



Modeling the Many-Body Interactions of Water within a Metal Organic Framework



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Introduction

MOFs (Metal Organic Frameworks) are versatile nanoparticles comprised of a metal node (such as cobalt, nickel, iron, etc.) and an organic ligand or linker. These particles have an astounding surface area (SA), with one gram of a MOF containing the SA between a basketball court and football field. With this expansive surface area comes innumerable applications, such as gas storage, water purification and collection, targeted drug delivery, and medical imaging based on MOF luminescence[1]. Initially, these frameworks were incredibly fragile and prone to collapse with exposure to water, changes in temperature, or varying pH levels. Fortunately, innovations in the field have created more structurally stable frameworks.

The objective of this research is to better understand MOF properties that relate to their potential applications for water collection. Atmospheric water (humidity) is a huge, yet untapped resource of fresh water, containing about ten percent of our fresh water supply (13 sextillion tons of water at any given moment) [1]. Using computer simulations, it is now possible to gain a more comprehensive understanding of both the process of adsorption and desorption of water, specifically regarding variant temperature and loading. For this project, a MOF with a cobalt node was used due to its previous applications for similar water collection experiments. This MOF is an ideal candidate for water adsorption and desorption, because it has an open site on the cobalt node. Prior research demonstrated it was able to adsorb 84.7 wt % of water [2].

Understanding the interaction between MOFs and water is integral to improving water adsorption and the process in which nanoparticles can be designed to be more structurally stable. These nanoparticles may be utilized for a multitude of possible applications, such as providing aid to those in dire need of a basic necessity: water.

Methods

It is now possible to model not only the interactions between two molecules, but interactions inside a molecule, as well as three, four, and even N-body interactions inside the system, increasing simulation accuracy. For this research, DL_POLY V2 was used to run the simulations with two different potential energy functions: q-TIP4/p, which models pairwise interactions, and MB-pol, which takes into account the short-range two and three-body interactions, along with the one-body interactions inside the molecule itself. Once the calculations are complete, it is then possible to view the simulation unfolding with VMD (Visual Molecular Dynamics) software using DL_POLY V2 to run the simulation.

$$E_N = \sum_i V^{1B}(i) + \sum_{i<j} V^{2B}(i,j) + \sum_{i<j<k} V^{3B}(i,j,k) + \dots + V^{NB}(1,\dots,N)$$

1-body
2-body
3-body
4-body
...

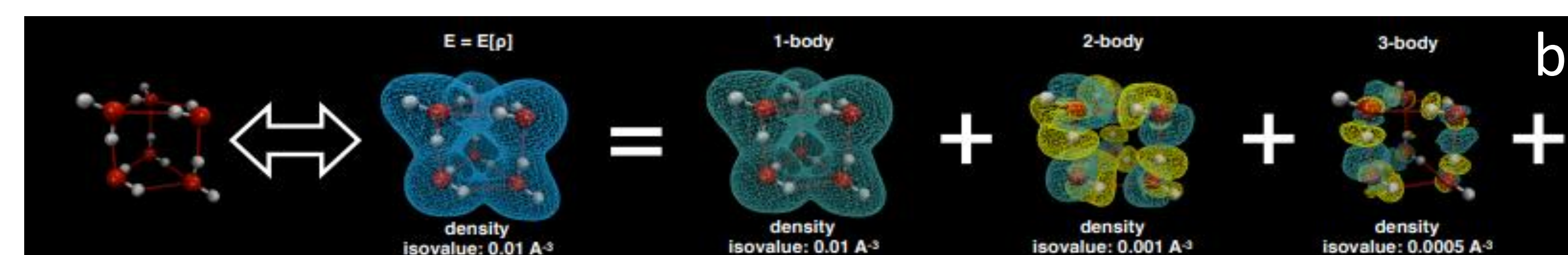


Figure 2: a. Equation for the different many-body interactions [3] b. Visual representation of the many-body dynamics [3] c. & d. Two VMD simulations of the Co₂Cl₂BTDD MOF with a loading of 162 water molecules

Xmgrace, a linux plotting tool, is then used to compile RDF (radial distribution function) graphs, which depict the probability of an atom/molecule being located at varying distances away from another specified atom/molecule.

