



Determining the Effects of Varying Pressures and Temperatures on the Stability of Methane Clathrate Compounds Using Molecular Dynamics

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Abstract

Methane clathrates, also known as methane hydrates, are crystalline compounds composed of water which contain a substantial amount of methane molecules. Water molecules (H_2O) form a cage-like structure around the methane molecules (CH_4), causing the latter to be trapped within the clathrate. Naturally forming under low temperatures and high pressures, methane clathrates are found deep in oceanic sedimentary structures. Due to their extreme location, the clathrates typically remain stable over long periods of time, entrapping the methane molecules. However, changes in pressure and temperature can affect the stability of the clathrate within picoseconds, causing the methane, one of the leading contributors to global warming, to be released into the atmosphere. To determine the physical stability of methane clathrates, molecular dynamics simulations were conducted, subjecting the methane clathrate model to different combinations of pressure and temperature. Understanding the stability of methane clathrate compounds can offer not only a method of prevention from further crises, but one of economic gain and innovation in the engineering and chemical fields.



Fig 1. Methane emissions from clathrates on Arctic Sea Floor

Methods

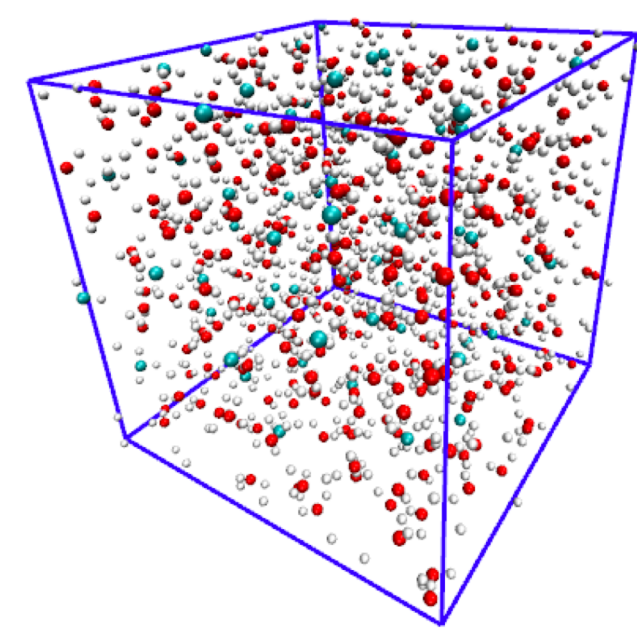


Fig 2a. Methane clathrate model 3-D view with bounding box

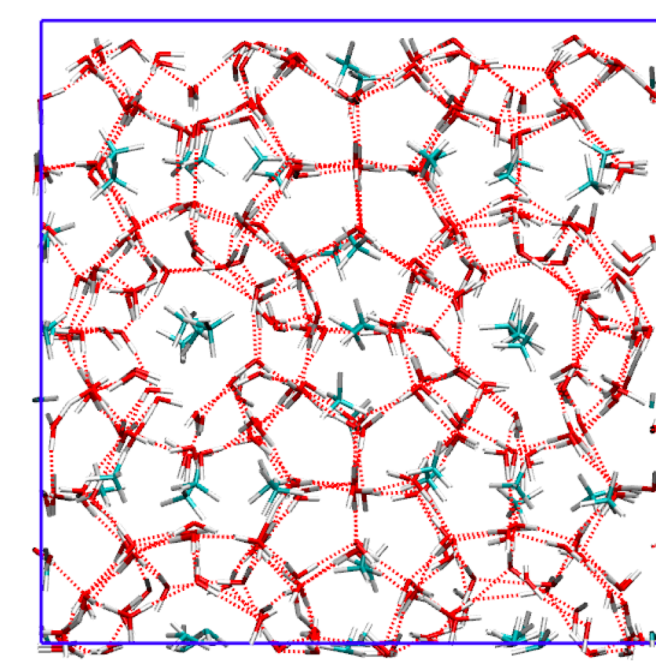


Fig 2b. Methane clathrate model side view with boundaries

We modeled the methane clathrate compounds in DL_POLY V2 computer simulations, and viewed it using Visual Molecular Dynamics (VMD) software. The lattice of water molecules was modeled using the MB-pol potential energy function, which calculates the molecular interactions through many-body polarization. Sixty-four methane molecules were modeled with the ttm4 potential, creating the clathrate. Each compound was subject to periodic boundary conditions, duplicating the clathrate (as seen in Figures 2a & 2b) infinitely in the x , y , and z directions.

