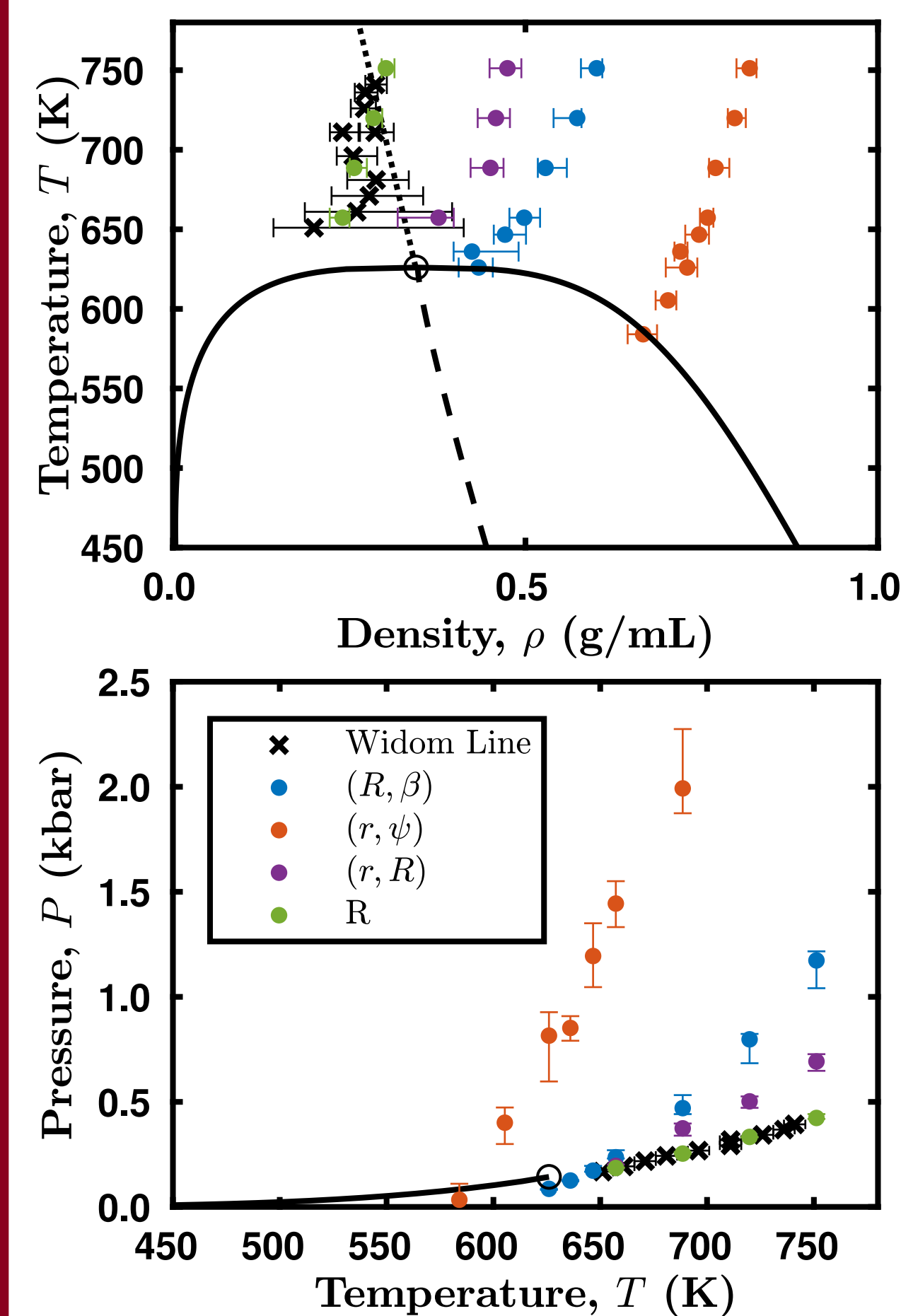


# WHISKEY IS FOR DRINKING; WATER IS FOR FIGHTING OVER

## ABSTRACT

Water is a fascinating liquid due to its many anomalous properties and their unique relevance to life. For example, as most liquids are cooled, their density increases monotonically. In water, on the other hand, the density increases but then at 4°C (at ambient pressure), the density begins to decrease. This density maximum is the reason that ice cubes float to the top of a glass of water and why lakes usually do not freeze solid during the winter, the latter being especially important for the survival of aquatic life. Most of the unique properties of water stem from the hydrogen bonds that form between water molecules. The Skinner Group studies water and the role of these hydrogen bonds in a wide variety of contexts, from supercooled water, to supercritical water, to biological water.