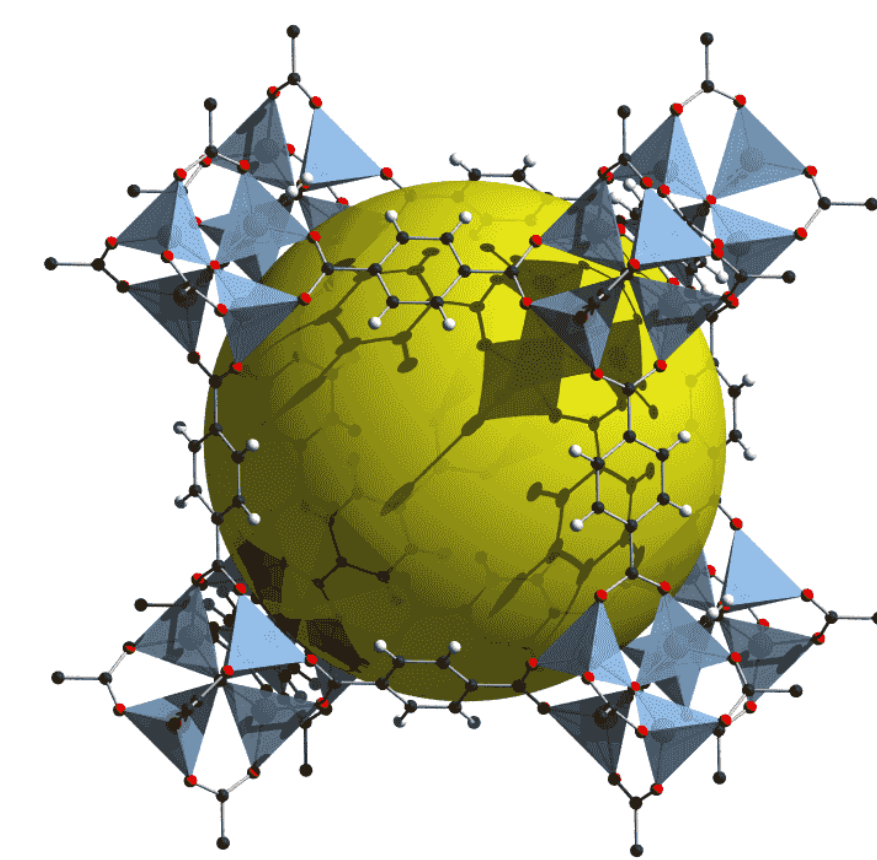


Figure 1. A cell of a Metal Organic Framework containing a guest molecule

After the Cobalt MOF was computationally constructed, it was tested with various stresses, such as different loadings of water (between 54 to 432 water molecules in a single cell of the framework), along with different temperatures ranging from 200K to 400K. Under these conditions, the distance between individual atoms of both the framework and the water molecules were recorded and graphed. Once it is possible to understand how the MOF responds to the stresses of water loading and temperature, the next step of research is how the water interacts with itself due to the presence of the MOF. The vibrational spectra of water provides further insight into this area of research. Therefore, the spectra of water inside the MOF was evaluated for various loadings in reference to the vibrational spectra of bulk water (Figure 4).