There were nine total methane clathrate compounds simulated, each of which was subject to a unique combination of temperature and pressure (as outlined in the Table 1). Two simulations were run on each of these clathrates: the NPT simulation and NVE simulation. Every one of the simulations modeled 40 to 350 picoseconds, but took between 7 and 60 hours to complete. While some simulation were run locally on the lab computers, the rest were run on the Triton Shared Computing Cluster (TSSC) at the San Diego Supercomputer Center (SDSC).

Temperature (K)	Pressure (atm)
283	1, 10, 100, 200, 500, 1000
288	100
293	100
338	100

Table 1. The various combinations of pressures and temperatures

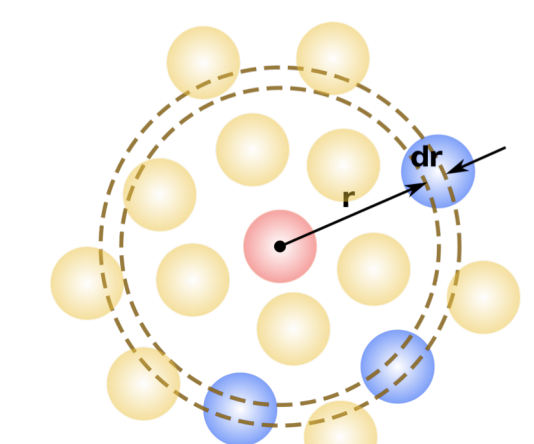


Fig 2c. A visualization of radial distribution functions

In NPT simulations, the number of molecules, pressure, and temperature are kept constant. As a result, volume is allowed to fluctuate as the simulation progresses. Since NPT simulations track the state of the system at various timesteps, it is possible to extract data regarding atomic or molecular distance, such as radial distribution functions (RDFs). Using a self-written python script, the distances between two types of atoms throughout the framework were measured for the RDF, which was used to calculate the most probable distance separating the two atoms.

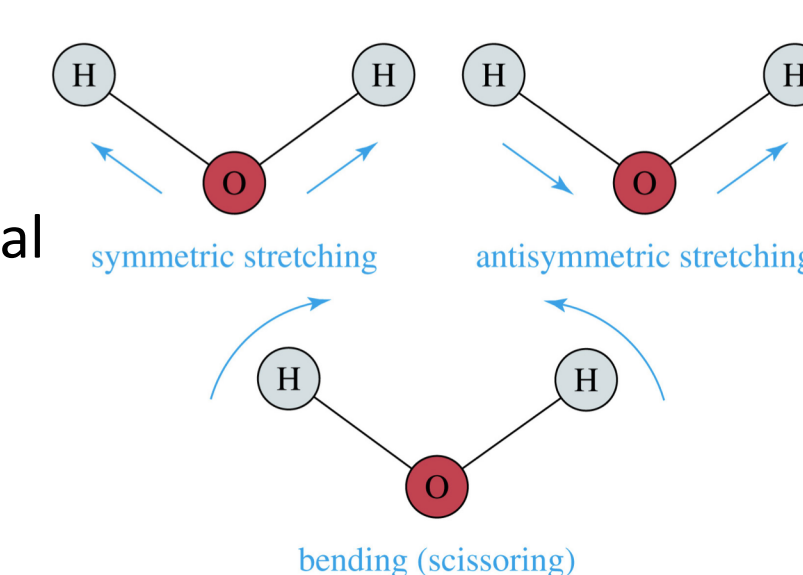


Fig 2d. Various ways that atoms of a molecule can move

The *xmgrace* Linux plotting tool allowed us to plot the radial distribution functions and the vibrational spectra for all of our simulations. Both of these graphs compare the effects of variance in temperature as well as pressure, and offer promising insights into understanding the stability of methane clathrates.

