Nuclear quantum effects in metal-organic frameworks

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Metal-organic frameworks (MOFs) make up a fairly recent class of nanoporous materials[1], which are built up out of inorganic bricks connected through organic linkers, thereby giving rise to a virtually unlimited number of possible structures, as different inorganic building blocks can be combined with various organic linkers. Due to this vast amount of possible structural combinations, MOFs can be tuned towards specific applications, such as gas storage[2], gas separation[3], and heterogeneous catalysis[4], research in which atomistic computer simulations can play a major role for screening and design purposes.

Most of the molecular dynamics (MD) simulations that are performed to that end rely however on the Born-Oppenheimer approximation, which allows to separate the electronic degrees of freedom from the nuclear degrees of freedom. The nuclei are then usually treated as classical particles. However, when considering lighter atoms, such as hydrogen, or lower temperatures, quantum mechanical effects such as zero-point energy and tunnelling can become important, so that an appropriate modelling of nuclear quantum effects (NQEs) is required[5]. This is most commonly achieved by using path integral molecular dynamics (PIMD). This work assesses the importance of nuclear quantum effects in three different MOFs: MOF-5, UiO-66(Zr), and MIL-53(Al). Both structural and thermal properties are reviewed for empty and guest loaded frameworks, showing some distinct differences with respect to classical MD simulations.

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4. S.M.J. Rogge et al., *Chemical Society Reviews* **2017**, vol. 46

5. T.E. Markland et al., *Nature Review Chemistry* **2018**, vol. 2