Electronic Supplementary Information (ESI)

Quantum mechanical predictions to elucidate the anisotropic elastic properties of zeolitic imidazolate frameworks: ZIF-4 vs. ZIF-zni

Jin-Chong Tan,[*a] Bartolomeo Civalleri,[‡b] Alessandro Erba[b] and Elisa Albanese[b]

[a] *Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, UK*

[b] *Department of Chemistry, NIS and INSTM Reference Centre, University of Turin, via P. Giuria 7, 10125 Torino, Italy*

*jin-chong.tan@eng.ox.ac.uk

‡bartolomeo.civalleri@unito.it

Table of Contents

1 *Ab Initio* Density Functional Theory (DFT) Calculations

1.1 CRYSTAL09 [1,2]: Additional Computational Details

The Pack–Monkhorst/Gilat shrinking factors for the *k*-point sampling of reciprocal space were set to 2 × 2, corresponding to 8 × 8 points at which the Hamiltonian matrix was diagonalized. The accuracy of the integral calculations was increased by setting the tolerances to 7, 7, 7, 7 and 16. For the numerical integration of the exchange–correlation term, 75 radial points and 974 angular points were adopted in a Lebedev scheme in the region of chemical interest. The self-consistent field iterative procedure was converged to a tolerance in total energy of $\Delta E = 1 \times 10^{-8}$ a.u.

2 Final Optimised Geometry (DFT) *vs*. Experimental Lattice Parameters

2.1 ZIF-4

- Orthorhombic space group: *Pbca*

Lattice parameters	*a* (Å)	*b* (Å)	*c* (Å)	Angles *α*/*β*/*γ* (°)	Volume (Å^3)
DFT PBE/BS1	15.576	15.837	18.543	90/90/90	4574.045
Expt. (233 K) Ref.[3]	15.3950(17)	15.3073(17)	18.426(2)	90/90/90	4342.2
% Deviation	+1.18%	+3.46%	+0.63%	0%	+5.34%

2.2 ZIF-zni

- Tetragonal space group: $I4_1cd$

Lattice parameters	*a* (Å)	*b* (Å)	*c* (Å)	Angles *α*/*β*/*γ* (°)	Volume (Å^3)
DFT PBE/BS1	23.763	23.763	12.496	90/90/90	7056.035
Expt. (298 K) Ref.[4]	23.5028(4)	23.5028(4)	12.4607(3)	90/90/90	6883.06
% Deviation	+1.11%	+1.11%	+0.28%	0%	+2.51%

3 Computed Elastic Stiffness Tensors C_{ij}'s and Compliance Tensors S_{ij}'s

Notations adopted:

Stiffness tensor $C_{ijkl} =$

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ & & C_{33} & C_{34} & C_{35} & C_{36} \\ & & & C_{44} & C_{45} & C_{46} \\ & & & & C_{55} & C_{56} \\ \textit{symm.} & & & & & C_{66} \\ C_{ij} = C_{ji} & & & & & \end{bmatrix}$$

Compliance tensor $S_{ijkl} = \left[C_{ijkl} \right]^{-1}$

3.1 ZIF-4 (Orthorhombic *Pbca*) with nine independent elastic constants

- ***Stiffness Tensor***

$$C_{ijkl} = \begin{bmatrix} 4.266 & 1.221 & 1.916 & 0 & 0 & 0 \\ & 3.492 & 1.526 & 0 & 0 & 0 \\ & & 5.015 & 0 & 0 & 0 \\ & & & 1.029 & 0 & 0 \\ & & & & 1.927 & 0 \\ \text{symm.} & & & & & 2.453 \end{bmatrix} \text{GPa}$$

- ***Compliance Tensor***

$$S_{ijkl} = \begin{bmatrix} 294.157 & -61.9845 & -93.5226 & 0 & 0 & 0 \\ & 343.35 & -80.7955 & 0 & 0 & 0 \\ & & 259.717 & 0 & 0 & 0 \\ & & & 971.817 & 0 & 0 \\ & & & & 518.941 & 0 \\ \text{symm.} & & & & & 407.664 \end{bmatrix} \text{TPa}^{-1}$$

3.2 ZIF-zni (Tetragonal $I4_1cd$) with six independent elastic constants

- ***Stiffness Tensor***

$$C_{ijkl} = \begin{bmatrix} 19.010 & 13.257 & 13.377 & 0 & 0 & 0 \\ & 19.010 & 13.377 & 0 & 0 & 0 \\ & & 23.384 & 0 & 0 & 0 \\ & & & 1.557 & 0 & 0 \\ & & & & 1.557 & 0 \\ \text{symm.} & & & & & 1.759 \end{bmatrix} \text{GPa}$$

- ***Compliance Tensor***

$$S_{ijkl} = \begin{bmatrix} 116.393 & -574.39 & -33.726 & 0 & 0 & 0 \\ & 116.393 & -33.726 & 0 & 0 & 0 \\ & & 81.351 & 0 & 0 & 0 \\ & & & 642.185 & 0 & 0 \\ & & & & 642.185 & 0 \\ \text{symm.} & & & & & 568.579 \end{bmatrix} \text{TPa}^{-1}$$

4 References

1. Dovesi, R., Orlando, R., Civalleri, B., Roetti, C., Saunders, V.R., and Zicovich-Wilson, C.M., *CRYSTAL: a computational tool for the ab initio study of the electronic properties of crystals.* Zeitschrift Fur Kristallographie, 2005. **220**(5-6): p. 571-573.

2. Dovesi, R., Saunders, V.R., Roetti, C., Orlando, R., Zicovich-Wilson, C.M., Pascale, F., Civalleri, B., Doll, K., Harrison, N.M., Bush, I.J., D'Arco, P., and Llunell, M., *CRYSTAL09 User's Manual, University of Torino, Torino*. 2009.

3. Park, K.S., Ni, Z., Cote, A.P., Choi, J.Y., Huang, R.D., Uribe-Romo, F.J., Chae, H.K., O'Keeffe, M., and Yaghi, O.M., *Exceptional chemical and thermal stability of zeolitic imidazolate frameworks.* Proceedings of the National Academy of Sciences of the United States of America, 2006. **103**(27): p. 10186-10191.

4. Spencer, E.C., Angel, R.J., Ross, N.L., Hanson, B.E., and Howard, J.A.K., *Pressure-induced cooperative bond rearrangement in a zinc imidazolate framework: a high-pressure single-crystal X-ray diffraction study.* Journal of the American Chemical Society, 2009. **131**(11): p. 4022-4026.