Results for Radial Distribution Functions

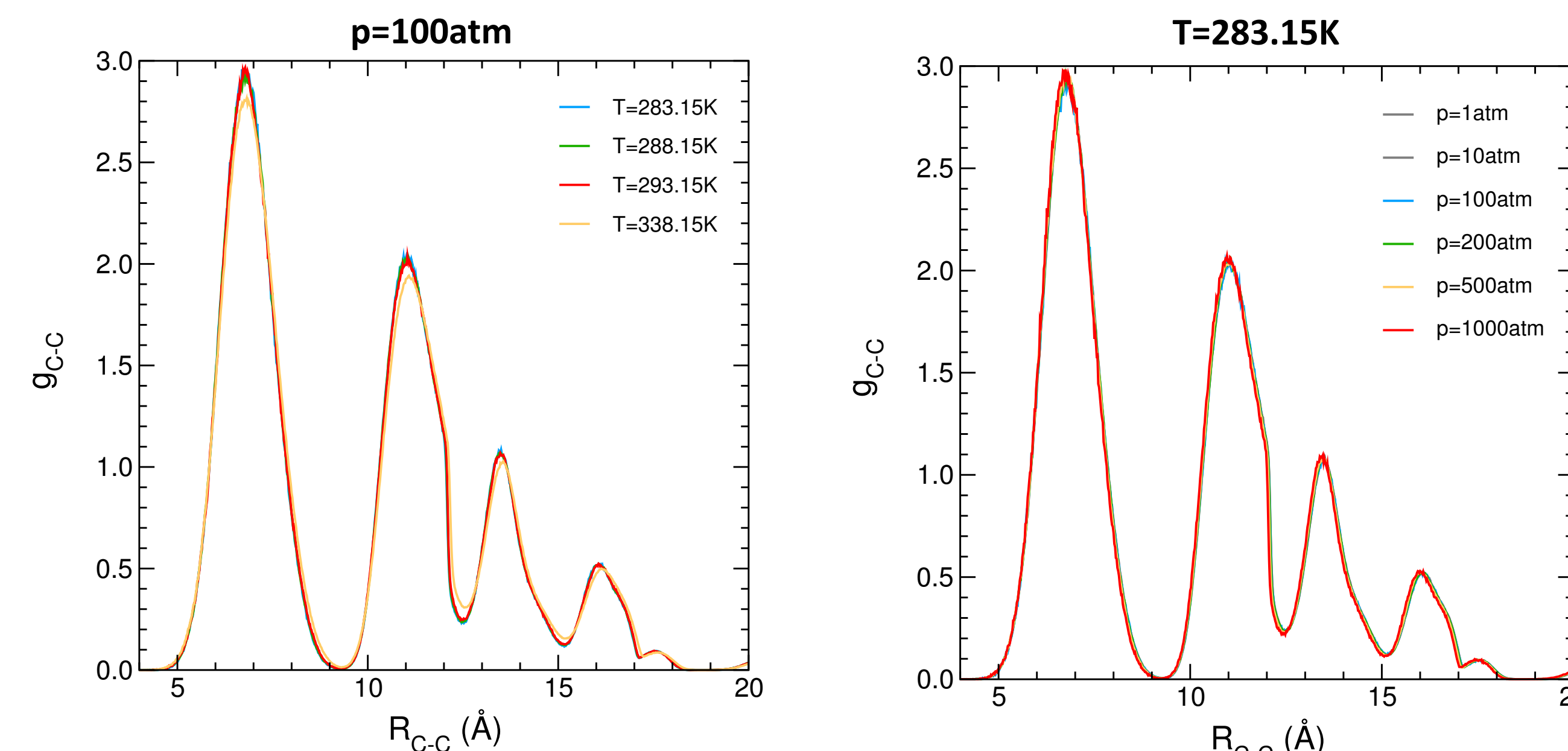


Fig 3a. The radial distribution functions for two carbon atoms (from methane)

