Framework Models

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Exceptional Negative Thermal Expansion in Isoreticular Metal–Organic Frameworks**

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The thermal-expansion properties[1] of substances are very important in materials design; for example, cracks form when joined materials expand or contract by different amounts upon heating. The most famous example of a substance that contracts when heated is ice: it transforms into water, which has a higher density than ice. Negative thermal expansion (NTE) in solids is relatively rare, although examples have been found in zeolites.[2] The underlying physics of NTE remains poorly understood. Herein, we show, on the basis of molecular simulations, that the recently synthesized isoreticular metal–organic frameworks (IRMOFs) consistently have negative thermal-expansion coefficients and are by far the most contracting materials known. Our simulations point to two competing effects: a local effect, where all bond lengths increase with temperature, and a second long-range effect, where the thermal movement of the linker molecules leads to a shorter average distance between corners upon heating.

MOFs are a new class of nanoporous materials that have good stability, large void volumes, and well-defined tailorable cavities of uniform size. Their potential appears great, because these are precisely the properties needed for catalysis, separations, and storage/release applications.[3] MOFs generally consist of metal or metal–oxygen vertices interconnected by rigid or semirigid organic molecules. A large variety of MOFs, featuring different linker molecules and different types of bonding between the vertices with the linkers, have been produced by various research groups. The specific examples shown in Figure 1 are IRMOFs developed by Yaghi and co-workers.[4–8] In general, the IRMOFs consist of zinc–oxygen complexes connected by carboxylate-terminated linkers, forming a three-dimensional lattice of cubic cavities.

Molecular simulations of adsorption in MOFs have shown very good agreement with experiment,[9–13] and it is interesting to note that simulations of diffusion in MOFs preceded experiments by almost two years.[9,14] In addition to predicting macroscopic observables, simulations can also provide useful molecular-level insights. To systematically investigate the thermal properties of MOFs, we herein simulate the (cubic) structures of several IRMOFs of varying linker length. We obtain information about the unit-cell length (L) as a function of temperature and about adsorbate loadings (q) as a function of pressure. We show that the experimental data scattered in the literature (for different adsorbate loadings and temperatures) are, in fact, consistent, and we elucidate the different effects of temperature and loading on L at the microscopic level.

Various models for MOF flexibility have recently appeared.[15–17] Our flexible framework model for IRMOF-1, IRMOF-10, and IRMOF-16 is described in the Supporting Information. It is similar in spirit to the model of Greathouse and Allendorf,[15] but differs in the treatment of the carboxylate group and has the advantage of being calibrated to experimental data. It reproduces the experimental unit-cell lengths (L; Table 1), bond lengths, and bond angles of the frameworks (see the Supporting Information), as well as the adsorption of molecules by the frameworks, not only qualitatively, but also quantitatively (Figure 2). The Zn_4O cluster is modeled using only Lennard-Jones and Coulombic potentials between the individual atoms, while the linker molecule is simulated using a combination of general force-field parameters (DREIDING/CVFF parameters) for bond, bend, and (improper) torsion constants. Quantum-mechanical calculations were performed to obtain partial charges for all atoms. The starting parameters for the Zn_4O cluster are the parameters of the core-shell models used with considerable success for metal oxides.[18–20] However, MOFs do not have the local periodicity of metal oxides, and further refinement was, therefore, unavoidable. The fitting process not only involved the unit-cell length, and the bond lengths and angles within the structure, but also the adsorption isotherms of methane and CO_2 at several temperatures. All simulations were carried out for one unit cell using high precision for the electrostatics (Ewald summation). Test simulations using $2\times2\times2$ unit cells gave equivalent results, but were deemed too expensive for production runs.