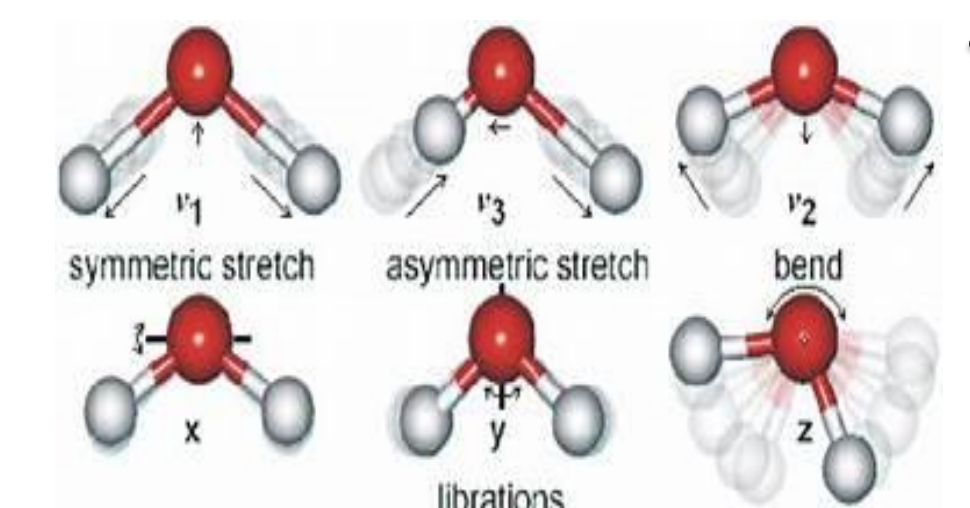
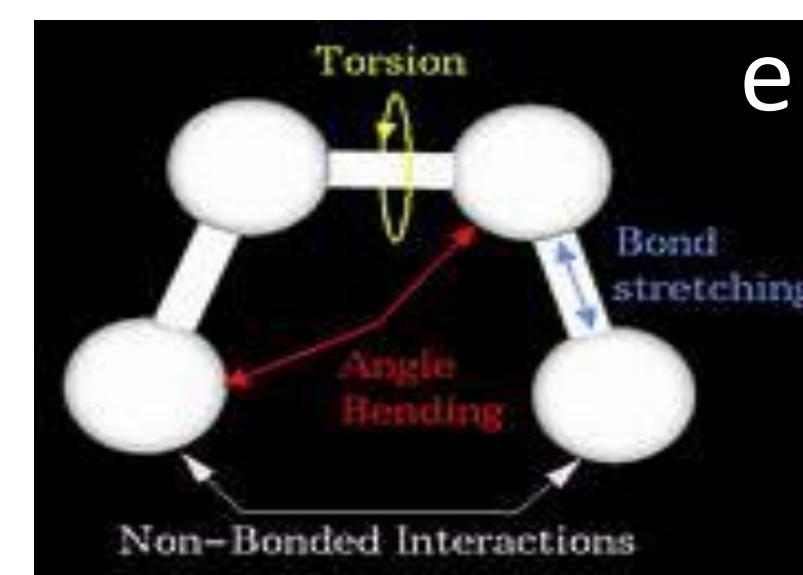


Figure 2e. & f. Different motions within a molecule

These results will yield further information regarding not only how the MOF interacts with different quantities of adsorbed water at different temperatures, but also how the water will alter its behavior under specified conditions.