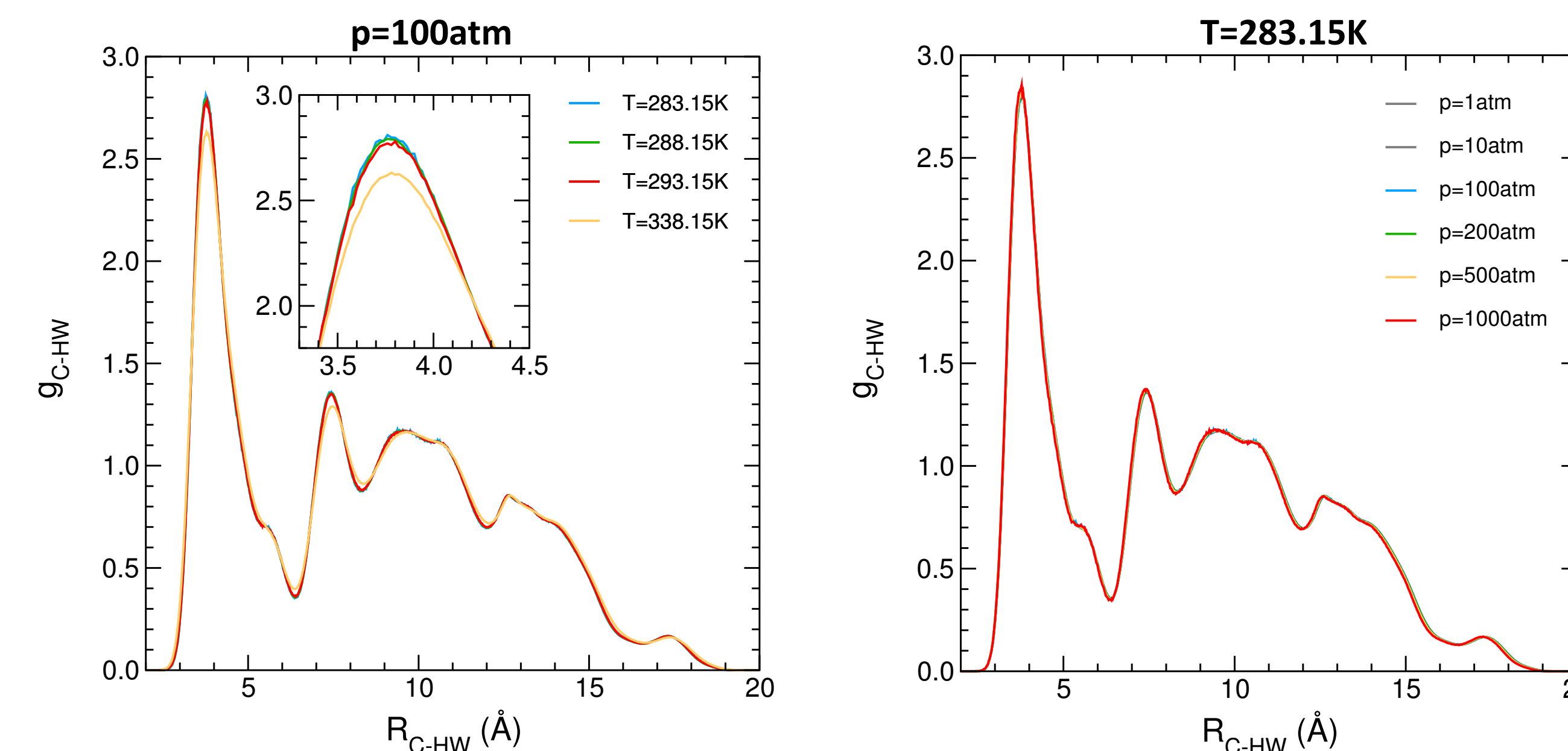


Fig 3b. The radial distribution functions for a carbon atom (from methane) and a hydrogen atom (from water)