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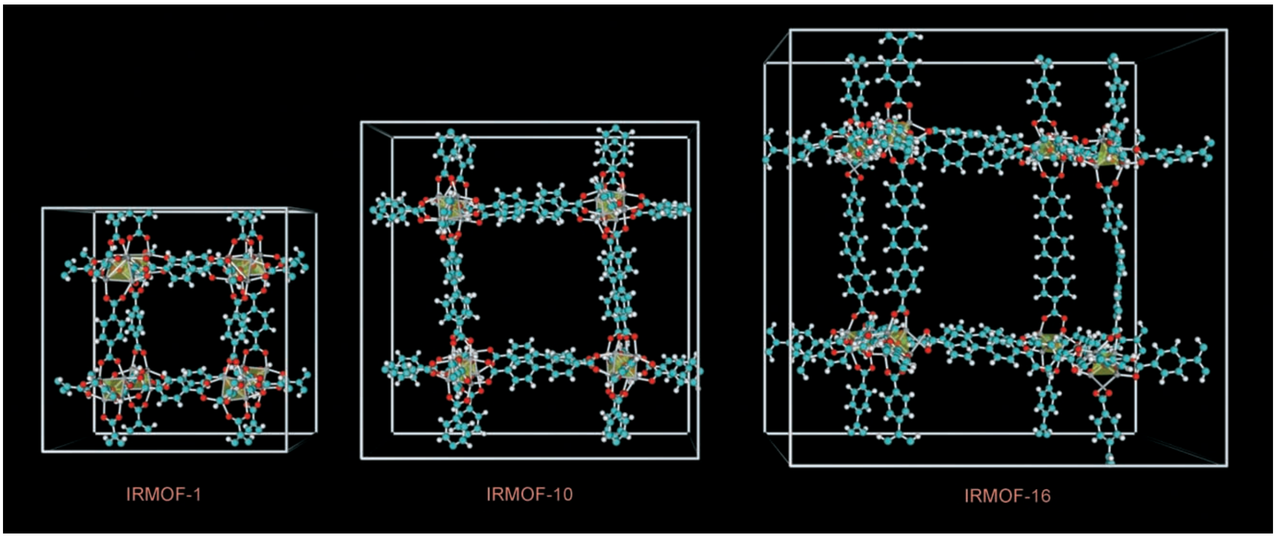

Figure 1. Simulated structures of IRMOF-1, IRMOF-10, and IRMOF-16. The IRMOFs consist of Zn_4O complexes (yellow) connected by carboxylate-terminated linkers, forming a three-dimensional lattice of cubic cavities. Zn silver, C cyan, H white, O red.

Table 1: The simulated unit-cell lengths (*L*) of the cubic structures of IRMOF-1, IRMOF-10, and IRMOF-16 compared to the experimental data of Li et al.[4] and Eddaoudi et al.[6]

Structure	*T* [K]	Experimental *L* [Å]	Simulated *L* [Å]
IRMOF-1	169	25.882[4]	25.88 ± 0.01
IRMOF-1	258	25.832[6]	25.83 ± 0.01
IRMOF-10	258	34.281[a], [6]	34.28 ± 0.02
IRMOF-16	258	42.980[b], [6]	43.00 ± 0.03

[a] The experimental value given for IRMOF-10 was actually inferred from the closely related structure IRMOF-12.[6] [b] The unit-cell length of IRMOF-16, which crystallizes in the primitive cubic space group $Pm\bar{3}m$, is doubled for comparison with those of IRMOF-1 and IRMOF-10, which crystallize in the face-centered cubic space group $Fm\bar{3}m$.[6]

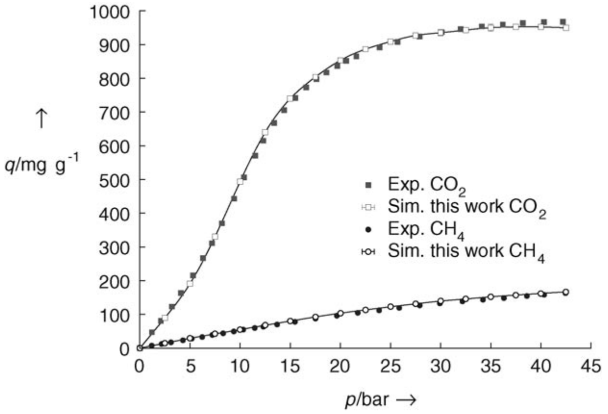

Figure 2. Simulated excess-adsorption isotherms (loading (*q*) as a function of pressure (*p*)) for CO_2 and CH_4 in IRMOF-1 at 298 K compared to the experimental data of Yaghi and co-workers.[5,21]