Results of the Simulations

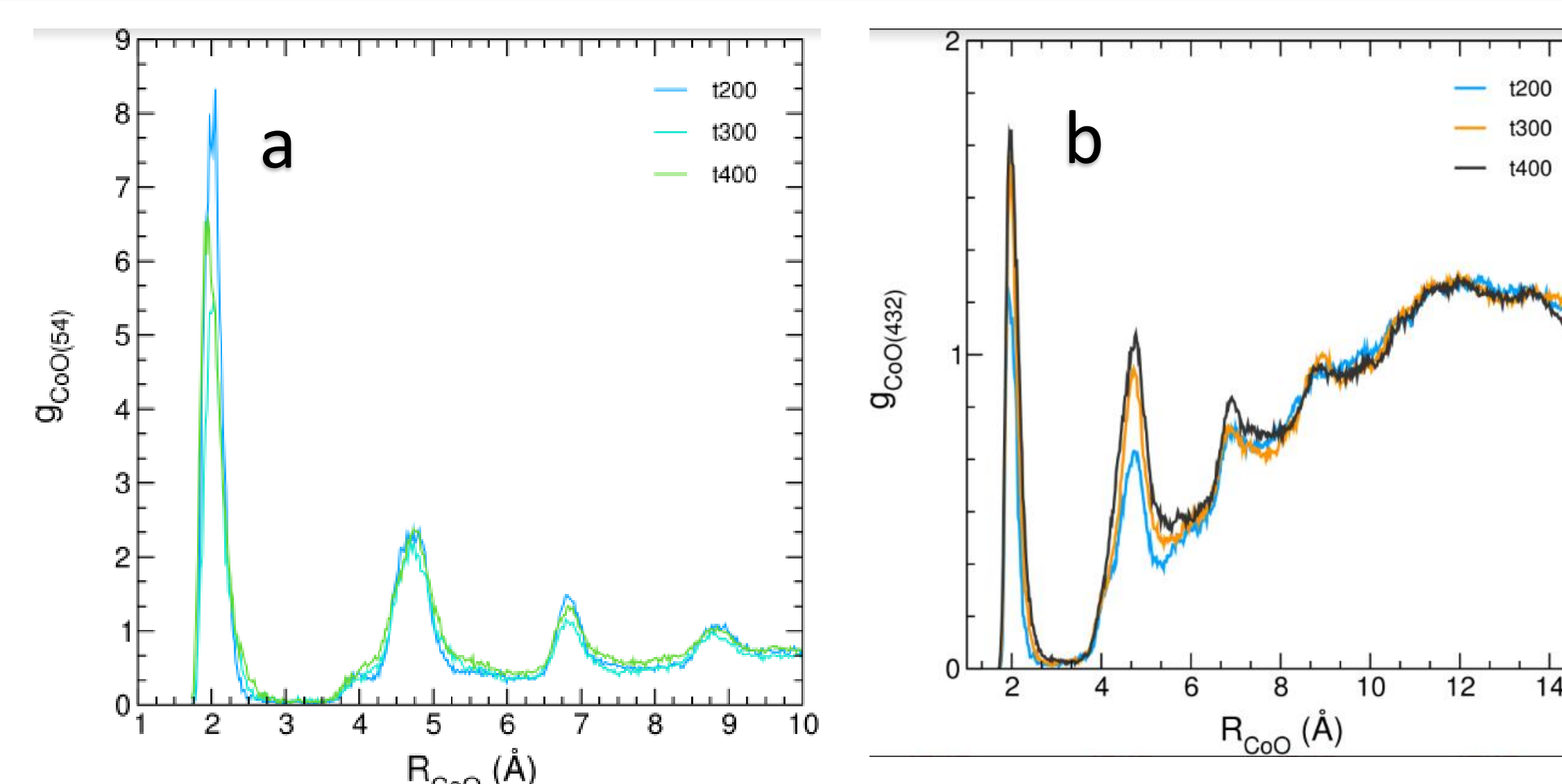


Fig 3: a. The RDF between the oxygen atoms (54 water molecules) and the cobalt nodes b. The RDF between the oxygen atoms (432 water molecules) and the cobalt nodes

