf{k}) e_{\alpha}(i, \mathbf{k}, m) = \sum_{\beta, j} D_{\alpha, \beta}(i, j; \mathbf{k}) e_{\beta}(j, \mathbf{k}, m)$$

When $e(i, \mathbf{k}_m)$ are normalized, they allow expanding the instantaneous positions of atoms ($i=1, \dots, 3n$) in terms of plane waves:

$$u_\alpha(l, i) = \frac{1}{\sqrt{m_i}} \sum_{\mathbf{k}, m} e_\alpha(i, \mathbf{k}, m) Q(\mathbf{k}, m) e^{i\mathbf{k}\mathbf{R}(l)}$$

The equations of motion of the coordinates $Q(\mathbf{k}, m)$ are independent from each other:

$$\ddot{Q}(\mathbf{k}, m) + \omega_m^2(\mathbf{k}) Q(\mathbf{k}, m) = 0$$

In the theory of dynamical systems such coordinates are called *normal modes*. The vectors $e(i, \mathbf{k}_m)$ define the space distribution of atomic position fluctuation corresponding to the mode m . Their symmetry is determined by the space group of the crystallographic structure.

Modes at the center of the Brillouin zone can be probed by means of vibrational spectroscopy (IR and Raman). However, it is worth remembering that the lowest energy vibrations (soft modes) can also be observed for $\mathbf{k} \neq 0$ and they usually indicate more intricate mechanism of transformation leading to bigger unit cell of the final (transformed) structure.

3. Structures and computational methodology

ZIFs are built up by metallic centers that are tetrahedrally coordinated by imidazole derivatives playing the role of the linkers. The prototypical framework analyzed in this work, ZIF-8, is composed of zinc centers connected by methylimidazolate molecules (Figure 1). This material is more stable than typical MOFs: it retains its structure up to 400°C [17]. It also shows very interesting phenomena related to adsorption. It was shown that the N₂ adsorption isotherm of ZIF-8 at 77 K has a step-like nature which was attributed to the gate-opening mechanism due to imidazolate linker rotations [18]. The vibrational properties of this material were previously studied both experimentally (FIR, inelastic neutron scattering INS), and using DFT methodology. Ryder et al. [15] showed that the mode which is characteristic for gate-opening occurs around 33 cm⁻¹, and described it as symmetric 4-member ring gate opening. Due to its symmetry, deformation of the structure induced by this mode does not change the dipole and hence it is not IR active. Tan et al. [19] pointed out that the mode responsible for gate-opening is located around 63 cm⁻¹ and is IR active. We will show that this apparent contradiction can be explained using the normal modes analysis.

Our study is focused on three materials based on ZIF-8 topology: the original ZIF-8 and two systems in which the methyl group attached to the imidazolate ring is replaced by a hydrogen atom (SALEM-2) or by an amino group (ZIF-8_amino), respectively (Figure 1). Table 1 gives the

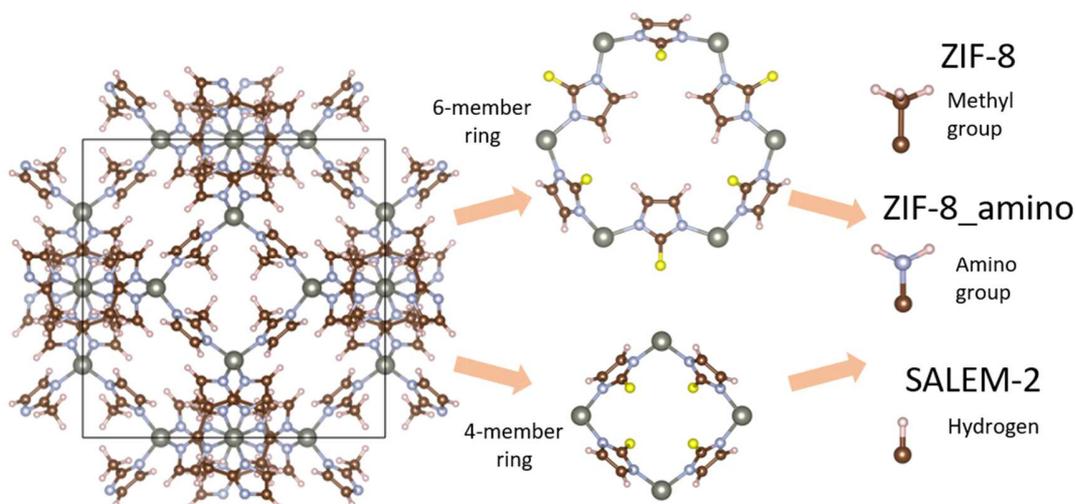


Figure 1. Unit cell of ZIF-8 of sodalite topology (left), types of gates present in the structure (middle) and functional groups attached to imidazolate for particular structures

