Development of reliable force fields for molecular simulations of metal-organic frameworks.

Louis Vanduyfhuys

Supervisor(s): Veronique Van Speybroeck

I. Introduction

Recently it was shown that Metal-Organic Frameworks could be successfully used as selective adsorbents for the extremely difficult and industrially relevant separations of mixed C8 alkylaromatic compounds [1]. The selective adsorption in MIL-47 was studied in a number of theoretical studies but without including the lattice dynamics [2,3]. For MIL-53 which is much more flexible, such approach is deemed to be unreliable. In this contribution, a generic forcefield (FF) is developed for MIL-53. The FF parameters are derived based on first principles density functional theory (DFT) calculations on nonperiodic model systems.

II. Theoretical and computational method

To be able to parametrize the FF for MIL-53, we performed DFT calculations (B3LYP/6-31G(d,p)) on 2 subsystems: the organic linker and the inorganic oxide. These results are used to construct the hessian to which the FF counterpart will be fitted.

Within the FF concept, the potential energy surface is devided into a covalent part and a non bonding part. The non bonding energy consists of electrostatic interactions and van der Waals interactions. The electrostatic interactions are described using constant atomic charges calculated from the DFT calculations. The van der Waals parameters are retrieved from literature [4]. The covalent energy is described as a sum of energy terms associated with stretch bonds, bending angles and dihedral angles. These energy terms have a known functional form and depend on a number of unknown parameters. We calculated these parameters by fitting the hessian generated by the FF to the DFT hessian.

III. Conclusions

A FF solely based on first principles was developed for the metal-organic framework MIL-53. It was tested for its ability to reproduce the geometry and we found a good agreement. The infrared spectrum was calculated and we found a fairly good agreement with the experimental spectrum. Finally, we observed the breathing mode in a NPT simulation.

Acknowledgments

I wish to thank Veronique Van Speybroeck, Michel Waroquier and Toon Verstraelen for their support and guidance in this research. Funding was received from the European Research Council under the European Community's Seventh Framework Programme (FP7(2007-2013) ERC grant agreement number 240483).

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L. Vanduyfhuys is with the Center for Molecular Modeling, Louis.Vanduyfhuys@ugent.be