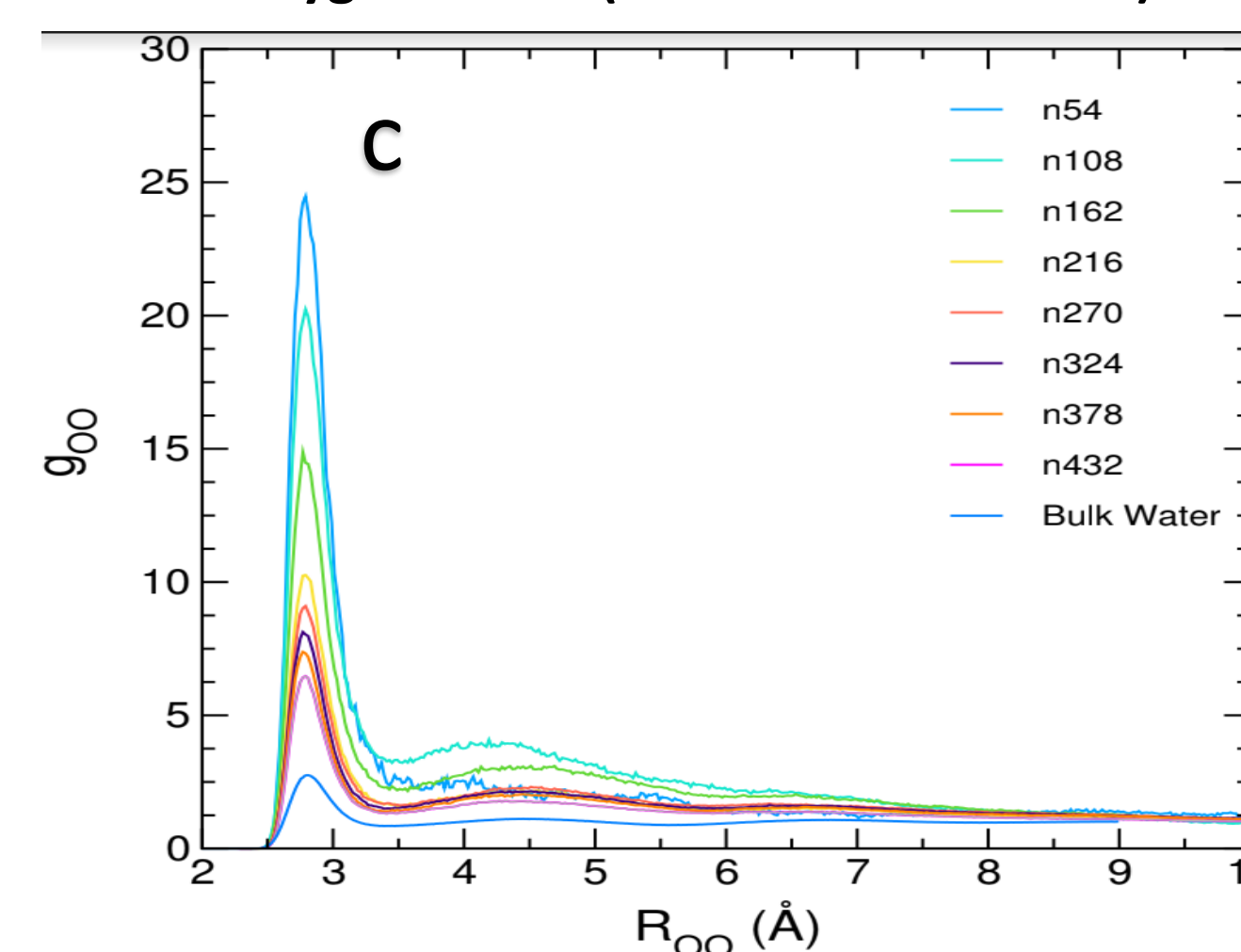


Fig 3c. RDF with different loadings of water at a constant temperature (300K)