crystallographic data for all studied structures. SALEM-2 is an existing compound, synthesized by solvent-assisted linker exchange in ZIF-8 [20]. Due to smaller van der Waals radius of hydrogen with respect to the methyl group, SALEM-2 possesses two types of apertures, one related to the 6-member ring (larger than for ZIF-8) and additional one, related to 4-member ring (Figure 1). Gate opening in this system may lead to broadening of the apertures; to the best of our knowledge the mechanism of this transformation has not been studied yet. ZIF-8_amino material has not been synthesized yet, but the analysis of the influence of this modification on the gate-opening is appealing due to well-known effect of enhanced affinity of the amino group to CO₂ [21].

Table 1. Experimental symmetry groups and lattice parameters of studied ZIFs, compared with corresponding values obtained from geometry optimization.

Framework	Symmetry group (exp.)	Lattice parameters (exp.)	Symmetry group (DFT)	Lattice parameters (DFT)	Reference
ZIF-8	I4-3m (217)	a = 16.9900	I23 (197)	a = 16.9484	[29]
SALEM-2	I4-3m (217)	a = 16.8303	P1 (1)	a = 16.8361 b = 16.7864 c = 16.8391 $\alpha = 88.6$ $\beta = 86.5$ $\gamma = 91.7$	[30]
ZIF-8_amino	-	-	I4-3m (217)	a = 16.9468	-

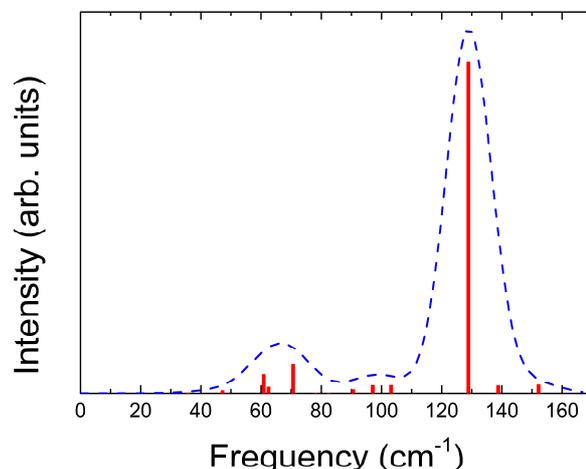


Figure 2. IR calculated intensities (red bars) with fitted Gaussian-based spectra (blue, dashed line) for ZIF-8.

The phonon frequencies have been calculated from the ab initio interaction model. We used the Density Functional Theory (DFT) method where electron density was approximated with plane waves, together with projector-augmented waves, as implemented in VASP package [22–25]. The dispersion correction to the density functional was incorporated [26–28]. Preparation of the calculations proceeded as follows: first the geometries of the structures were optimized using conjugate-gradient method. Optimized structures were then used in phonon calculations with finite-displacements (FD) method, within harmonic approximation. In this method, position of atoms is slightly distorted, at least six times per atom - $\pm\Delta x$, $\pm\Delta y$, $\pm\Delta z$. To improve the accuracy we also added second displacement in each direction, namely $\pm 2\Delta x$, $\pm 2\Delta y$, $\pm 2\Delta z$ with the displacement of $\Delta x = \Delta y = \Delta z = 0.015 \text{ \AA}$. In FD the matrix of force constants of energy second derivatives $V_{\alpha\beta}$ is created and after the Fourier transform the dynamical matrix is calculated. Its eigenvalues are the squares of frequencies ω of the normal modes, and eigenvectors are the vectors indicating atomic displacement of these modes. The symmetry of the eigenvectors indicated whether the vibration is IR active or not. We have limited the analysis to the center of the Brillouin zone.

