Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


# Metal Defects in HKUST-1 MOF Revealed by Vibrational Spectroscopy: A Combined Quantum Mechanical and Experimental Study

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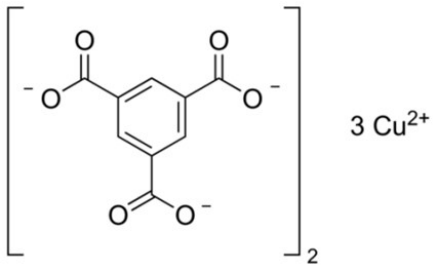
## Supplementary Data

### Table of contents




***Scheme S1.*** *Molecular formula of CuBTC.*

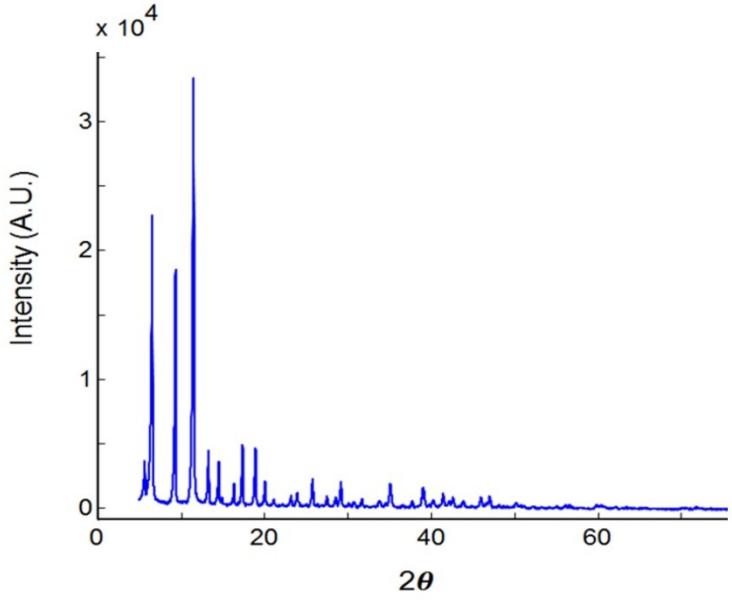



***Figure S1.*** *Wide Angle X-ray Scattering (WAXS) spectrum of CuBTC after the pressing and activation protocol.*

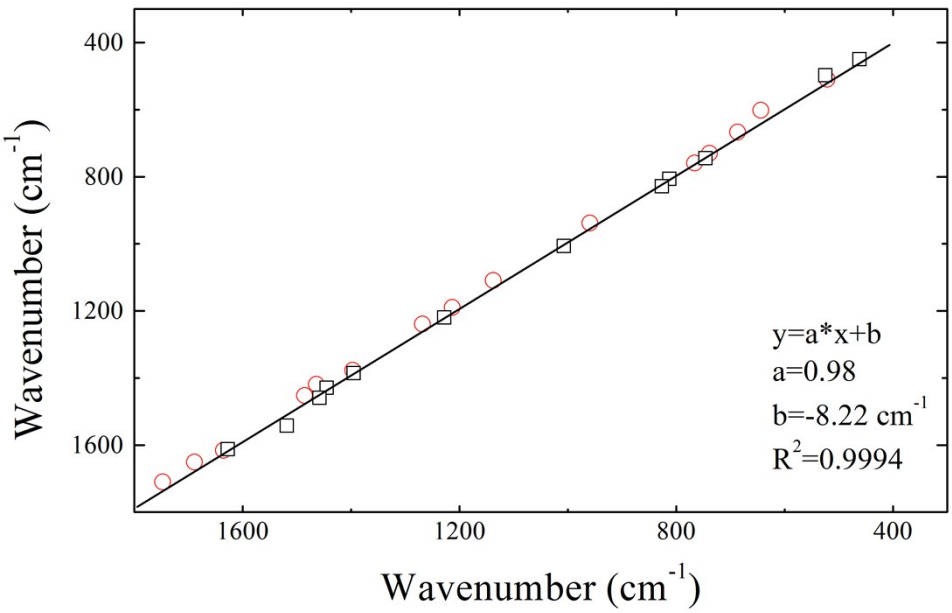



***Figure S2.*** *Observed vs calculated frequencies for the 3DP model.* ○: IR; □: Raman.

**The fragment strategy for the calculation of the vibrational modes of functional groups.**

A further analysis of the vibrational behavior of the localized defects has been performed according to the strategy developed in [1, 2]. It has been shown that, when subgroups of vibrational modes of the full lattice, or modes associated with subunits of the lattice (or large system), are described by wave vectors that are well localized, spatially, around the group of interest (in our