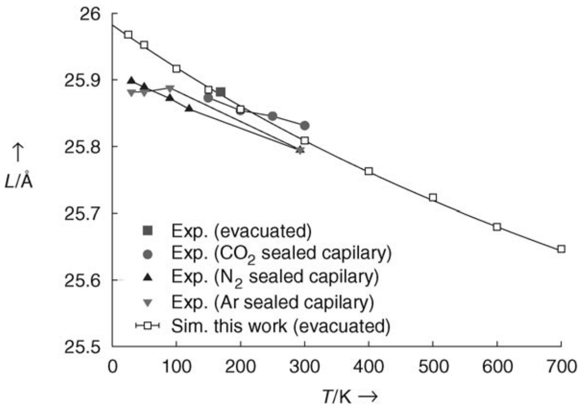

Figure 3. Simulated unit-cell length (*L*) of evacuated IRMOF-1 ($Fm\bar{3}m$) as a function of temperature (*T*) compared to the experimental data of Yaghi and co-workers for CO_2-, Ar-, and N_2-loaded IRMOF-1.[4–6,21,22]

In Figure 3, a plot of the unit-cell length of IRMOF-1 as a function of temperature obtained from simulations is compared to experimental data from the literature.[4–6,21,22] The unit-cell lengths for N_2- and Ar-loaded IRMOF-1[22] were taken from the Cambridge Structural Database (CCDC-277428–277437), and those for the CO_2-loaded structure were taken from the doctoral thesis of Millward.[21] Both literature studies examined the primary adsorption sites upon lowering the temperature. After loading a capillary with 700 Torr of fluid and sealing it at ambient temperature, the adsorption sites were refined from X-ray diffraction data obtained at progressively lower temperature. The authors only hinted at a possible NTE. A clear trend is observed when the data are plotted as in Figure 3: there is an exceptionally large NTE.

The experimental results are not straightforward to interpret, because they are for CO_2-, Ar-, or N_2-loaded structures at 700 Torr in a sealed capillary. The experimental data at 700 Torr actually exhibit two separate trends. The first effect is the strong NTE of the structure as a function of temperature. The second trend is the complex behavior of the unit-cell length as a function of loading. We note that at 300 K the structure is close to evacuated, because almost no CO_2, Ar, or N_2 is adsorbed under these conditions. At 250 K a small amount is adsorbed, while at 200 and 150 K the framework is roughly half-saturated.[5] Our simulations show that the general trend with increasing sorbate loading is a contraction of the unit cell up to medium loading, followed by an expansion at close to saturation capacity. This loading dependence of the unit-cell size is in agreement with experiments on other MOFs (see, for example, reference [23]). Extrapolating the experimental data to the evacuated case (by correcting loading effects) would lead to larger values for the unit-cell size at the lower temperatures. Therefore, the agreement between the simulation and the experimental data (for different adsorbates, loadings, and temperatures) is even better than Figure 3 suggests.

Recently, there has been a renewed interest in materials exhibiting the unusual phenomenon of NTE. This property finds applications in electronics and optics, sensors and actuators, and in the design of materials, for example, dental-filling materials. Examples of materials showing a large NTE are the mixed-metal oxide ZrW_2O_8,[24] the zeolite chabazite (CHA; framework code of the International Zeolite Association),[25] and the aluminophosphate $AlPO_4$-17 (ERI topology).[26] MFI, one of the most famous zeolites, also shows NTE.[27] Barrera et al. provide a nice discussion on the NTE of many substances,[1] and Lightfoot et al. present a table of the thermal-expansion coefficients for a variety of nanoporous materials.[2] It is believed that strong bonds play a role in the NTE mechanism. Pryde et al. showed that the correlated movement of polyhedra must also be taken into account (such correlated motions are called rigid-unit modes (RUMs)).[28,29] Goodwin and Kepert showed that the topologies of a number of simple cyanide-containing frameworks support a very large number of low-energy RUMs, all of which give rise to NTE.[30] The magnitude of the NTE in the IRMOFs makes them by far the most contracting materials known, as shown in Figure 4. To our knowledge, the previous record holder is the aluminophosphate $AlPO_4$-17.[26] Our simulations indicate a much larger NTE for the IRMOFs than for $AlPO_4$-17.

