Quasi-1D Physics in Breathing Metal-Organic Frameworks

Danny E. P. Vanpoucke¹, Jan W. Jaeken¹, Stijn De Baerdemacker¹, and Veronique Van Speybroeck¹

¹ Center for Molecular Modeling, Ghent University, Technologiepark 903, 9052 Zwijnaarde, Belgium.

Introduction

Metal-organic frameworks (MOFs) present a class of materials showing properties akin to both solids and molecular systems. They consist of inorganic metal or metal-oxide clusters (nodes) connected through organic molecules (linkers), giving rise to porous, highly tunable frameworks. Their porous nature, with internal surface areas of >1000 m² g⁻¹, and chemical tunability, through the choice of nodes and linkers, makes them versatile materials that are receiving a rapidly growing interest with a large focus on industrial, chemically oriented processes, such as catalysis, gas separation and gas storage.

In this work, we focus on MOFs with the MIL-47 topology (cf. Fig. 1), which contain 1D transition-metal (TM) oxide chains. These MOFs belong to the class of so-called breathing MOFs because they can reversibly switch between a large-pore (LP) and narrow-pore (NP) configuration under the influence of guest molecules, temperature or pressure. The presence of transition metals on the other hand make these MOFs of interest for magnetic and/or multiferroic applications. We have studied the mechanical and electronic properties of such MOFs using ab initio methods, and found these MOFs to present an interesting test bed for quasi-1D physics.

Results and Discussion

In case of the MIL-47(V) MOF, the unit cell used contains 4 TM sites, which contain a single unpaired electron. This leads to 2⁴ possible configurations of which 5 are inequivalent (cf. Fig. 2).

For each of these 5 configurations we fully optimized the structure. [1] The final atomic structures are nearly indistinguishable, and the calculated Hirshfeld-I charges [2,3] on the vanadyl chains show only very small variations between the different spin configurations. In contrast, the calculated mechanical properties (cf. below) vary strongly, showing these very small variations to be of importance.

The inter- and intra-chain coupling of the unpaired electrons is investigated by mapping the obtained ab initio energies onto a simple Ising-spin model showing that both interaction couplings are anti-ferromagnetic, although the inter-chain coupling is 2 orders of magnitude smaller than the intra-chain coupling. This shows that the TM oxide chains can be regarded as quasi-1D systems. [4]
For the optimized structures also the bulk-modulus and its pressure derivative are calculated, and from these we derive a transition pressure at which the MOF is expected to show a phase-transition from the LP to the NP geometry (cf. Fig 3). Interestingly, it was found that the different spin configurations give rise to a clearly different bulk modulus of 6 GPa for ferromagnetic chains and 8 GPa for anti-ferromagnetic chains. This means that under a strong magnetic field the MIL-47(V) becomes softer. Also the transition pressure varies significantly: from 82 MPa to 124 MPa for the ferromagnetic and anti-ferromagnetic chains, respectively. [4] This is in perfect agreement with the pressure range, of 85 up to 125 MPa, observed in Hg intrusion experiments. [5] This shows that for polycrystalline samples, there may be a relation between the crystallite size and the fraction of ferromagnetic chains in the crystallite.

Conclusions

In this first principles study of the MIL-47 breathing MOFs, we have shown that the TM oxide chains behave as quasi-1D systems. The spin configuration plays an important role in the system stability, although the system geometry is barely modified. Ferromagnetic and anti-ferromagnetic chains give rise to clearly different mechanical properties, which provides us fundamental understanding regarding the experimentally observed broad range of transition pressures during pressure induced breathing.

References