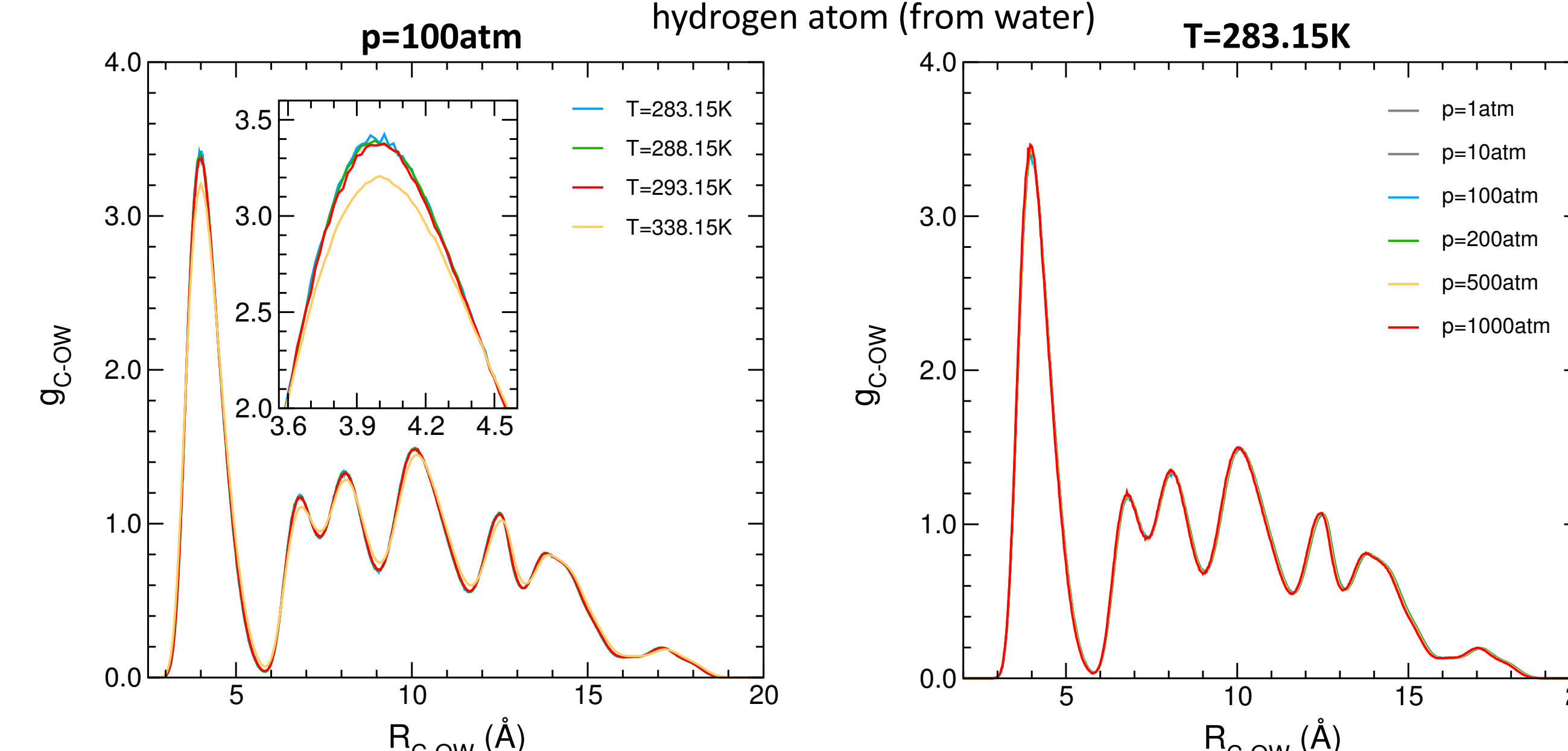


Fig 3c. The radial distribution functions for a carbon atom (from methane) and an oxygen atom (from water)

