

Understanding the water structures by near-infrared and Raman spectroscopy

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Funding information

Haihe Laboratory of Sustainable Chemical Transformations; Fundamental Research Funds for the Central Universities, Nankai University, Grant/Award Number: 63211019; Frontiers Science Center for New Organic Matter, Nankai University, Grant/Award Number: 63181206; Natural Science Foundation of Tianjin, Grant/Award Number: 20JCYBJC01480; National Natural Science Foundation of China, Grant/Award Number: 22174075

Abstract

The structure of water in different systems has been extensively studied due to the complexity and flexibility of the hydrogen-bonded network and the important role in chemical and biological processes. Near-infrared (NIR) and Raman spectroscopy has been used to investigate the structures of water and the interactions in aqueous systems. In this review, works for structural analysis of water by NIR and Raman spectroscopy were summarized. From resolution-enhanced spectra, the spectral components of water were obtained. The spectral features correspond to the structures of water with different hydrogen bonds and the interactions of water and solutes. Following the concept of aquaphotomics, the changes of the spectral pattern of water with different perturbations, such as the variation of composition and temperature, were studied. The spectral pattern was found to be related to the analytes in the analyzing system and can be used to reflect the properties of the solutes and even disease diagnosis. Furthermore, water structures in the conformational change of macromolecules such as proteins and polymers were analyzed. Water was proved to be an indicator of the changes, and the water structures with two or three hydrogen bonds (S_2 or S_3) were found to have an important role in the phase transition of the proteins and polymers.

KEY WORDS

aquaphotomics, near-infrared spectroscopy, Raman spectroscopy, water structure

1 | INTRODUCTION

Water is important for human life and plays a significant role in biological and chemical systems. Due to the flexibility of the hydrogen bonding between water molecules and the complexity of the hydrogen-bonded network, the structure of water is yet to be well understood.^[1,2] Different models have been proposed to describe the structure of water in pure state and solutions.^[3,4] Particularly, the

exploration of the structural and binding properties of small water clusters provides deep insights into the hydrogen bonding of bulk water and hydration water.^[5–7] Therefore, as an interesting and important subject, the structure of water has been extensively studied for decades.

Molecular spectroscopy has been employed as a powerful tool for the study of water structures. Spectral changes of water under different perturbations can reveal

the structural changes and interactions in aqueous systems. Raman spectroscopy was employed to study the solute-induced variation of water structures. The promotion and destruction of ordered water by glucose^[8] and NaCl^[9] were observed, respectively, by the changes in Raman spectra of OH stretching vibration. Near-infrared (NIR) spectroscopy has been recognized as a sensitive technique to investigate water structure.^[3,10] Due to the strong absorbance, the spectral information of water structures with different hydrogen bonds can be distinguished by the NIR spectrum. A two-state structural model of water structures with weak (WHB) and strong hydrogen bonds (SHB) was proposed by investigating the temperature-dependent NIR spectra of water.^[11] Aquaphotomics proposed by Tsenkova provides a framework for understanding the structural change of water caused by various perturbations in aqueous and biological systems.^[12,13] Terahertz (THz) spectroscopy was also used to study the influence of carbohydrates on the solvation of water.^[14,15] The change in THz absorbance was found to be correlated with the number of hydrogen bonds between the solute and water. According to the difference between the absorption coefficients, bulk water and the hydration water were distinguished and the size of the hydration shell was determined.^[16,17] Furthermore, quantum chemical calculations were adopted in the studies of aqueous systems.^[18] The hydrogen bonding between water molecules and C=O/N-H in nucleobase was found in the calculated infrared (IR) spectrum. The influence of hydrogen-bonded interactions on the vibrational frequencies of hydroxyl stretching, carbonyl stretching, and amide bending modes was shown.^[19,20]

In this review, water structures obtained from NIR and Raman spectra were summarized, including the structures in liquid mixtures of water and other compounds with different mixing ratios and aqueous solutions of different solutes. At first, the complexity of water structures was shown by the spectral features. Then, the change of spectral pattern with temperature and concentration, which is able to reveal the composition of solutions and the properties of the analytes in aqueous samples, was summarized. At last, the water structure in the phase transition of proteins and polymers, which can be used to indicate the aggregation and explain the role of water in these processes, was reviewed.

