



## Local statistical interpretation for water structure

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### ABSTRACT

In this Letter, Raman spectroscopy is employed to study supercooled water down to a temperature of 248 K at ambient pressure. Based on our interpretation of the Raman OH stretching band, decreasing temperature mainly leads to a structural transition from the single donor–single acceptor (DA) to the double donor–double acceptor (DDAA) hydrogen bonding motif. Additionally, a local statistical interpretation of the water structure is proposed, which reveals that a water molecule interacts with molecules in the first shell through various local hydrogen-bonded networks. From this, a local structure order parameter is proposed to explain the short-range order and long-range disorder.

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### 1. Introduction

Water is certainly the most essential of all molecules on our planet. However, in comparison with its simple molecular composition, liquid water exhibits a fascinating array of unusual thermodynamic and dynamic properties both in pure form and as a solvent, and these anomalous behaviors are strongly enhanced in the supercooled regime [1,2]. So far, many theories have been proposed to account for supercooled water, such as the stability limit (SL) conjecture [3], the liquid–liquid critical-point (LLCP) scenario [4], the singularity-free (SF) scenario [5], and the critical-point free scenario [6]. The most prominent of these theories is the LLCP hypothesis [4], which postulates the existence of two liquid phases of water that can interconvert through a first order transition terminating at a critical point located deep in the supercooled liquid region of the water phase diagram. Based on a study by Mishima and Stanley [7], the LLCP of water could be located around 220 K and 100 MPa. A more recent estimation based on a scaled equation of state, yields a similar critical temperature, 232 K, and a considerably lower critical pressure, 27 MPa [8]. Additionally, recent Letter by Mishima indicates that, if there is a LLCP, it would be located at 50 MPa and 223 K [9].

The structure of liquid water has been intensively investigated, and most models of water can be partitioned into two broad categories: (a) mixture models and (b) distorted hydrogen bond or continuum models [1]. For the mixture model, it postulates the simultaneous existence of two distinct types of structures. The view from the latter model is that water comprises a random, three-dimensional network of hydrogen bonds encompassing a broad distribution of O–H···O hydrogen bond angles and distances, but the water networks cannot be ‘broken’ or separated into distinct molecular species as in the mixture models. Liquid water is

generally classified as a tetrahedral liquid according to the first coordination number, which is defined as,

$$N_c = 4\pi\rho \int_{r_{\min}}^{r_{\max}} r^2 g_{OO}(r) dr$$

where  $\rho$  is the number density of water,  $r_{\min}$  and  $r_{\max}$  are the lower and upper limits of integration in oxygen–oxygen radial distribution function,  $g_{OO}(r)$ . For ambient water, this gives values for  $N_c$  of 4.3 [10] and 4.7 [11], respectively. However, from X-ray absorption and Raman spectroscopy (XAS and XRS) experiments, Wernet et al. [12] claimed that the distribution of water molecules around a molecule was asymmetric, resulting in only two hydrogen bonds per water molecule. This view was challenged by Smith et al. [13], which proposed that the XAS spectra were consistent with the tetrahedral model based on a Boltzmann analysis of the temperature-dependent variation in spectral features. Recently, Huang et al. [14] conducted small angle X-ray scattering (SAXS) to study the water density inhomogeneity on the nanometer length-scale, and proposed that the density difference was due to fluctuations between tetrahedral-like and hydrogen-bond distorted structures, which was also consistent with the liquid–liquid phase transition between low and high density water in supercooled water [14]. This interpretation was contested by Soper et al. [15] and by Clark et al. [16]. To date, there remains strong debate on water structure.

The Raman OH stretching band is sensitive to hydrogen bonding, and has been widely applied to investigate the water structure. For liquid water, the complex nature (inhomogeneously broadened) of the Raman OH stretching band has long been recognized. Many studies have attempted to explain the band of water [17–22]. Recently, from discussions of water structure and molecular clusters [22], we suggested that the Raman OH stretching band can be fitted into five sub-bands, where each peak can be assigned to OH groups engaged in different local hydrogen bonding motifs.

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In this study, following our interpretation of the Raman OH water stretching bands, Raman spectroscopy is applied to investigate the water structure down to 248 K at ambient pressure. Additionally, a local statistical interpretation for the water structure is proposed, which means that a water molecule interacts with molecules in the first shell through various local hydrogen-bonded networks.

## 2. Experimental

In this Letter, deionized water was produced by a MilliQ water purification system, and its conductivity was  $5.5 \times 10^{-6}$  s/m. Raman spectra of supercooled water were recorded down to 248 K at 0.1 MPa. The temperature uncertainty was 0.1 K.

The unpolarized Raman spectra were recorded using a confocal micro-Raman system in a backscattering geometry (Renishaw 1000). An Ar<sup>+</sup> ion laser with an excitation wavelength at 514.5 nm was operated at 25 mW. The spectrometer with an entrance slit of 50  $\mu\text{m}$  was used to collect the signals. The resolution was about  $1 \text{ cm}^{-1}$ . Each Raman spectrum was recorded for 10 s with a 50 $\times$  objective.

The Raman spectra were analyzed by the Jandel Scientific Peakfit v4.04 program. The Raman spectra were first smoothed until the noise diminished, and the baselines were corrected. Later, GAUSSIAN functions were used to fit the Raman OH stretching bands.

