Observing the complexity of water structures from near infrared spectra and simulation

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Summary: The complexity of water structures was discussed through the high order derivative NIR spectra and molecular dynamics (MD) simulation. The high order derivative was calculated by continuous wavelet transform (CWT), from which the spectral features of different water species can be observed, including the free and differently hydrogen bonded water. MD simulation was further employed to investigate the possible structures in pure water and different solutions. Nine types of water species with different number of hydrogen bonds were observed and the percentage of each type at different temperature was statistically calculated.

Introduction: Aquaphotomics is a new discipline that provides a framework for understanding the bio-systems through the spectra of water under perturbations such as temperature and additives [1]. NIR aquaphotomics achieves both quantitative and structural analysis by uncovering the hidden information in NIR spectra of water [2]. Water was used as a mirror to explore the spectral changes related to saccharide in the aqueous systems [3]. NIR water spectral patterns were used to discriminate different DNA structures [4]. Taking water as a probe, quantitative analysis of the components in mixtures and the glucose in human serum samples was succeeded [5-7]. In these studies, extracting the water absorbance pattern that can discriminate the samples is clearly an important issue. However, due to the low resolution of NIR spectrum and the complexity of water structures, it is still difficult to analyze the NIR spectrum of water or aqueous solutions. Therefore, various chemometric techniques have been employed for analyzing NIR spectra to reveal the structures of water in different solutions. Six components were observed in the second derivative spectrum of water [8]. Two-state structural model (water species with weaker and stronger hydrogen bonds) and three-component model (strongly and weakly hydrogen bonded species and an intermediate state) were employed for the explanation of water spectrum [9,10].

For observing the complexity of water structure, high order derivatives, which is calculated by CWT, were studied using the NIR spectra of water and its mixture with ethanol. The spectral features of OH and CH with various intermolecular interactions were observed. MD simulation was further used to investigate the structures in pure water and different solutions. Water structures with different hydrogen bonding were observed and the effect of temperature was discussed.

Methods: Derivative calculation has been a technique widely used in signal processing. It has been employed for reducing the variant background, correcting the drifting baseline, enhancing the resolution, and resolving the overlapping peaks. In this study, CWT was used for derivative calculation. Compared with the conventional methods, there are advantages of this technique, e.g., the simplicity in calculation, the flexibility of the parameters, and the smoothing effect [11–13]. CWT with Haar, Sym2, Sym4, Sym6 filter and scale parameter 20 were used for calculating the first, second, fourth and sixth derivative, respectively.

A large water box was built and simulated with periodic boundary conditions using SWM4 water model at different temperatures. All the MD simulations were conducted employing the popular MD engine NAMD. The distribution of different water species and its variation with temperature were investigated. The hydrogen bonds formed by each water molecule and its surrounding molecules are analyzed by VMD software based on the MD trajectories. Nine water species are identified according to the number of acceptors (A) and donors (D) of each molecule in its formed hydrogen bonds, which are denoted as A_mD_n (m = 0,1,2; n = 0,1,2).

Results and Discussion: To investigate the complexity of the NIR spectra of water, the first, second, fourth and sixth derivative were calculated using CWT. It was found that the resolution of the spectra can be significantly improved with the increase of the derivative order. The drifting baseline or background can be eliminated even in the second derivative and the peaks are greatly sharpened, and more peaks can be seen in the fourth and sixth derivative, although the improvement from the order four to six is not so significant any more. Figure 1 shows the measured and the fourth derivative spectra of water, ethanol and a mixture (v/v = 50/50). In the spectrum of water, peaks at 7325, 7109, 6974 and 6835 cm^{-1} can be clearly seen, which can be attributed to the $v_1 + v_2 + v$ mode of water (S_r), the $v_1 + v_3$ mode of free water (S_0), and water with one (S_1) and two (S_2) hydrogen bonds, respectively. In the derivative spectra of ethanol, six or seven peaks can be found. Obviously, the complexity of the spectra originates from the interactions in the liquids. For examples, the peaks at 7371, 7271, 7197, 7109, 6980 and 6835 cm^{-1} for ethanol, the first three are related to the $v_1 + v_3$ vibrational mode of CH, and the last

three correspond to the free OH, OH in linear aggregates and OH in cyclic aggregates of ethanol, respectively. In the fourth derivative spectra of the mixture, a new peak appears at 5176 cm^{-1}. The peak is apparently related to the interaction between ethanol and water. Therefore, high order derivative may provide a way to discover the spectral features in complex NIR spectra and investigate the interactions in aqueous solutions.
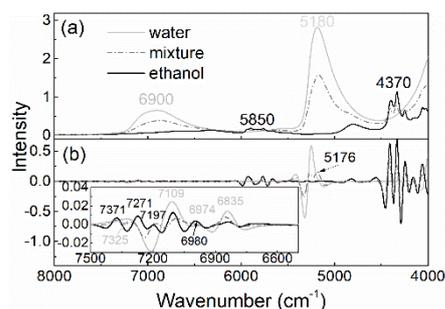

Figure 1. Measured NIR spectra (a) and their fourth derivative (b) of water, ethanol and their mixture
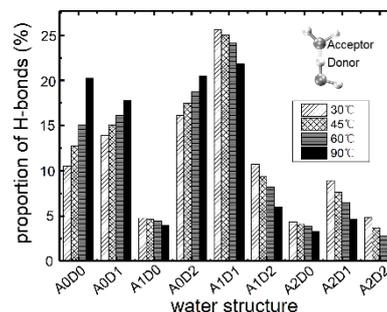
Figure 2. Water species and their percentage obtained from the simulation at different temperature

  Figure 2 shows the distribution of the water species with different hydrogen bonding obtained from the result of the simulation of pure water. It can be seen that nine species with different hydrogen bonding were obtained, demonstrating a much complicated composition even in pure water. Furthermore, A1D1 is the most dominant species and then A1D0, A0D1, and A0D0 (free water). Only 11% of the water molecules are in free form in 30 $^{\circ}$C. On the other hand, when temperature rises, the percentage of the species with less hydrogen bonds ($m+n = 0$ or 1) increases but that with more hydrogen bonds ($m+n >= 2$) decreases. This is obviously caused by the temperature effect. More importantly, the changes of the percentage may be a criterion to evaluate the stability of the hydrogen bond in the species.

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