case, around the interstitial O atom and its neighbours), a viable approximation, which is economic in terms of computer time without loss of accuracy, can be made. In this approximation, the construction and diagonalisation of the complete hessian matrix, which, in the case of no symmetry ($P_1$), would require (3N+1) SCF gradient calculations, where N is the number of atoms in the cell, can be replaced by the construction and diagonalization of a smaller matrix of (3M+1) size, where M is the number of atoms belonging to a fragment centered around the defect.

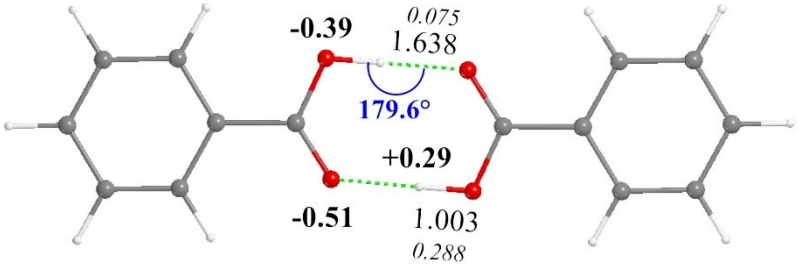



***Figure S3.*** *A molecular model of the benzoic acid dimer. Distances (in Å), bond populations (α+β electrons, in |e|; italic), Mulliken net charges (in |e|; bold) and H-bond angles (in degrees; blue) are highlighted in the figure.*

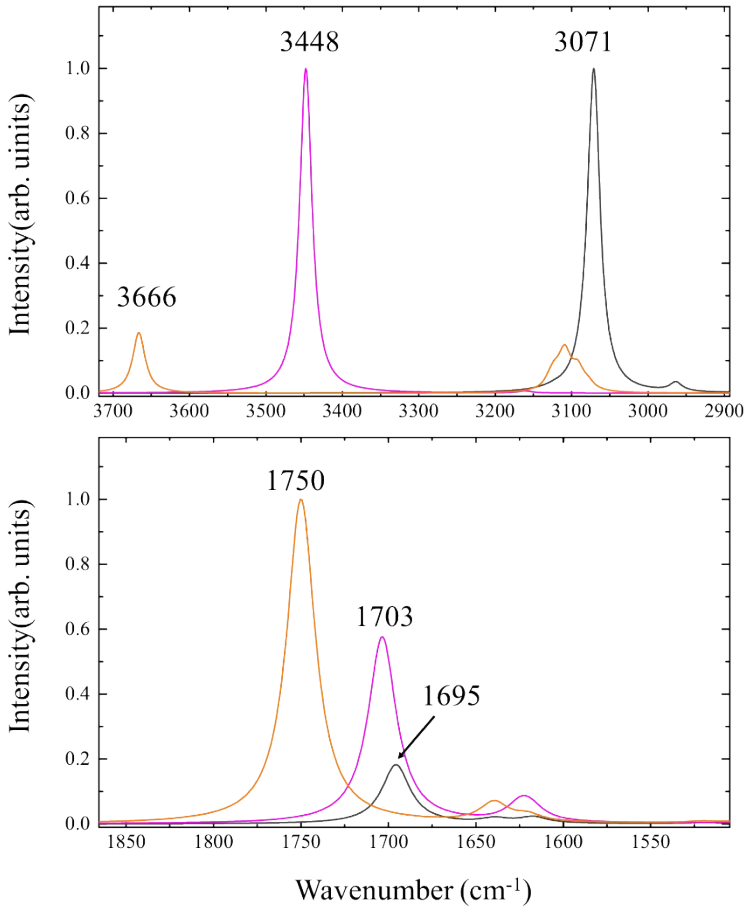



***Figure S4.*** *Calculated infrared spectra of benzoic acid monomer (orange trace), benzoic acid dimer (black trace) and defective fragment on the 3DP structure (purple trace) in the 3700 – 2900 cm$^{-1}$ range (top) and 1860 – 1500 cm$^{-1}$ (bottom).*