2 | COMPLEXITY OF WATER STRUCTURE

Water is the main component of aqueous solutions and most biosystems. The interaction of water and solutes is

of great importance for understanding the properties of the analyzing samples. However, the hydrogen bonding between water and different compounds is complex and flexible, and the spectral bands are generally broad and overlapping; therefore, it is very difficult to obtain the tiny spectral change induced by the interactions. Great efforts have been made for extracting the spectral features reflecting the water structures and the interactions of water and different compounds.

To understand the structures of water in pure water and aqueous solutions, spectral components relating to different water structures were obtained by Gaussian fitting of NIR spectrum.^[21] Six spectral components were used to fit the spectra, corresponding to the water structures with no and one to four hydrogen bonds, as well as the rotational vibration (S_r) of water molecule. To describe the water structures with different hydrogen bond more exactly, $AmDn$ was used to represent the water molecule with m hydrogen bonds on proton acceptor (A) and n hydrogen bonds on proton donor (D), where $m, n = 0, 1, \text{ or } 2$.^[22] Nine water structures are defined, that is, A0D0, A0D1, A1D0, A0D2, A1D1, A2D0, A1D2, A2D1, and A2D2. Assuming that the NIR spectrum of water is composed of the peaks of the nine structures and a peak of S_r , the position and intensity of 10 peaks were obtained from the spectrum of water by Gaussian fitting with a knowledge-based genetic algorithm. Through the variation of these peaks, the temperature effect on the nine water structures was investigated, revealing that with the increase of the temperature, hydrogen bonds are weakened and the large water clusters dissociate into small ones. Furthermore, through the variation of the peaks with glucose concentration, the enhancement of the ordered (tetrahedral) water structures induced by glucose was observed. The results provide an evidence for the protective effect of glucose on the biomolecules in aqueous solutions.

The interaction in liquid water was analyzed by NIR and Raman spectroscopy using the mixture of H₂O and D₂O. For describing the structures in the mixture, $AmDn$ can be extended as $A_{m(H/D)}D_{H(D)n}$, for example, A_{1H1D}D_{D1} to represent the structure of OD with two hydrogen bonds connecting to a hydrogen and a deuterium on the oxygen (acceptor) and one hydrogen bond on the deuterium (donor). It was found that most of the structures of OH can be identified from the NIR spectrum, due to the high sensitivity to OH stretching vibration. Generally, the signal of NIR spectrum is generated from the molecular vibrations that cause the change in dipole moment. However, O—D···O has more symmetric configurations,^[23,24] which results in the sensitivity of NIR spectra to OD group that is comparatively lower. As complementary information, Raman spectrum arises

from the change in polarizability, which usually occurs in symmetric mode of vibration.^[25] Thus, Raman spectrum may provide information for the interaction of OD groups. Figure 1 shows the Raman spectra of H₂O-D₂O mixtures and the resolution-enhanced spectra by wavelet packet transform (WPT).^[26,27] In Figure 1a, there are only two bands around 3400 and 2500 cm⁻¹ corresponding to the stretching vibration of OH and OD, respectively.^[28] In Figure 1(b1–b5), however, the peaks overlapped in the latter band can be resolved into several peaks corresponding to the spectral features of OD in different way of hydrogen bonding with OD and OH. According to the variation of the intensity with the mole fraction, the attribution of these peaks can be identified, because the intensity goes up exponentially in different scale for the structures of A_{mD}D_n and goes up and then down with a different maximum for the structures of A_{mH/DDn}. Nine of the 12 possible structures of OD in the mixture were identified as labeled in the figure.

