Supplementary information for:

Phonons and Adsorption-Induced Deformations in ZIFs: Is It Really a Gate Opening?

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Table S1. Experimental symmetry groups and lattice parameters of studied ZIFs, compared with corresponding values obtained from geometry optimization. Numbers in brackets in the space group columns refer to the International Tables of Crystallography A.

Framework	Space group (exp.)	Lattice parameters (exp.) (Å)	Ref.	Space group (DFT)	Lattice parameters (DFT) (Å)
ZIF-8	I4-3m (217)	a = 16.9900	[1]	I23 (197)	a = 17.0239
SALEM-2	I4-3m (217)	a = 16.8303	[2]	I4-3m (217)	a = 16.9600
ZIF-8(amino)	-	-	-	I4-3m (217)	a = 16.8483
ZIF-65	-	-	-	I4-3m (217)	a = 17.4288
ZIF-90	I4-3m (217)	a = 17.2715	[3]	I23 (197)	a = 17.1748
CdIF-1	I4-3m (217)	a = 18.1206	[4]	I23 (197)	a = 18.1069
ZIF-67	I4-3m (217)	a = 16.9589	[5]	I23 (197)	a = 16.8847
BIF-3Li	P-43n (218)	a = 16.0311	[6]	P-43n (218)	a = 16.0148
BIF-3Cu	P-43n (218)	a = 16.0184	[6]	P-43n (218)	a = 15.9603

1. Adsorption isotherms

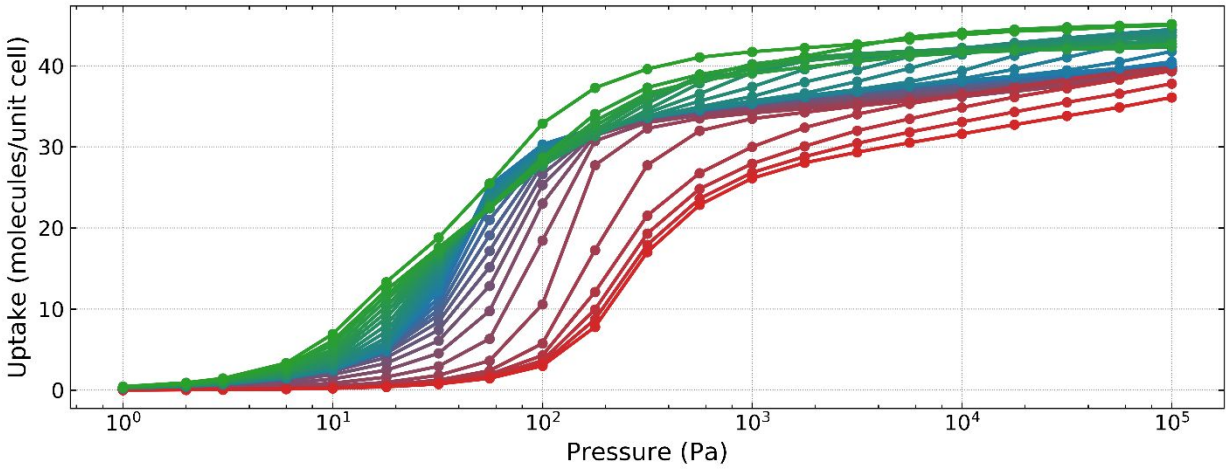

Figure S1. N_2 adsorption isotherms in ZIF-8. Blue represents undistorted (optimized) structure Linear change of isotherm color from blue to green represents structures deformed according to ν_{go2} phonon mode and from blue to red - ν_{go1}.

Visualizations of all modes related to linker-rotation are available on:

https://drive.google.com/file/d/1dJs84YrSlUbZhDHBZxpSrP9pmLis7opF/view?usp=sharing

Visualization of process of construction of accessible surface is available on:

https://drive.google.com/file/d/1PjjOnvzDR_R5XNKMDPXvZ8bN2-pzycQe/view?usp=sharing