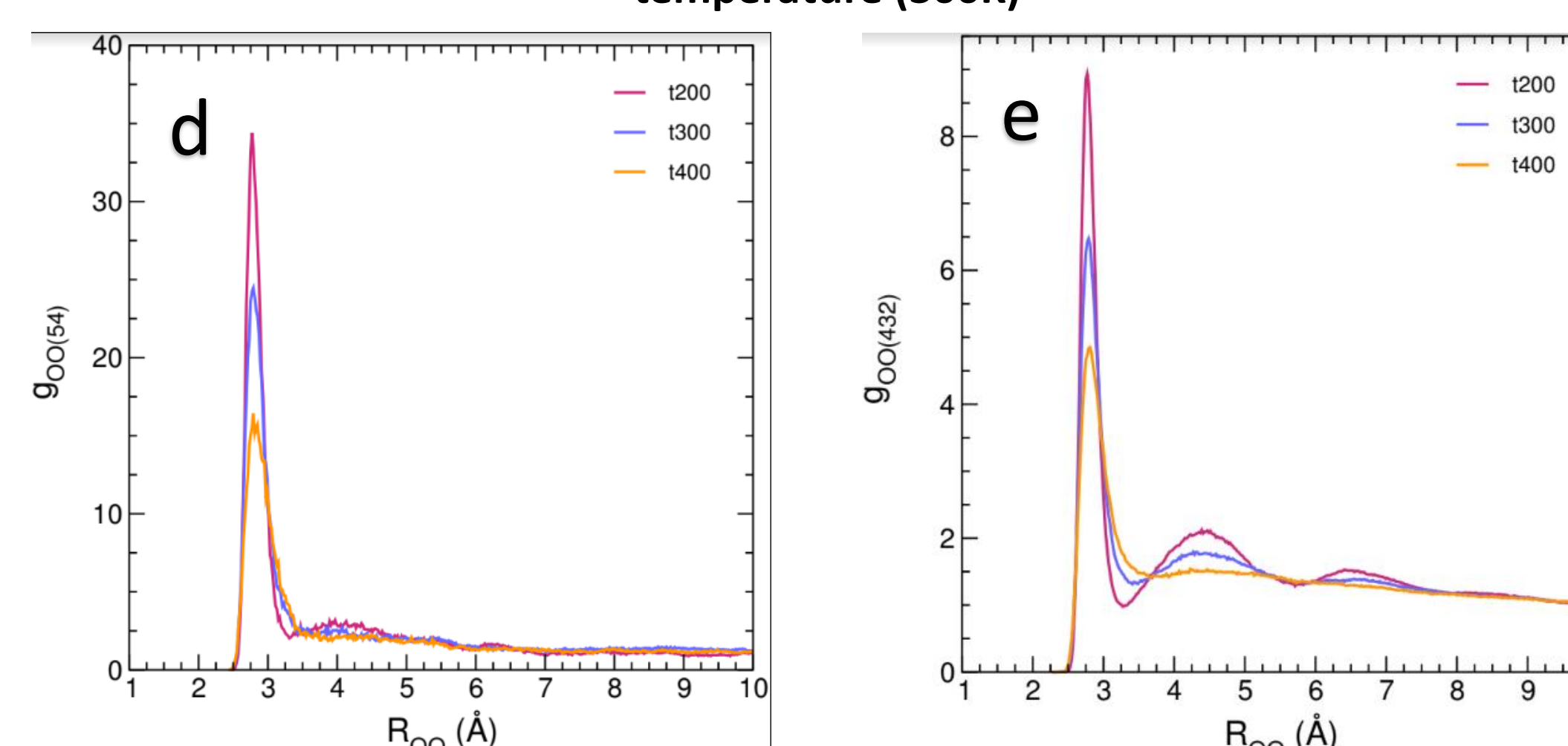


Fig 3: d. RDF (O-O), with 54 water molecules at varying temperatures e. RDF (O-O) with 432 water molecules at varying temperatures