The interactions in alcohol–water mixtures have been studied using temperature-dependent NIR spectroscopy and two-dimensional correlation spectroscopy (2D-COS). Compared with the absorption peaks in bulk water, those in the mixtures are red-shifted, implying that the interaction of water and alcohol is stronger than that between water molecules.^[29] Water molecules interact with the free OH groups of alcohol at lower water content (the mole fraction less than 0.3), while water–water interaction is more favorable at higher water content.^[30,31] Spectral features of the water–alcohol interaction were observed by high-order chemometric algorithms.^[32] It was found that the content of hydrated CH₃ group decreases with the rise of temperature. Ethanol promotes the formation of water clusters, but the predominant structures of water in the mixture are one and two

hydrogen-bonded water regardless of concentration. Through the resolution enhancement of the high-order derivative spectra, the spectral information about the interactions of water and ethanol was further obtained.^[33] By analyzing the derivative spectra of the mixtures and the pure components, the information of the spectral changes caused by the interactions was extracted. More than seven peaks can be seen in the spectral range 7100–6500 cm⁻¹, indicating the complex structures in the mixture, such as water and ethanol clusters of different sizes and the heteroclusters of ethanol–water.

The interaction of water and solute may change the properties of bulk water. For example, the freezing point of water reduces when an antifreeze is added. The structure of water at low temperatures and the mechanism of the cryoprotectant dimethyl sulfoxide (DMSO) in reducing the freezing point of water were investigated.^[34] Figure 2a,b shows the measured NIR and Raman spectra of DMSO–water mixtures, respectively, and Figure 2c,d shows the resolution-enhanced spectra by continuous wavelet transform (CWT). In Figure 2c, the peak at 6442 cm⁻¹ is absent in the spectra of pure water and DMSO but appears in the spectra of the mixtures. Therefore, the peak can be assigned to S=O···H–O. Two inflection points at 30% and 60% can be observed from the change of peak intensity. This implies that there are two hydrogen-bonded DMSO–water structures in the mixtures, that is, DW2 and D2W (the mole ratio of DMSO and water is 1:2 and 2:1). NIR spectrum is sensitive to the groups containing hydrogen, including OH, CH, and NH but not to the group S=O. Therefore, the spectral features of S=O with different hydrogen bonds cannot be distinguished in NIR spectrum. As the complementary technique, Raman spectroscopy was used to investigate the hydrogen bonding of S=O. The two