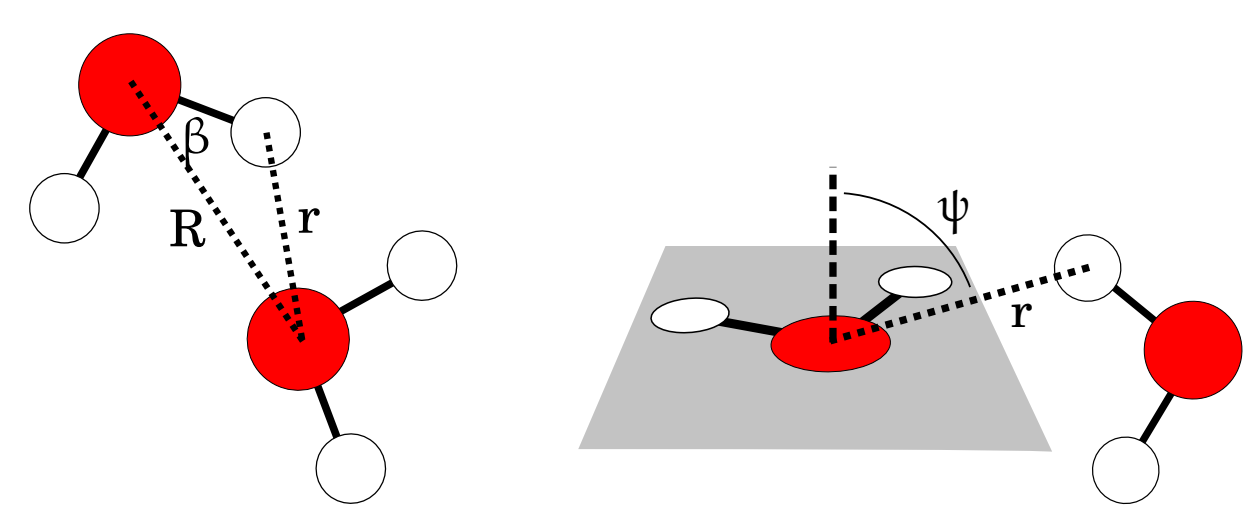
## HYDROGEN BOND PERCOLATION



Water's interesting and unique properties stem from its hydrogen bonding network. In water vapor, however, there is no hydrogen bonding network because the density is too low. Therefore, by tuning water from the liquid, around the critical point, and into the vapor phase, at some point the hydrogen bonding network must break down. One might expect this breakdown to occur near the critical point, where the thermodynamic susceptibilities are

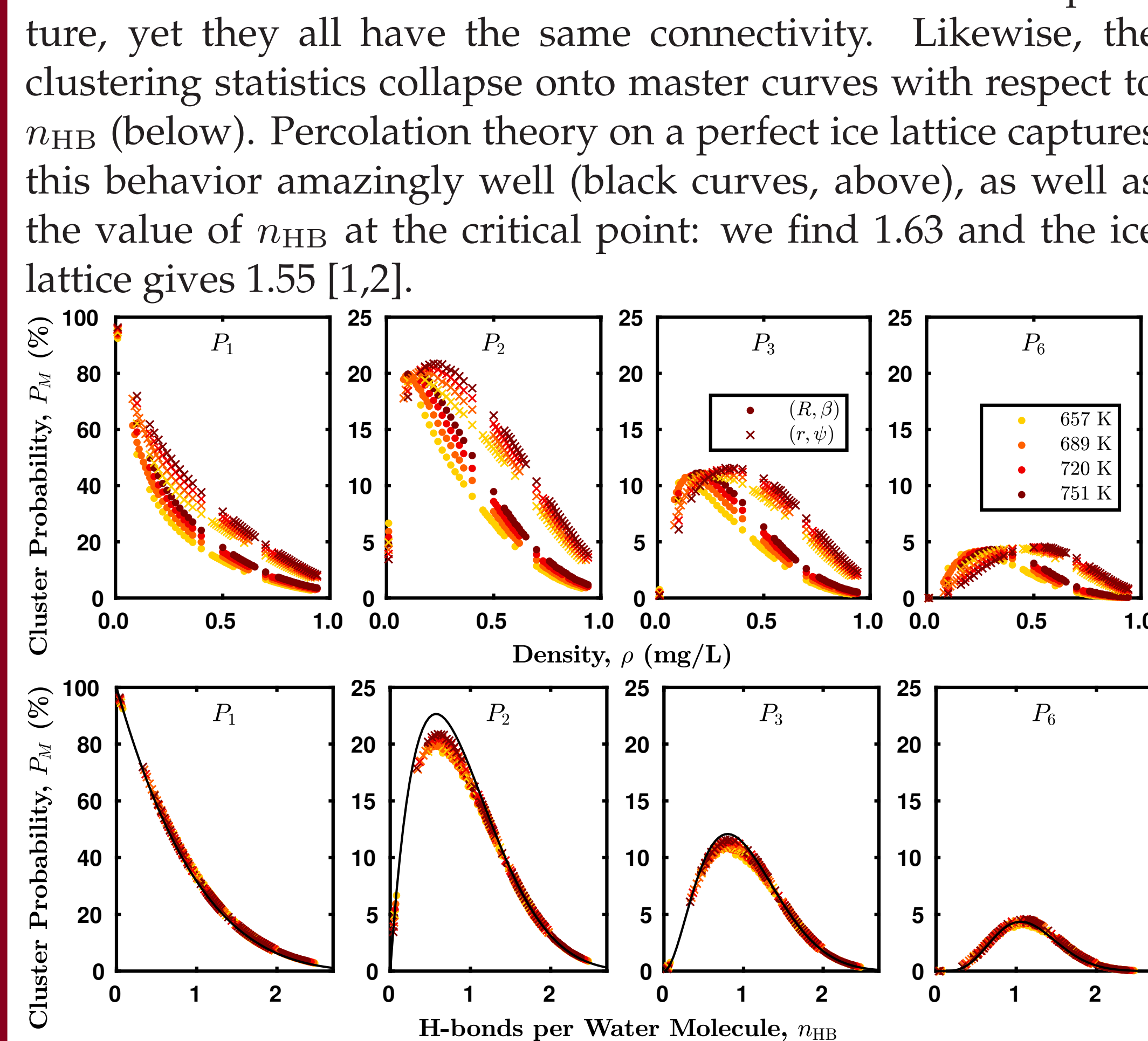
largest and the fluid is changing most quickly from liquid-like to gas-like. We use percolation theory to locate where in the phase diagram the hydrogen bonding network breaks down. While the location of the percolation line in the phase diagram depends on the hydrogen bonding definition used (below), we find that the percolation line is distinct from the Widom line, which traces the maxima in compressibility along isobars (above left) [1].