2. Symmetry of positive and negative deformation of ν_{go2} mode

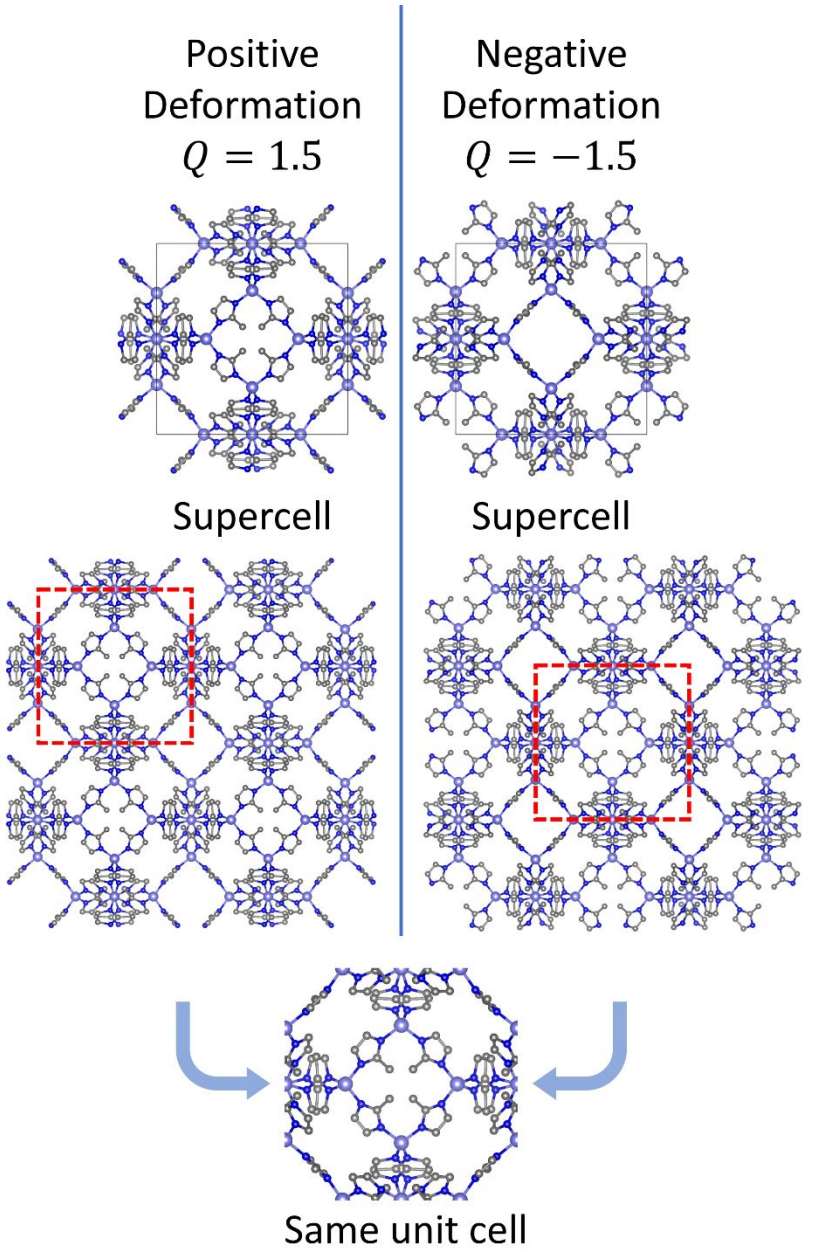

Figure S2. Negative and positive deformation related to ν_{go2} mode generate a structure with the same unit cell. Structure generated with $Q = 1.5$ equal to structure generated with $Q = -1.5$ and transformed by a lattice vector $\left[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right]$.

3. Selection of the SOD-topology structures

We focus our analysis on materials based on ZIF-8 with SOD topology and two types of chemical modifications of the: (i) exchanged linkers with the substituted methyl group and (ii) substituted metal ions in tetrahedrally coordinated metallic center. Table S1 gives crystallographic data of all structures.

SALEM-2 is a framework where the methyl group is replaced by hydrogen atom [7]. Due to smaller van der Waals radius of hydrogen with respect to the methyl group, SALEM-2 exhibits two types of apertures, one related to the 6-member ring (larger than for ZIF-8) and additional to 4-member ring (which is not penetrable in ZIF-8). Gate-opening may result in further broadening of the apertures and to the best of our knowledge its mechanism has not been studied yet.

ZIF-65 possess linker with nitro group ($-NO_2$) which is known to be highly selective for CO_2 molecules. Adsorption and desorption of N_2 in 77 K results in large hysteresis [8] which was suggested to be related to gate-opening although no explicit proof has been found.

Framework with amino ($-NH_2$) group was also analyzed. This material was not synthesized yet, but the analysis of the influence of this modification on the gate-opening is appealing due to well-known effect of enhancing the affinity to CO_2. Theoretical studies of CO_2/CH_4 separation showed for instance that the ZIF-96, a RHO-topology framework with amino group shows very high selectivity [9].

Finally, we used ZIF-90, a framework with aldehyde group. Gate-opening was suggested to occur in this material by terahertz spectroscopy [10] and a hysteresis on the N_2 adsorption isotherm was observed also indicating the presence of this phenomenon [11]. Due to strong polarity, aldehyde groups are good candidates for enhanced CO_2 capture as well.

We have also selected four systems with different metal ion mass starting from heavy cadmium, through base zinc and slightly lighter cobalt to boron imidazole frameworks (BIFs) with the mixed composition of boron with copper and lithium.

CdIF-1 (cadmium imidazolate framework) was synthesized with cadmium acetate dihydrate which replaced zinc nitrate dihydrate used in ZIF-8 synthesis as the ion source, and 2-methylimidazole as a linker. It was shown that the exchange of the ion causes significant elongation of the M-N (metal-nitrogen) bond, from 2.05 Å to 2.20 Å [4]. The elongation of the cation-nitrogen bonds causes higher degree of the flexibility of the framework such as gate-opening and 6- and 4-member ring breathing. Gate-opening, although not explicitly proven to exist, leaves its footprint on the adsorption isotherm of H_2 as a step [4].

The other material is ZIF-67 where Zn^{2+} is replaced by Co^{2+}. Many studies have been published describing this material, covering wide range of potential application such as separation [12], or adsorption and catalysis [13]. Due to the shortening of the M-N bonds, ZIF-67 emerges as material with higher selectivity, which is suggested to be caused by the reduced aperture of the gates [14].

Two remaining materials represents the group of boron imidazolate frameworks (BIFs) [6]. In this framework, the metallic center is occupied by B^{3+} and it is coordinated by MeIm linkers connected to the center with either Li^+ (BIF-3_Li) or Cu^+ (BIF-3_Cu). As the system is significantly

lighter than the base material – ZIF-8, and the M-N bonds are shorter, stiffening the framework. It has been shown by Fischer and Bell [15] that the long-range dispersion interactions of the atoms in metallic centers with adsorbed gases is reduced, and therefore it may influence adsorption of nonpolar gases such as H_2 without affecting adsorption of polar gases where the electrostatic interactions are significant, e.g. CO_2. Nevertheless, there is no systematic studies of the flexibility of those structures related to gate-breathing and gate-opening phenomena.

3. Bibliography

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