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Low Frequency Vibrations as the Indication of the Structural Transformations in Zeolitic Imidazole Frameworks –Density Functional Theory Study

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Low frequency lattice vibrations (<100 cm-2) are indicators of variety of structural transformations in the metal-organic frameworks (MOFs) [1]. In the case of zeolitic imidazole frameworks (ZIFs) ZIF-4, ZIF-7 and ZIF-8, the terahertz vibrations which are responsible for such phenomena as gate opening mechanism, shear-induced deformations or breathing. ZIFs are promising materials not only for the classical porous materials applications (CO¬2 capture, separation of hydrocarbons) but also as possible hosts for catalytically active compound (nanoparticles), drug delivery or even as shock-wave mechanical absorbers.
We selected ZIF-8 as the precursory framework for our research. This well-known sodalite-type cage material allows introducing a variety of chemical and structural modifications. We defined three groups of ZIF-8-derivateve materials with (i) different metal ions in metallic centers (B3+ and Li+ or Cu+ at the tetrahedrally coordinated positions - BIF-3 family, Co2+ - ZIF-67, Cd2+ - CdIF-1), (ii) different functionalization of imidazolate ring (-H –SALEM-1, –NO2, –H, -NH2, –CHO –ZIF-90) and (iii) different geometry (ZIF-7 and ZIF-9 – Zn- and Co- based frameworks with benzimidazole as a linker and with elongated 6-meber ring). We used density-functional theory in conjunction with the finite displacement method to predict and visualize the normal modes (vibrations) of the lattice. The results allows us to determine how changes in composition or geometry affect the presence and frequency of the mode related to the gate opening mechanism. We show that there are several participating modes. The first one is a symmetric distortion of the framework leading to the opening of the pore (IR inactive due to its symmetry) and a collection of IR active modes which might lead to asymmetric gate-opening. We claim that the frequency of the IR inactive "gate opening"mode is determined by the interactions between the linkers, therefore depending on attraction/repulsion force competition in the attached functional groups. At the same time, the frequencies of the IR active modes are sensitive to the variation of the linker mass. Additionally, we show that that the elongation of the M-N (M = metal ion) distance when Zn in ZIF-8 is substituted by heavy Cd ion leads to the shear deformation of the 4-meber ring. This corresponds to a mode at around 22 cm-1 in the precursory ZIF.
In conclusion we show that the potential structural deformations (or transformations) which occur in zeolitic imidazolate frameworks can be predicted from vibration in the low frequency phonon spectrum.

References

1. M. R. Ryder, et al., Identifying the Role of Terahertz Vibrations in Metal-Organic Frameworks: From Gate-Opening Phenomenon to Shear-Driven Structural Destabilization, Physical Review Letters, 113 (2014), 215502-21550

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