To understand why the percolation transition is unrelated to the critical point or the Widom line, we study the connectivity of the hydrogen bonding network at the percolation transition (right).

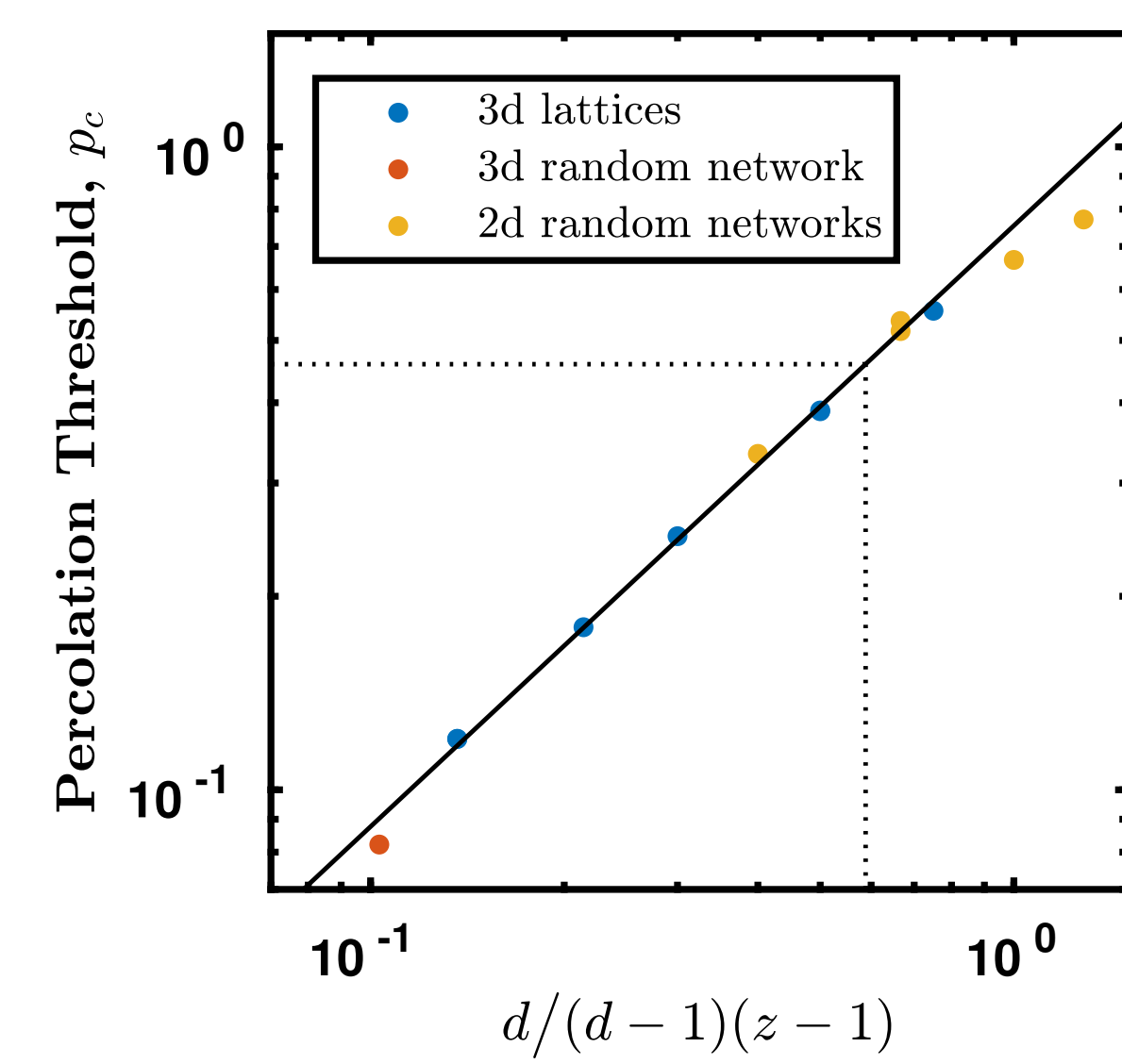


## PERCOLATION IN WATER IS ICE-LIKE

The connectivity of the hydrogen bonding network is quantified by  $n_{HB}$ , the average number of hydrogen bonds per water molecule. We find that the connectivity is exactly the same at the percolation transition, regardless of the temperature and hydrogen bonding definition (left) [1]. In the figure to the left, each point of the same color corresponds to the percolation transition in a system at a different temperature, yet they all have the same connectivity. Likewise, the clustering statistics collapse onto master curves with respect to  $n_{HB}$  (below). Percolation theory on a perfect ice lattice captures this behavior amazingly well (black curves, above), as well as the value of  $n_{HB}$  at the critical point: we find 1.63 and the ice lattice gives 1.55 [1,2].