4. Results

In our work we focused on the vibrations having low frequency (and hence, energy), up to 170 cm^{-1} . First, we analyze normal modes related to the adsorption-induced deformations of the internal structure of ZIF-8, which we will consider as the reference material. The two other structures will be compared to this reference system. In our calculations we observe two types of gate-opening modes in ZIF-8: one symmetric IR-inactive mode and several IR-active asymmetric modes. Symmetric mode is located at around 40 cm^{-1} . The asymmetric modes

located at 35.7 cm^{-1} , 47.2 cm^{-1} , 60.9 cm^{-1} , and 70.7 cm^{-1} forming a peak in the IR spectrum with maximum located at around 67 cm^{-1} (Figure 2). It covers the frequencies of modes predicted independently by Ryder et al. [15] and Tan et al. [19]. The small difference between ours and Ryder et al. [15] results is due to the use of different dispersion corrections in the calculations (D3(BJ) [27] in our case instead of D2). However, it does not change the qualitative picture.

Comparison of the symmetric and asymmetric gate-opening mechanism is depicted on the Figure 3. In both cases the mechanism involves the rotation of the linkers in 4-member rings. The highest peak on the IR spectra located around 129 cm^{-1} (Figure 2) is caused by vibration of the metallic centers. This, however does not affect the gate size since it is related to M-N bond vibration and not to the reorientation of the aromatic rings within the linker. There are also very weak breathing-related vibrations at 100 cm^{-1} . Concluding (see Table 2), one can divide the calculated IR spectra into three regimes related to: (i) asymmetric gate-opening modes, with the maximum around 67 cm^{-1} , (ii) breathing-related vibrations at 100 cm^{-1} ,

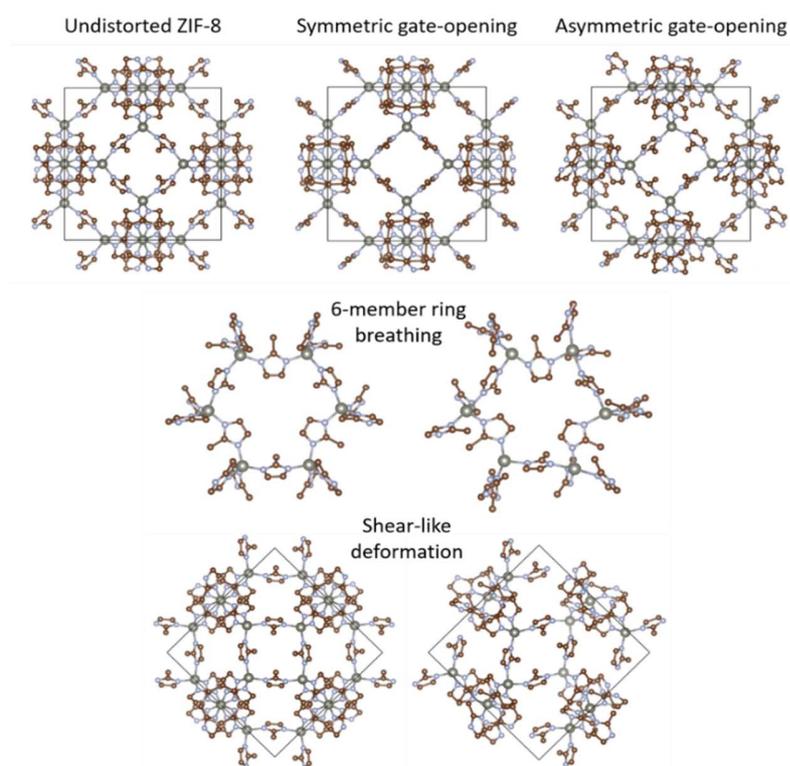


Figure 3. Visualization of the symmetric and asymmetric gate-opening (first row) together with breathing-like deformation of the 6-member ring (second row) and shear-like deformation (third row).

and (iii) the higher frequencies modes, related to metallic centers rocking. Besides the symmetric gate-opening mode, there still is one IR-inactive soft mode worth mentioning. It is

located at 22 cm^{-1} and it indicates shear-like deformation of 4-member ring (Figure 3). This mode should be tracked to monitor the effect of structure chemical modifications, as an indicator of the framework stability [31].