## 3. Discussion

For a single H<sub>2</sub>O molecule, the vibrational normal modes are  $2A_1$  (including a symmetric stretching vibration  $\nu_1$  at  $3657.05 \text{ cm}^{-1}$  and a bending vibration  $\nu_2$  near  $1595 \text{ cm}^{-1}$ ) +  $B_1$  (anti-symmetric stretching vibration  $\nu_3$  at  $3755.97 \text{ cm}^{-1}$ ) [23]; they are all Raman active. When a hydrogen bond forms between two water molecules, electron redistribution occurs. This results in both the cooperativity (accepting one hydrogen bond encourages the donation of another, such as single donor–single acceptor (DA)) and anti-cooperativity (accepting one hydrogen bond discourages acceptance of another, such as double acceptor (AA)) in hydrogen bonded networks of water. The concept of cooperativity between hydrogen bonds was postulated by Frank and Wen [24]. In pure water clusters, a cooperativity rule has been developed over the years [25–27] where the maximum hydrogen bond strength is obtained when there is a balance between donor and acceptor bonds. In this study, for a given water molecule, the hydrogen bonding is divided into the local hydrogen bonding structure (hydrogen bonding within the first shell) and hydrogen bonding beyond the first shell.

For water clusters, hydrogen bond formation increases the O–H bond lengths, while causing a 20-fold greater reduction in the H $\cdots$ O and O $\cdots$ O distances [28], in addition to causing a red shift of the hydrogen-bonded OH stretch frequency, the magnitude of which increases with cluster size [27]. Previous theoretical and experimental studies on water clusters provide a foundation to investigate how the OH vibrational frequency depends on the hydrogen bonding environment (Figure 1). Theoretical calculations have demonstrated that trimer, tetramer, and pentamer clusters should assume quasi-planar structures, where each H<sub>2</sub>O can interact with neighboring molecules by single donor–single acceptor (DA) hydrogen bonds [26,27,34]. From Figure 1, as water cluster size ( $n < 6$ ) increases, the peak of the DA–OH stretching vibration shifts to lower wavenumbers. However, when three-dimensional hydrogen bonding occurs ( $n > 6$ ), different local hydrogen bonding motifs correspond to various OH vibrational frequencies.

Additionally, increasing the cluster size does not affect the OH vibration frequency. This is also in accordance with the convergence of the DA–OH frequency for clusters larger than (H<sub>2</sub>O)<sub>6</sub>. From these data, it can be implied that once three-dimensional hydrogen bonding emerges, the OH stretching vibrations are mainly dependent on local hydrogen-bonded networks, and the effects of hydrogen bonding beyond the first shell on OH vibrations can be neglected.

Much work has been devoted to the study of the nature and strength of hydrogen bonding. According to Isaacs et al. [40], the hydrogen bond in water is mostly (about 90 %) electrostatic (dipole-dipole interaction) and partially (about 10%) covalent. Additionally, in comparison with a typical OH covalent bond strength ( $\sim 492 \text{ kJ mol}^{-1}$ ), hydrogen bonding energies are weak (3–8  $\text{kcal mol}^{-1}$  [41]). The dipole–dipole interactions are highly dependent on the intermolecular distances and the orientational correlation between them. These may lead to the weak hydrogen bonding effects beyond the first shell on OH vibrations. Of course, further study is necessary, especially with regard to the orientational correlation of dipoles.

Based on this analysis, it is reasonable to assign different OH vibrational frequencies to various local hydrogen bonding motifs. For a water molecule, the local hydrogen-bonded network can be differentiated by whether the molecule forms hydrogen bonds as a proton donor (D), proton acceptor (A), or a combination of both with neighboring molecules. Under ambient conditions, the main local hydrogen bonding motifs for a water molecule can be classified as DDAA (double donor–double acceptor), DDA (double donor–single acceptor), DAA (single donor–double acceptor), and DA (single donor–single acceptor) [22] (Figure 2). At 293 K and 0.1 MPa, the Raman OH stretching band can be deconvoluted into five sub-bands, located at 3041, 3220, 3430, 3572, and  $3636 \text{ cm}^{-1}$ , and can be assigned to the  $\nu_{\text{DAA-OH}}$ ,  $\nu_{\text{DDAA-OH}}$ ,  $\nu_{\text{DA-OH}}$ ,  $\nu_{\text{DDA-OH}}$ , and free OH symmetric stretching vibrations, respectively (Figure 3).

The OH vibrational frequency is mainly dependent on the water molecule's local hydrogen-bonded network. This can be demonstrated by Raman spectroscopic study on the effects of dissolved NaCl and increasing pressure on water structure [42]. Based on our interpretation of the Raman OH stretching bands, dissolved NaCl only significantly affects water molecules in the first hydration shell, and increasing pressure up to 400 MPa at 293 K has no obvious effects on the first shell of a water molecule [42]. These results are also in agreement with other studies [43–45].

The isosbestic point refers to the wavelength at which a series of spectra cross – where the spectral intensity is a constant. The existence of an isosbestic point has commonly been considered a fingerprint of two-state behavior. Recently, after considering the electric field experienced by the proton projected onto the OH covalent bond, Smith et al. [46] suggested that the isosbestic points could be explained as a consequence of a continuous distribution of local environments that correspond to increasing distortions around a single-component tetrahedral motif. In fact, along with the isosbestic point, both increasing temperature and adding NaCl lower the second peak at 4.5 Å in the oxygen–oxygen pair correlation functions, which indicates the breakage of tetrahedral hydrogen bonding. Therefore, the isosbestic point actually signifies a structural transition between tetrahedral and non-tetrahedral hydrogen bonding motifs.

For the Raman spectra of water from 298 to 248 K at 0.1 MPa, based on normalized intensity, an isosbestic point can be found around  $3330 \text{ cm}^{-1}$  (Figure 4). Following our interpretation of the Raman OH stretching bands, the isosbestic point should indicate the structural equilibrium between various hydrogen bonds, which can be expressed as follows,



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