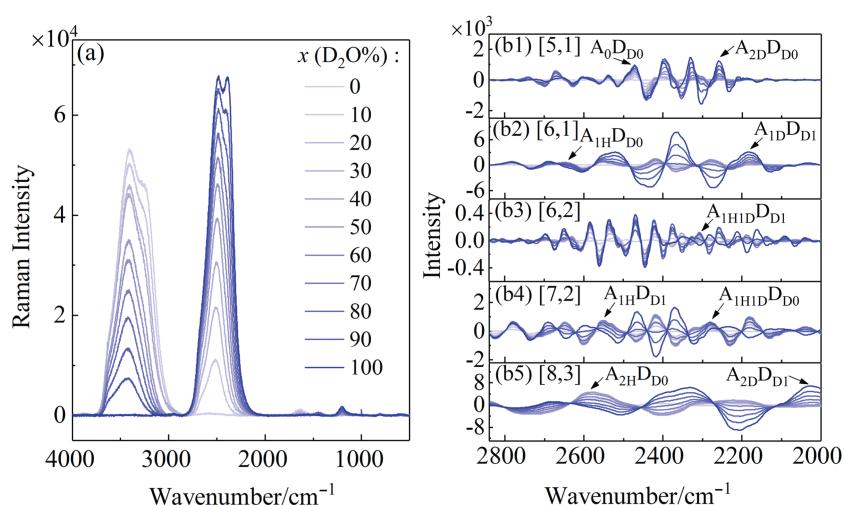
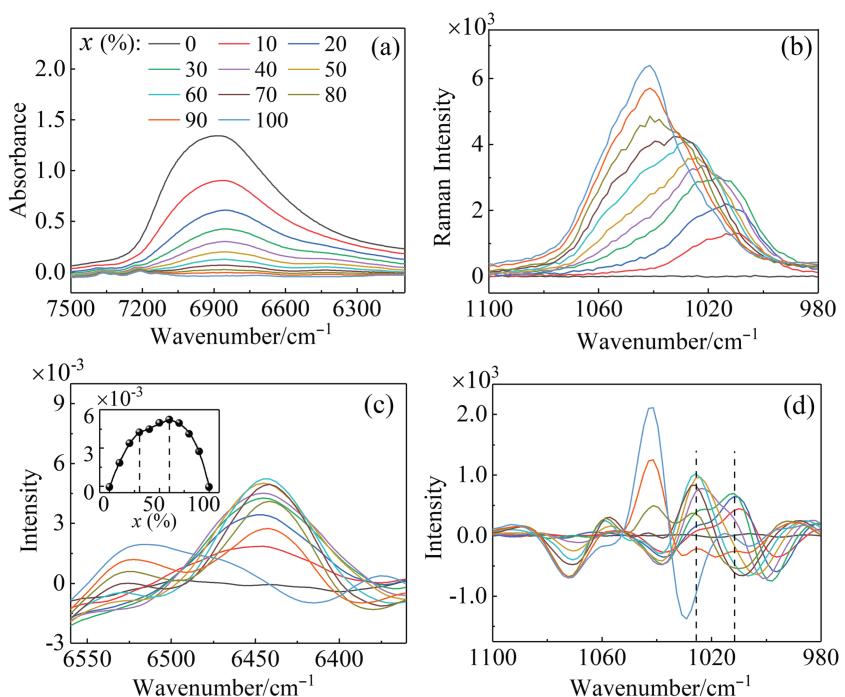


FIGURE 1 Measured Raman spectra (a) and processed spectra (b, b1–b5) calculated by wavelet packet transform (WPT) of xD₂O–H₂O mixture. x(D₂O) is the mole fraction of D₂O and the numbers in the brackets show the index of the wavelet coefficients in WPT calculation

FIGURE 2 Near-infrared (NIR) spectra (a, c) and Raman spectra (b, d) of x DMSO–water mixture at 20°C. Panels (a) and (b) are measured spectra, and panels (c) and (d) are the processed spectra calculated by continuous wavelet transform (CWT) in the region of 6560–6360 cm^{-1} and 1100–980 cm^{-1} , respectively. The inset shows the variation of the peak intensity at 6442 cm^{-1} . x is the mole fraction of dimethyl sulfoxide (DMSO)



structures (DW2 and D2W) were further confirmed by the Raman spectra in Figure 2d. The peak intensities at 1026 and 1012 cm^{-1} reach a maximum at 60% and 30%, respectively. Through the spectral variation with temperature, it was found that DW2 structure inhibits the formation of tetrahedral water structures, which may be the reason for DMSO reducing the freezing point of the mixture. Therefore, the combination of NIR and Raman spectra provides abundant information for understanding water structures, including the hydrogen bonds of water molecules and the hydration of solutes.

To further understand the effect of protein on the antifreezing performance of the DMSO–water system, the influence of formamide (FA) on the hydrogen bonding of DMSO and water was studied using temperature–dependent NIR spectroscopy.^[35] A peak at 6437 cm^{-1} depicting the interaction of DMSO and water through hydrogen bonding ($\text{S}=\text{O}\cdots\text{H}-\text{O}$) was observed in the CWT spectra. When FA exists in the mixture, the intensity of the peak decreases with the increase of FA content, showing that FA may replace the water to form the hydrogen bond of $\text{S}=\text{O}$ and $\text{H}-\text{N}$ and weaken the hydrogen bonding between DMSO and water. In the results by alternating trilinear decomposition (ATLD), two varying spectral features due to water and DMSO were obtained, but no spectral feature that significantly varies with the content of FA was found. The result implies that, although FA may reduce slightly the antifreezing effect, DMSO is still the key component to prevent water from icing.