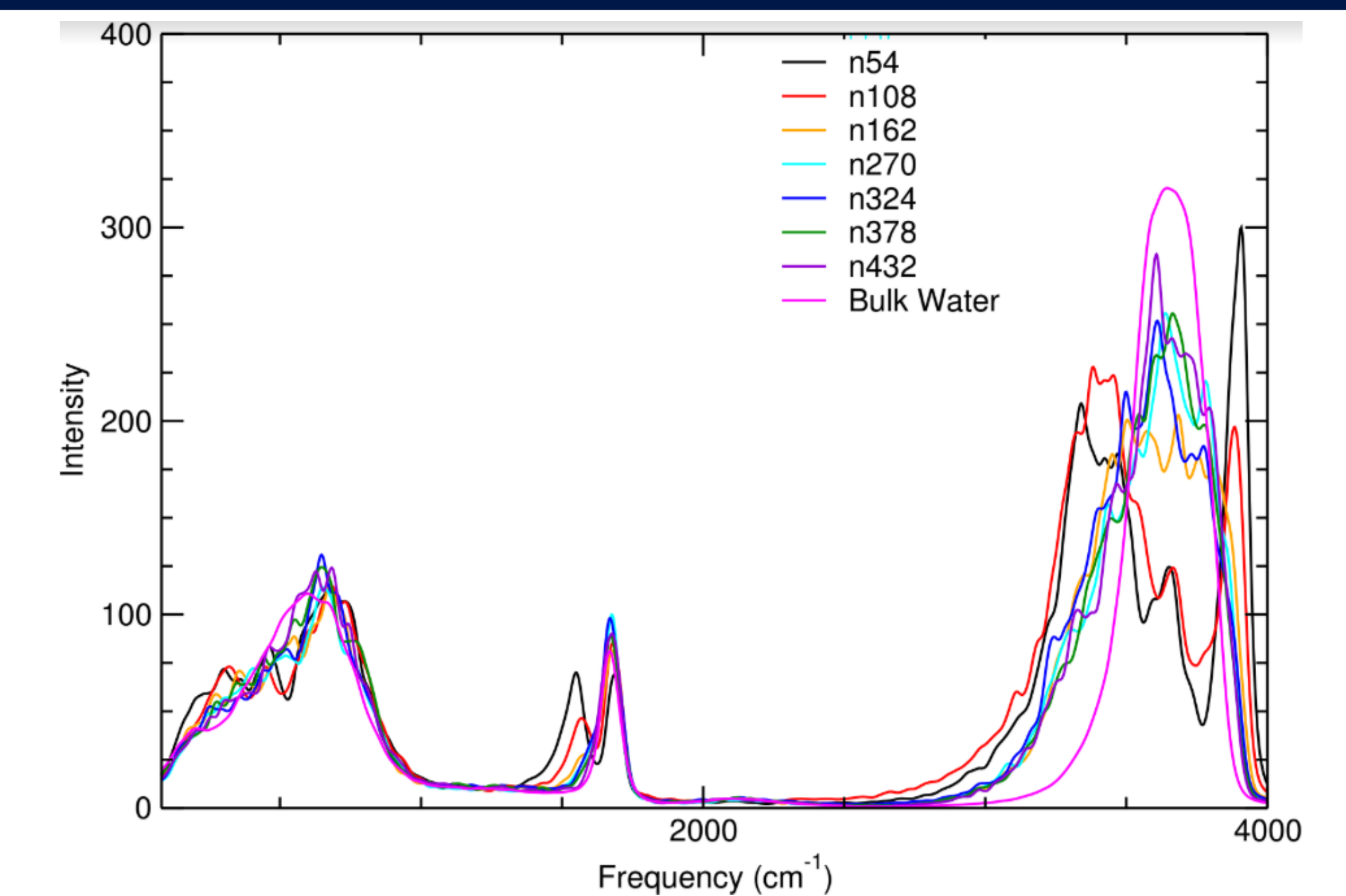


Fig 4. The infrared vibrational spectra of water at different loadings (54-432) vs. that of bulk water.

Analysis and Conclusions

From the data collected, it is evident that water within a MOF will behave differently than that of bulk water. With a small number of water molecules adsorbed into the framework, they will remain localized near the cobalt nodes, as the water's oxygen will be attracted to the open site on the cobalt atom. As this space becomes more occupied, the water will be distributed more throughout the cell (Figure 3a & b). This is also shown in Figure 3c as there is a much higher probability of the adsorbed n54 molecules to be closer to each other than in bulk water. They also become more dispersed throughout the framework across a range of temperatures and loadings (Figure 3d & e). The vibrational spectra of water is also impacted as the water molecules enter this new environment. The three peaks seen in Figure 4 describe the separate motions of water: libration (left peak), bending (middle peak), and stretching (right peak). The rightmost peak in the stretching range is caused by the free water molecules not hydrogen-bonded to any other waters, which is unlikely in bulk water due to the proximity of the water molecules. The molecules that are hydrogen-bonded inside the cell exhibit stretching at a lower frequency, meaning said hydrogen bonds are stronger due to their attraction to the cobalt node, decreasing the distance between molecules. As the loading size increases, the water begins to exhibit more bulk-like characteristics, such as the lack of the rightmost peak, due to a larger percentage of the water population being hydrogen-bonded to each other as space becomes more scarce within the cell. Further research would include more extensive tests regarding temperature-specific ad/desorption for water collection applications to better understand the capabilities of these nanoparticles, as well as optimization of adsorption for future implementations.

References

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Acknowledgements

I would like to thank Professor Paesani for his time, dedication, and patience. This research experience would not be possible without his guidance and support. I would also like to thank the Paesani lab team, including Daniel Moberg, Kelly Hunter, Diana Mendez, Marc Riera, Alan Hirales, Kimmy Fogliatti for helping with this project.

Lastly, I would like to thank Dr. Komives and Dr. Eduardo Ramirez for their support and organizing the Research Scholars program.