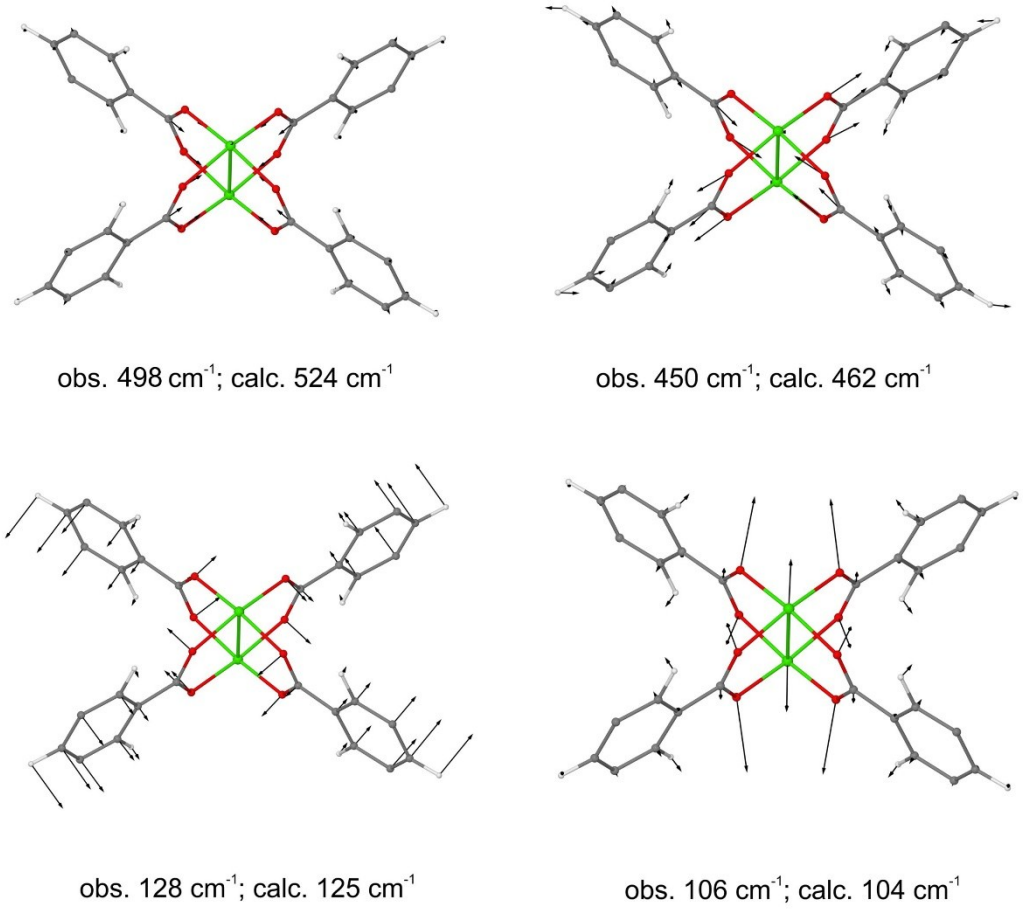



***Figure S5.*** *Vector representation of the Raman modes observed at 498, 450, 128 and 106 cm$^{-1}$..*

## References

[1] F. Pascale, S. Salustro, A.M. Ferrari, M. Rérat, P. D'arco, R. Dovesi, The Infrared spectrum of very large (periodic) systems: global versus fragment strategies—the case of three defects in diamond, Theoretical Chemistry Accounts, 137 (2018) 170.

[2] F.S. Gentile, Difalco, A. Pascale, F., Salustro, S., Mackrodt, W.C., Dovesi, R., The Spectroscopic Characterization of Interstitial Oxygen in Bulk Silicon. A Quantum Mechanical Simulation, The Journal of Chemical Physics, in press, (2020).