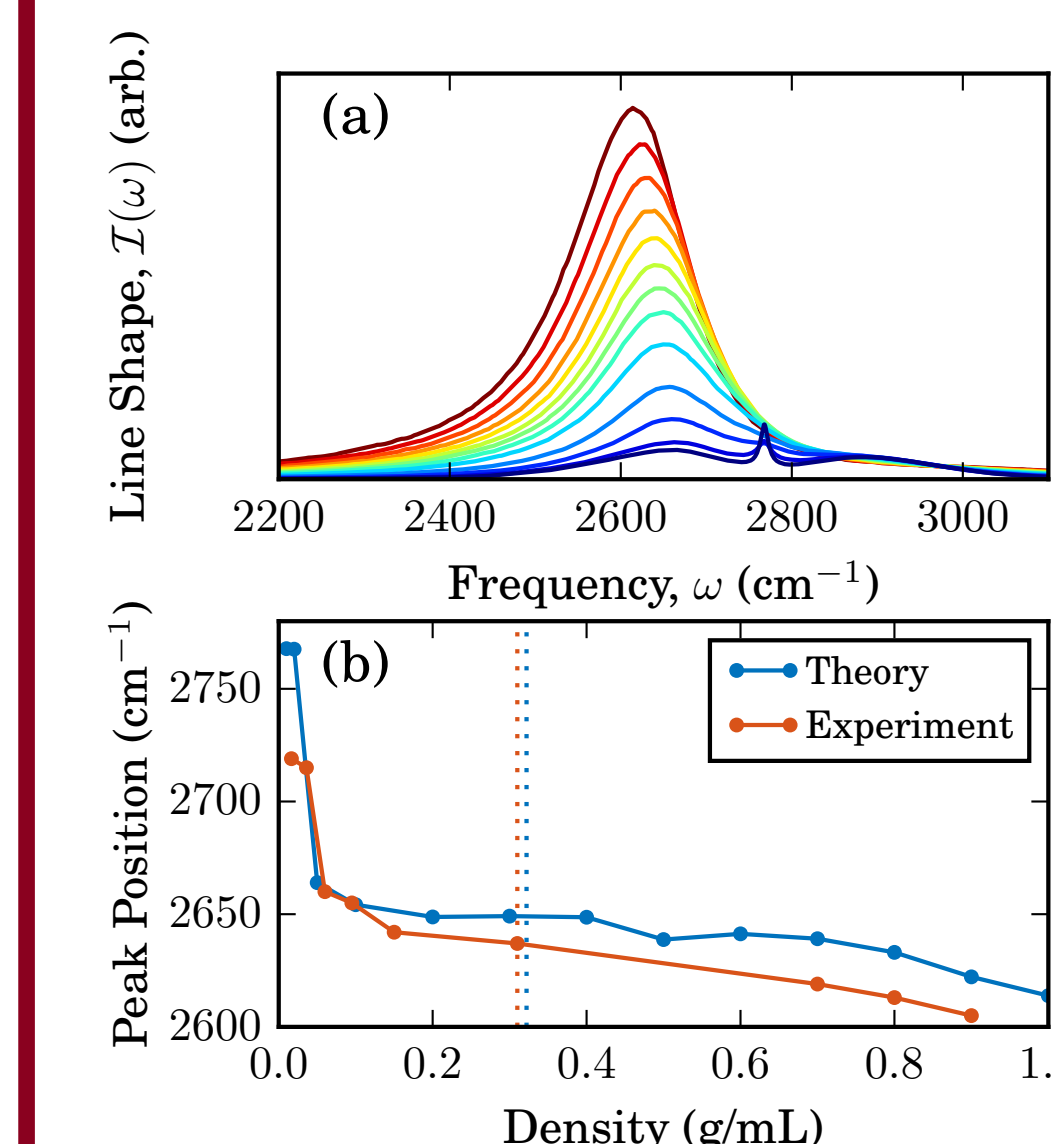
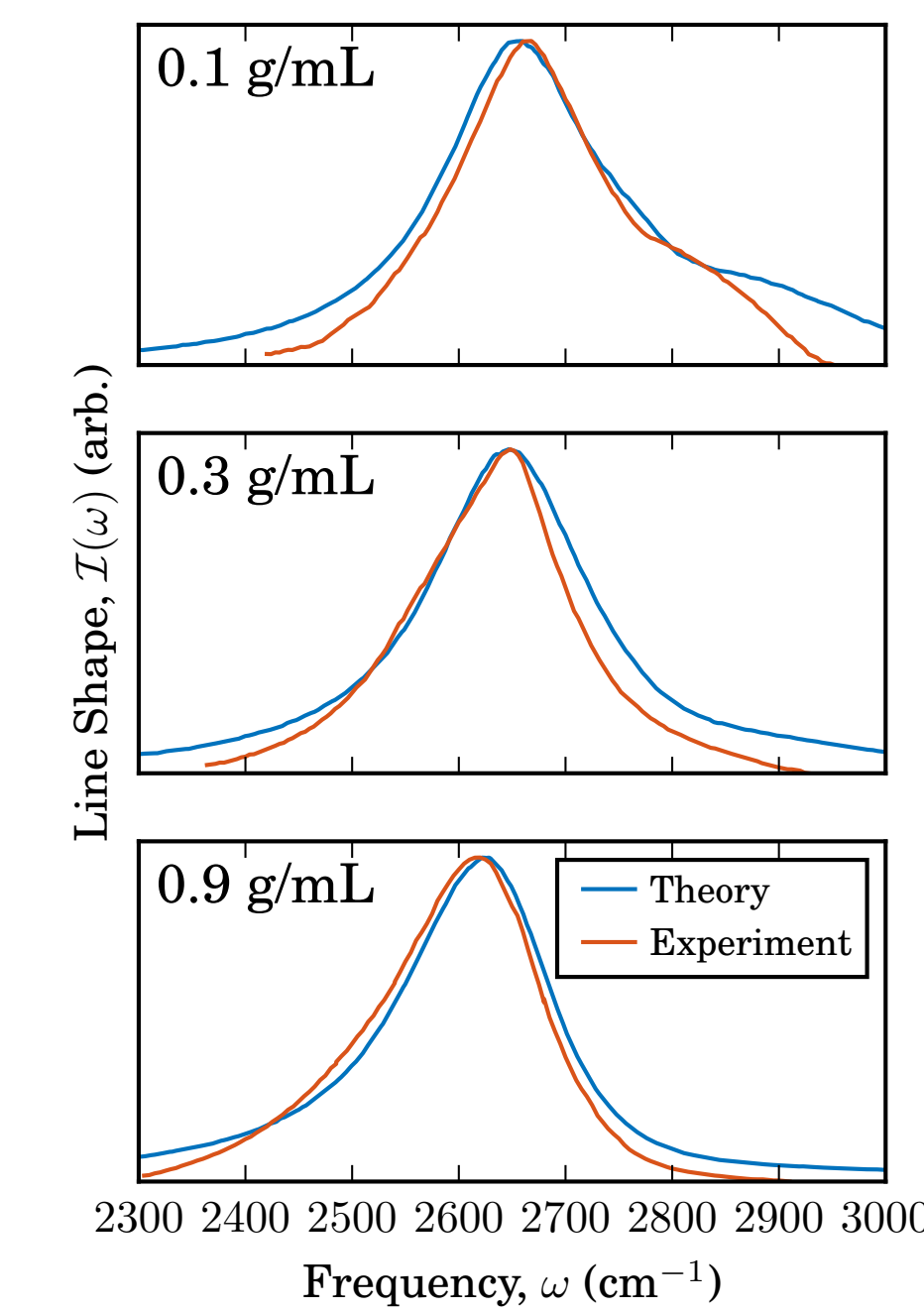


While the ice lattice does a surprisingly good job describing the structure of the hydrogen bonding network, we can elucidate the structure in more detail using the empirical Galam-Mauger relationship (right). Applying this to supercritical water, we can extract information about the underlying lattice, on which hydrogen bonds are broken and formed. We find that this lattice has an average number of nearest neighbors of 3.55. Water at ambient conditions has 3.4–3.7 hydrogen bonds per water molecule, meaning that the underlying lattice is largely unchanged all the way from ambient conditions to the supercritical state [1].



