Designing temperature-responsive flexible metal-organic frameworks by tuning the balance between dispersion and entropy

Kurt Lejaeghere(1), Jelle Wieme(1), Georg Kresse(2) and Veronique Van Speybroeck(1)

(1) Center for Molecular Modeling, Ghent University, Technologiepark 903, BE-9052 Zwijnaarde, Belgium

(2) Faculty of Physics and Center for Computational Materials Science, University of Vienna, Sensengasse 8/12, A-1090 Vienna, Austria

The unique combination of metal nodes and organic linkers has endowed some metal-organic frameworks (MOFs) with an unparalleled flexibility. A particularly fascinating example is MIL-53(Al). This so-called breathing framework undergoes a large and abrupt volume change as a function of temperature, switching between a narrow- and large-pore phase. However, the underlying physics has thus far remained unclear, prohibiting rational design for sensing and actuator applications.

We show that tuning the temperature-dependent phase stability of breathing MOFs results requires shifting the delicate balance between dispersion interactions and entropic effects. Dispersion favours the narrow-pore phase at low temperatures, while the high-temperature stabilization of the large-pore structure is entropy-driven. Because standard dispersion-corrected density-functional methods do not describe these aspects correctly, we present an accurate theoretical framework based on the random-phase approximation to the correlation energy, including single-excitation corrections. Many-body dispersion effects prove to be crucial to get the relative phase stability at 0 K right.

Based on insights for MIL-53(Al), the design of temperature responsivity is illustrated by means of a series of isoreticular materials. Linker substitution is found to affect the breathing capability quite drastically, while metal substitution allows more subtle tuning. Among MIL-53(Al), MIL-53(Al)-FA, DUT-4, DUT-5 and MIL-53(Ga), only MIL-53(Al) and MIL-53(Ga) were confirmed to display a phase transition within physically relevant temperature ranges.

[1] J. Wieme, K. Lejaeghere, G. Kresse, V. Van Speybroeck, "Tuning the balance between dispersion and entropy to design temperature-responsive flexible metal-organic frameworks", submitted.