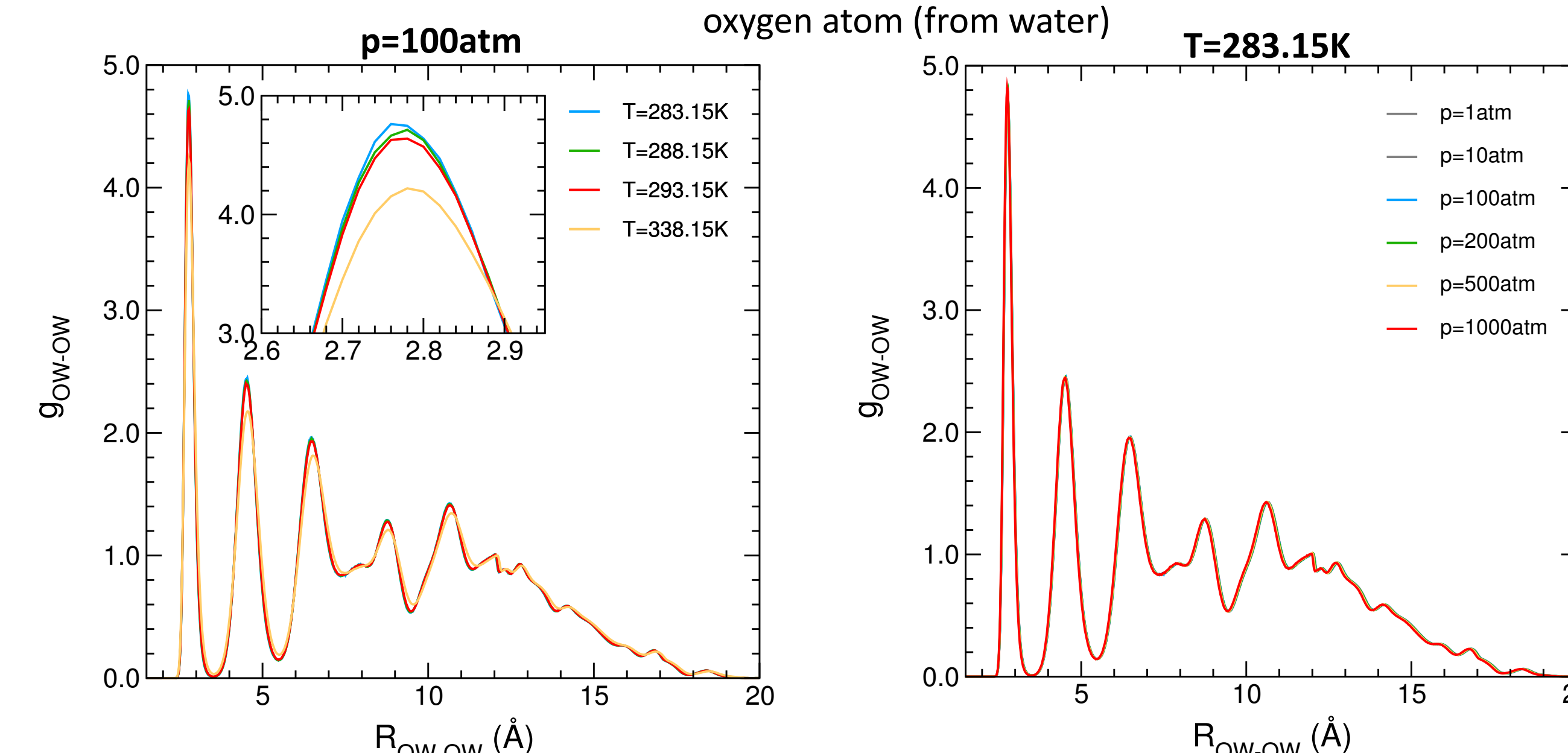


Fig 3d. The radial distribution functions for two oxygen atoms (from water)