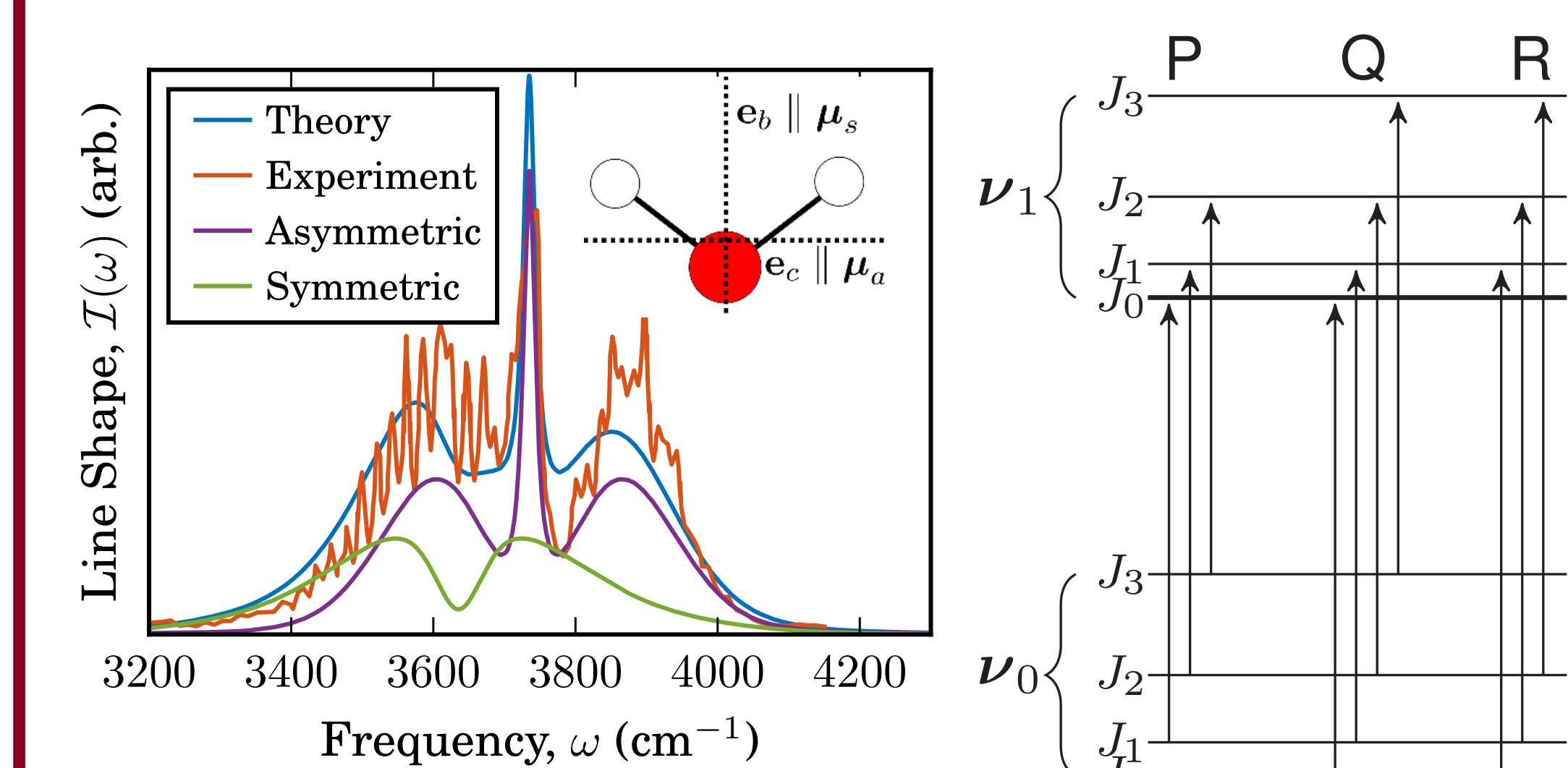
## OD STRETCHING SPECTROSCOPY

The percolation transition discussed to the left may be observable experimentally through IR spectroscopy of HOD, which is a sensitive reporter on the local hydrogen bonding environment that each water molecule experiences. We use a mixed quantum-classical approach to compute the IR spectrum. Even though the mixed quantum-classical approach is parameterized based on calculations at ambient conditions, it still does an excellent job reproducing experimental spectra [3] of supercritical water over a wide range of densities (right) [4].