3 | AQUAPHOTOMICS

Aquaphotomics has been proposed as a new discipline involving the study of water and aqueous systems.^[12,13] The aim is to extract information about the structure of water from the spectra and understand the function of the specific structures in aqueous or biological systems. The spectral pattern defined by water absorbance patterns (WAPs), that is, the absorbance at 12 specific wavelengths in the spectrum of water, is employed to provide an overall characteristic “signature” of analyzed samples and to understand the changes in the water structures caused by various perturbations. WAPs can be visualized by using radar chart, named as aquagram, which is plotted with the normalized water absorbance of 12 bands on a polar coordinate.^[36] With the help of an aquagram, it is easy to observe the difference between the spectral patterns of water induced by perturbations. With the knowledge of aquaphotomics, the spectral change of water can be used to reflect the properties of the solutes in aqueous solutions^[37] and illustrate the diseases or abnormalities in chemical or biological systems or processes.^[38] The fibril formation of proteins^[39,40] and ultraviolet radiation-induced mutation of DNA^[41] can be detected by the structural variations of water. For real biological samples, spectral changes of water in body fluids have been utilized to diagnose cow mastitis^[42,43] and indicate estrus in dairy cows^[44] and giant pandas.^[45,46] In the field of quality control, aquaphotomics approach has been applied for the quality monitoring of water^[47–49] and food.^[50,51]

Changes in water structure and the role of water during metabolism processes were analyzed. In food preservation, the storage of rice germ can be described as a decreasing process of bulk water.^[52] The variation of the water structures (free water, hydration water, adsorbed water, and bound water) during storage at different water activity (aw) can be shown by a radar chart, as displayed in Figure 3. It can be found that samples stored at higher aw level are characterized by high intensities of the bands associated with strongly bonded water (1518 nm), solvation water (1375 nm), and proton hydrates (1364 nm). The increase of the band at 1392 nm related to trapped water by dehydration can be clearly seen, indicating that water molecules become more confined upon the depletion of bulk water and free water. The enhancement of the band at 1436 nm, that is, carbohydrate–water interaction band, is related to the hardness of the germ, suggesting that the changes in hydration of biological structures lead to the change in hardness. Besides, the state of water in the leaves of a drought enduring plant *Haberlea rhodopensis* was investigated.^[53] A drastic decrease of free water molecules, an increase of water molecules with four hydrogen bonds, and a massive accumulation of water dimers were found in the full desiccation stage. The results suggest that the water dimer may hold special importance for the drought stress tolerance. Furthermore, yogurt fermentation was studied to find the spectral features reflecting the information about the progress.^[54] Weakly hydrogen-bonded water seems to be important for the first stage of fermentation, indicating that milk is still more liquid-like, not coagulated. In the

second stage, the rapid decrease in pH was observed when denaturation and the gel matrix are formed. Free water molecules, small protein hydrates, and weakly hydrogen-bonded species deplete to be bonded into the formed gel matrix of the yogurt. In the third stage, when the yogurt is produced, the majority of water is strongly bonded in ice-like structures.

In order to obtain the variables (wavenumbers) related to the interactions of water and solutes, a method based on the difference between the spectrum of pure water and the separated spectrum from that of the mixture was applied.^[55] Figure 4a shows the difference between the calculated and experimental spectra of water in the range of 6400–7500 cm⁻¹. Seven variables related to structural changes of water were found as labeled in the figure, which should be induced by the interaction with ethanol. The result clearly shows that there are at least seven differently hydrogen-bonded water structures (or OH) that changed due to the interaction. This may provide a proof of the rationality of WAPs that reflect an overall characteristics of analyzed samples.