Results for Vibrational Spectra

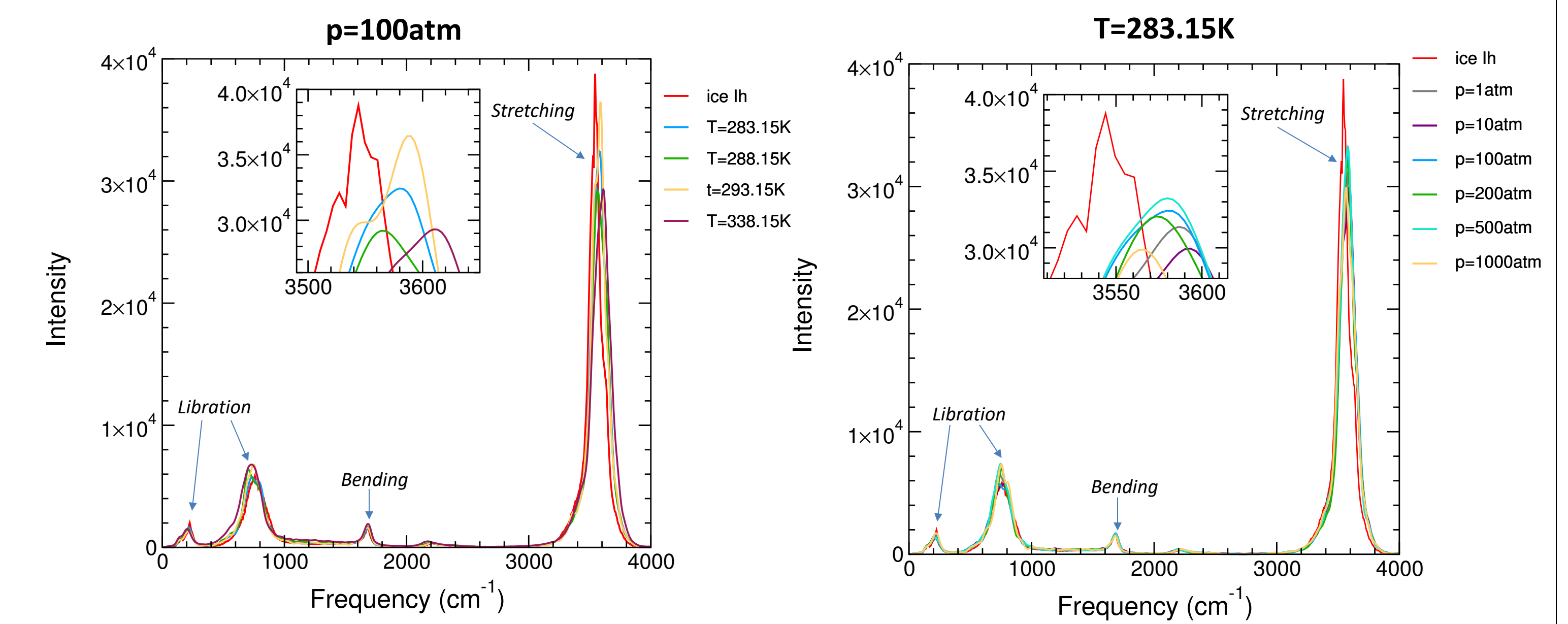


Fig 4. The vibrational spectra for each of the nine simulations, relative to ice Ih (the most common form of ice)

Analysis and Conclusions

For all depicted graphs, the radial distribution functions across different temperatures and pressures were nearly identical. Thus, we concluded that the methane clathrate compound remained relatively stable as the distances between various pairs of atoms did not alter significantly. The only exception was the radial distribution function of the simulation run at 338.15 Kelvin with a pressure of 100 atmospheres, which slightly deviated from the rest. This was exemplified at the first peak (the absolute maximum), showing that the compound was beginning to lose its stability. However, the methane clathrate compounds predominantly maintained their structure throughout the duration of the simulations.

Furthermore, the vibrational spectra illustrate the various motions of the molecules. In Figure 4, the peak at the highest frequency represents stretching, the second peak from the right represents bending, and the left-most peaks represent librational motion. As shown, the librational motion and the bending peaks are almost identical across the different simulations, inferring that changes in temperature and pressure do not affect the respective motions within the molecules. However, the stretching peak varies marginally across ranges of pressures and temperatures. As temperature increases or pressure decreases, the stretching peak moves further to the right, away from that of ice Ih. This is due to the weakening of the hydrogen bonds between the water molecules, which increases the frequency of the water O-H stretch and causes the clathrate to degenerate into a less stable fluid form. Therefore, we can conclude that increasing the temperature or decreasing the pressure of the methane clathrate decreases its overall stability.

In future work, additional simulations could be run at different pressures and temperatures, as well as for longer periods of time. Furthermore, studies could be conducted on the plausibility of real-life applications, which would help to avoid the collapsing of clathrates, therein preventing methane from being released into the atmosphere. We hope that our research can help in understanding the stability of methane clathrates, and guide the future direction of their study.

References

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