The IR spectrum redshifts and increases in intensity as the density increases (blue to red), but we do not see any qualitative changes near the critical point or the percolation transition (left). This is because IR spectroscopy is a reporter on the *local* hydrogen bonding network, while the critical phenomena at the critical point and the percolation transition are characterized by *long-range* correlations. We do, however, observe the development of a rovibrational lineshape at very low densities, characterized by the three P, Q, and R branches (dark blue) [4].

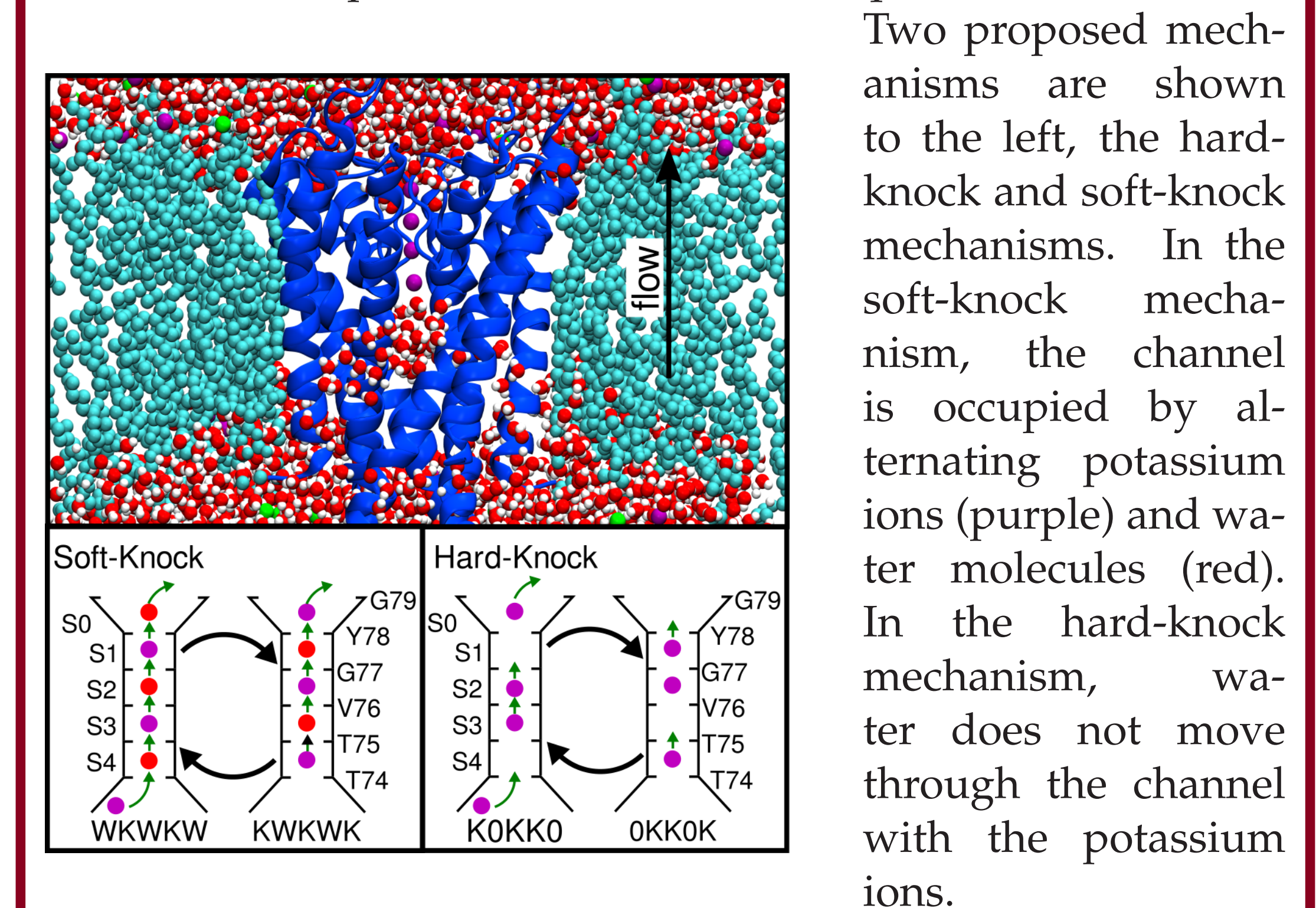
## H<sub>2</sub>O ROVIBRATIONS



The rovibrational lineshape is usually understood from a quantum mechanical perspective (above right). We show that it can be understood from a classical perspective in terms of the dynamical stability of various rotational motions, as described by the tennis racket theorem (above left) [4]. This provides a unique approach to understanding quantum mechanical selection rules that can be experienced by simply tossing a smartphone.