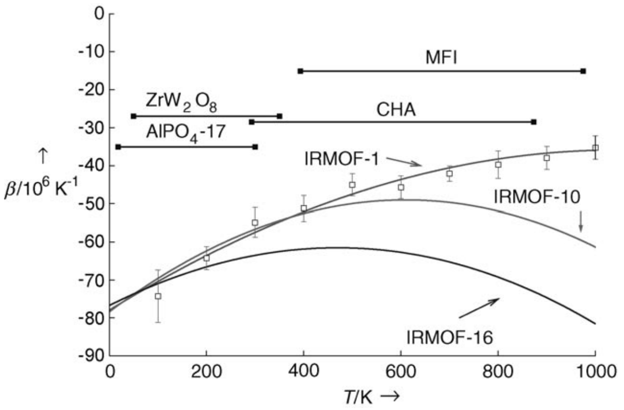

Figure 4. Simulated volumetric thermal-expansion coefficients (β) of IRMOF-1, IRMOF-10, and IRMOF-16 as a function of temperature (T). For comparison, the experimental data for $AlPO_4$-17,[26] ZrW_2O_8,[24] CHA,[25] and MFI[27] are plotted as a line at the highest NTE (lowest β value) over the temperature range examined. The IRMOFs consistently shrink when heated. Over the full temperature range, the simulated β values of the IRMOFs are more negative than that of the previous record holder $AlPO_4$-17, and at low temperatures, the β values of the IRMOFs are almost twice as negative as that of $AlPO_4$-17. The β values of the IRMOFs (lines) were determined from a numerical calculation of $\beta = 3\alpha$, where $\alpha = (1/L)(\partial L/\partial T)_P$, by a spline fit of the unit-cell length (L) as a function of temperature. The β values of IRMOF-1 (squares) were also determined from a fluctuation formula. The results of both methods agree well. See the Supporting Information for details. Note that the IRMOFs are stable to several hundred degrees Celsius.[4] Temperatures higher than the experimental stability limit were also considered in the simulations.

While the NTE in zeolites and metal oxides is not fully understood at the molecular level, the "simplicity" of the IRMOF structures (corners connected by fairly rigid linker molecules) allows for a more straightforward analysis. The volume-expansion coefficients ($\beta = (1/V)(\partial V/\partial T)_P$) decrease in the order IRMOF-1 > IRMOF-10 > IRMOF-16; that is, the NTE is greater for increased linker length. However, because the effect of the change in linker length is relatively small (compared to the total magnitude of the NTE) and because the Zn_4O cluster expands upon heating, the main contribution to the large NTE originates from the coordination bonds of the oxygen atoms of the carboxylate groups to the zinc atoms of the corners. The thermal motion of the linkers and the shearing of the cages result in a shorter average effective length of the linkers, even though all the bond lengths in the structure increase with temperature (see the Supporting Information). Figure 1 contains actual snapshots from our simulation. The flexibility, internal freedom, and shearing increase in the order IRMOF-1 < IRMOF-10 < IRMOF-16; that is, the phenyl rings of the longer linkers have more rotational freedom, and these linkers are less rigid. A single linker can bend, deform, and shear between the Zn_4O clusters, owing to the relatively weak coordination bonds, without affecting the other linkers much. In addition, the full cage shears in cooperative motion. Clearly, the IRMOFs possess a high degree of flexibility.[31–34]

We have shown that, besides having exceptional adsorption properties, the IRMOFs are also the most contracting materials known. The origin of the NTE is much longer-ranged than bond stretching and RUMs. It involves the rigid motion of the linker and the whole cubic cage. The simulations show that the IRMOFs possess very interesting thermal properties, owing to their inherent design. These properties can, in principle, be tailored to specific applications by a proper choice of linker molecules. In addition, it should be possible to further control the amount of NTE by changing the metal, the connectivity of the cluster, and/or the amount and type of solvent or adsorbates present.

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