SALEM-2 is the modified structure with lightest linker, where the methyl group present in ZIF-8 is replaced by a hydrogen atom. As for ZIF-8, the first peak on the spectrum (Figure 4) refers to the collection of vibrational modes which generally may be related to different representations of the gate-opening. It is interesting to note that its maximum is shifted to the value of about 37 cm^{-1} which is approximately the half of the value observed in ZIF-8. In comparison with the methyl groups of ZIF-8, which experience a significant mutual attraction across the four-ring due to dispersion interactions, the interaction between the hydrogen atoms is much weaker, lowering the energy required to open the gate. The IR-inactive mode, responsible for gate-opening is however slightly higher than in ZIF-8 and split into two modes at 43.6 cm^{-1} and 46.0 cm^{-1} . The observed small splitting of the modes results from the low symmetry (P1) used in DFT calculations. In fact in DFT calculations the structures are static, and they correspond to the absolute energy minimum. This results in reduced symmetry of the 4-member ring, with a small distortion and orientations of the imidazolate linkers not related by any symmetry. The symmetry of the experimental structure is a consequence of the dynamical nature of the imidazolate linkers which jumps in time between two orientations; their mean orientation corresponds to structure with higher symmetry. The peak positioned at 105 cm^{-1} on the IR spectra is the breathing mode. Its position is not significantly distorted by the change of the linker functionalization (see Table 2).

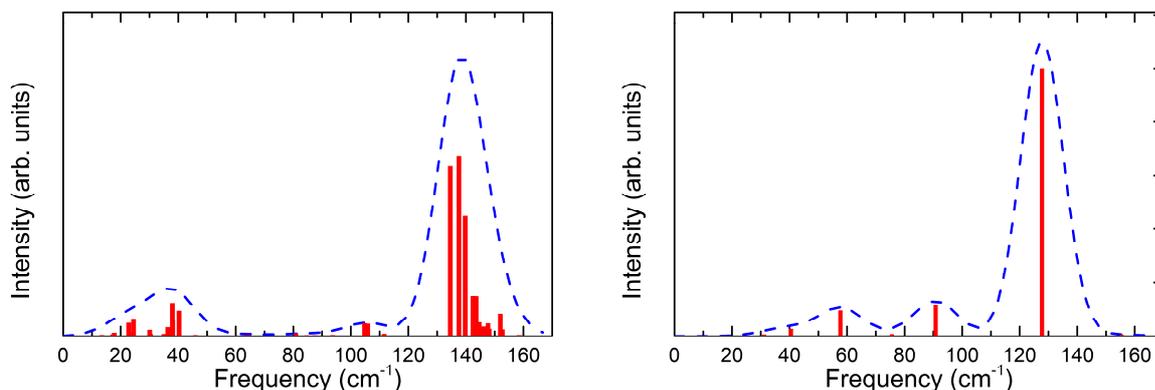


Figure 4. IR calculated intensities (red bars) with fitted Gaussian-based spectra (blue, dashed line) for SALEM-2 (left) and ZIF-8_{amino} (right).

The collection of the modes with the highest intensity is again related to vibration of the metal ions and does not influence the size of the 4- and 6-member ring in the material. Shear-like mode is present at the frequency of 23 cm^{-1} , almost equal to ZIF-8, indicating similar stability of both systems.

The IR spectrum of ZIF-8_ amino reveals only few active modes, which again may be divided into three peaks. In this case we observe only 3 active modes which are creating the spectra. In addition, as the amino group has very similar mass to methyl group and hence the mode has similar frequency as in ZIF-8 system. First of them, with the frequency of 58 cm⁻¹ represents deformation related to asymmetric gate-opening. The mode at 97 cm⁻¹ (no significant shift with respect to both ZIF-8 and SALEM-2) corresponds to breathing of the 6-member ring. The ion-rocking vibration at 128 cm⁻¹ is located at almost the same frequency as in ZIF-8, and it emerges to be linker-independent mode. The symmetric gate opening is found at a higher frequency than for previous structures, at around 50 cm⁻¹. Finally, the shear-deformation mode at 37 cm⁻¹ indicates that ZIF-8_ amino is more stable than two preceding structures. Frequencies of the analyzed modes are compared in [Table 2](#).

Table 2. Frequencies deformation-related modes in the analyzed systems.

	ZIF-8	SALEM-2	ZIF-8_ amino
Symmetric gate opening	40 cm ⁻¹	43 cm ⁻¹ 46 cm ⁻¹	50 cm ⁻¹
Asymmetric gate opening	67 cm ⁻¹	37 cm ⁻¹	58 cm ⁻¹
6-mr breathing	100 cm ⁻¹	105 cm ⁻¹	97 cm ⁻¹
Shear-like mode	22 cm ⁻¹	23 cm ⁻¹	37 cm ⁻¹

5. Summary

The role of phonons in the solid-state materials science has been confirmed for more than 50 years [1]. However, it is a new methodology in the field of structural studies of MOF compounds. The soft mode notion was evoked in some cases [5-7] in the context of adsorption-induced MOF deformations, without fundamental theoretical justification. In particular, the relation between the deformation and the symmetry properties of the soft mode was not determined.