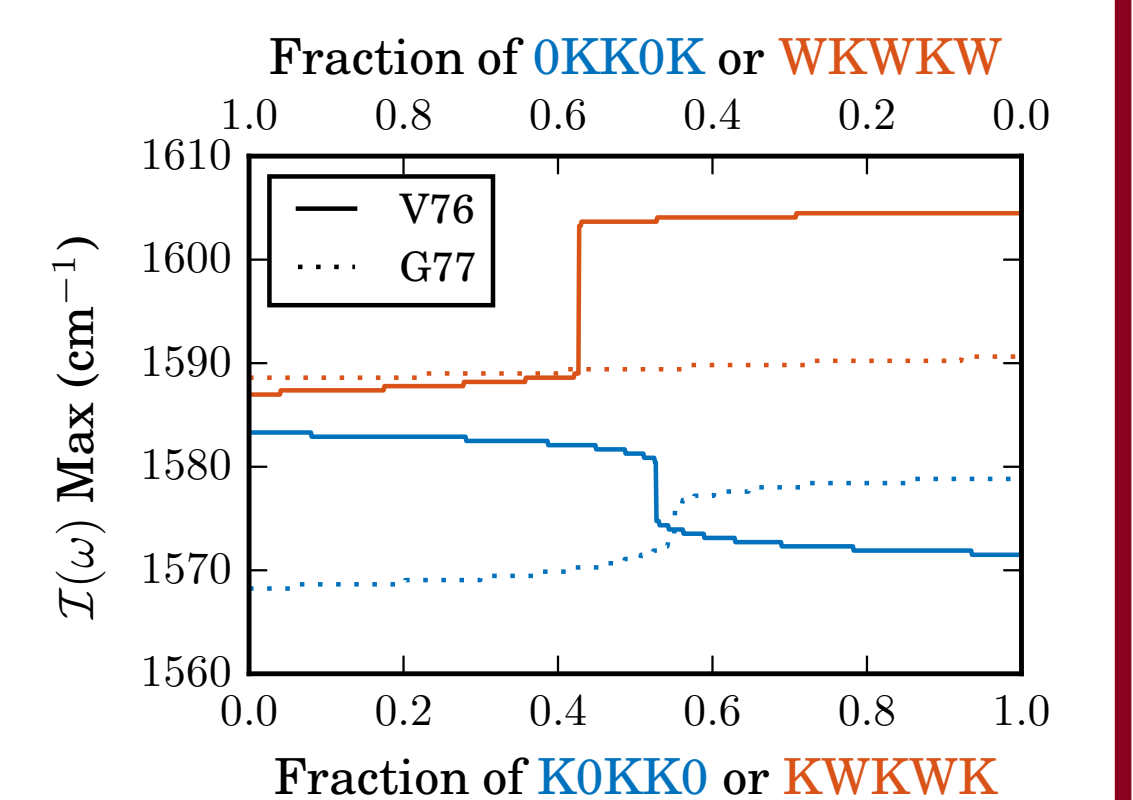
## ION CHANNEL TRANSPORT

Ion channels are central to nerve function and are involved in many cellular processes. These channels only permit certain ions to pass through, yet maintain high passage rates. The mechanism that gives rise to this behavior is hotly debated. Here, we use theoretical predictions of IR spectroscopy to propose an experiment that will discriminate between two proposed mechanisms [5]. This also serves as a proof of principle for a general approach to designing IR experiments that elucidate protein function in an aqueous environment.



Two proposed mechanisms are shown to the left, the hard-knock and soft-knock mechanisms. In the soft-knock mechanism, the channel is occupied by alternating potassium ions (purple) and water molecules (red). In the hard-knock mechanism, water does not move through the channel with the potassium ions.

By isotopically labeling backbone carbonyl groups with <sup>13</sup>C<sup>18</sup>O, specific sites in the ion channel can be isolated and probed. This approach has been used in the past in attempts to discriminate between the hard-knock and soft-knock mechanisms, but the results have not been conclusive, due to the wide variety of states that may contribute to the hard-knock mechanism, and the relative weights of these different states [6]. While previous work has studied at a triply-labeled protein, we find that, with careful choice of labeled sites, and by synthesizing the information from two single-labels rather than one triple-label, the two mechanisms are distinguishable. The two sites we label are V76 and G77, which probe the middle of the channel, where the two mechanisms differ the most. We find that the two mechanisms result in IR peak maxima at different frequencies (right) [5]. Critically, these two labels are able to distinguish the two mechanisms for any choice of weights between the ion occupation states shown above. While each label alone can only distinguish the mechanisms for some ranges of weights, together, they are robust to the choice of weights.



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