Here, we have shown that the rigorous calculations of the phonons energies and symmetry allow for the detailed interpretation of the deformation mechanism and the relation with the experimental phonon spectra. The phonon symmetry and their space distribution (represented by the atom displacement vectors) can be related geometrically to the lattice deformation. The low frequencies of the relevant vibrations indicate the relevant deformation and give the atomic displacement vector defining the structural transformation. In the case of the ZIF-8 based structures studied in this paper we have shown that the gate opening mechanism is controlled by group of phonons of different energies and different symmetries. The contribution and symmetry of different modes have been determined and the corresponding IR spectrum was calculated.

In general, the phonon analysis always indicates the vibrations which can deform the system under consideration. The low-energy vibrations, if they exist, should be always considered as

the most probable precursors of the system deformation. These dynamical fluctuations become static deformations when enough of the thermal (temperature), mechanical (pressure) or interaction (adsorption) energy is provided.

It is important to recall that the soft modes can also exist at different points of the Brillouin zone, not only at its center. This option has not yet been explored in the case of the MOF structures. Also, the phonon methodology requires additional developments in the case of deformable structural transformations in MOF systems. In particular, an extension of the purely harmonic phonon methodology into strongly anharmonic situations is necessary. However, even at its preliminary stage, the phonon analysis is recommended as a standard tool to characterize mechanism of structural transformations.

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Declarations of interest: None

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Figure captions:

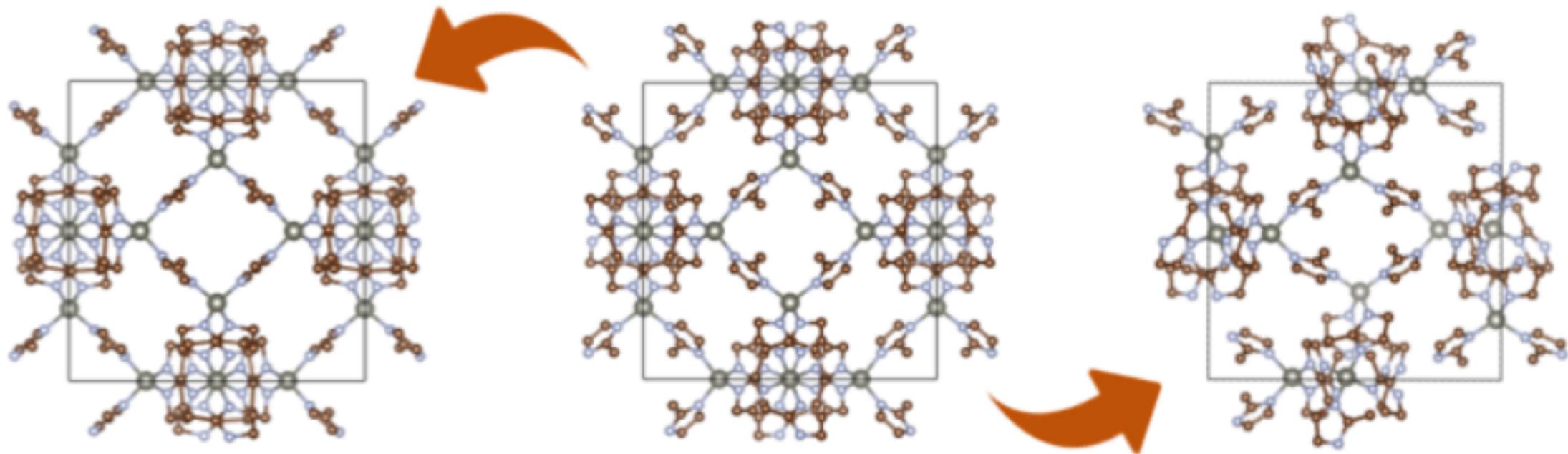
Figure 1. Unit cell of ZIF-8 of sodalite topology (left), types of gates present in the structure (middle) and functional groups attached to imidazolate for particular structures

Figure 2. IR calculated intensities (red bars) with Gaussian-based spectra (blue, dashed line) for ZIF-8.

Figure 3. Visualization of the symmetric and asymmetric gate-opening (first row) together with breathing-like deformation of the 6-member ring (second row) and shear-like deformation (third row)

Figure 4. IR calculated intensities (red bars) with Gaussian-based spectra (blue, dashed line) for SALEM-2 (left) and ZIF-8_amino (right).

Gate opening



Shear deformation