Assuming that water is composed of the molecules (or OH) with different hydrogen bonds, the relative contents of these structures will change under the perturbations such as the change of solute and temperature. To detect the structures in aqueous solutions, the spectral variables that change with temperature were selected by a method combined CWT and Monte Carlo uninformative variable elimination (MC-UVE).^[56] Interestingly, seven variables in the spectral range of 6300–7800 cm⁻¹ were obtained, as shown in Figure 4b, suggesting that

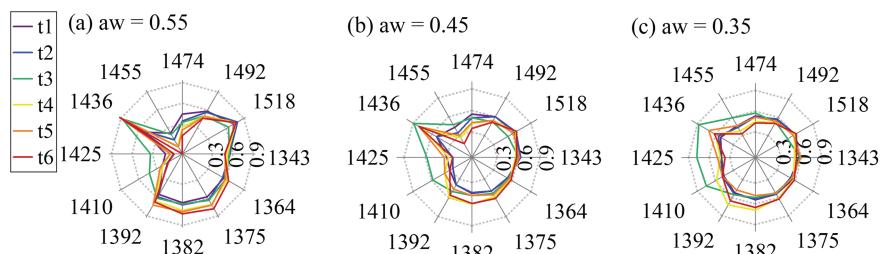


FIGURE 3 Aquagrams for rice germ during storage at different initial water activity (aw) level. Reprinted from Malegori et al.^[52] Copyright (2021), with permission from Elsevier

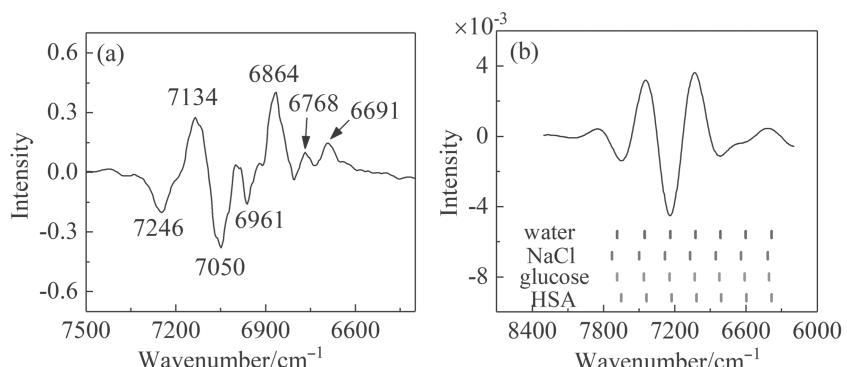


FIGURE 4 Difference spectrum of water between the calculated and experimental spectra (a) and the temperature-sensitive variables in the spectra of water, NaCl, glucose and human serum albumin (HSA) solutions (b)

there are seven structures changed by the variation of temperature. It is more interesting that the variables selected for different solutions are located at similar but not identical wavenumbers, showing that water interacts differently with different solutes. Compared with the variables of water, those of NaCl, glucose, and human serum albumin (HSA) are at larger, similar, and smaller wavenumbers, respectively. The result may be accounted for by that NaCl is capable to promote the formation of hydrogen bonds in the solution, HSA destroys the hydrogen-bonded network of water, and glucose is mild to the water structure. Therefore, water spectrum can be a mirror to reflect the difference of the aqueous solutions.

4 | WATER STRUCTURES IN BIOLOGICAL AND CHEMICAL CHANGES

Water plays a key role in the phase transition of macromolecules such as proteins and polymers.^[57–59] Detecting the structures of water during the conformational change of macromolecules is helpful to understand the role of water in the process. The structures of water during the dehydration of poly(N,N-dimethylacrylamide) (PDMAA) hydrogel were investigated by Raman spectroscopy.^[60,61] Gaussian fitting of the spectral band of OH stretching was conducted in order to investigate the water structure in the gel and dried glassy PDMAA. Five peaks corresponding to the water molecules with four hydrogen bonds and weakly or nonhydrogen bonds (NHB) were obtained. The intensity ratio of the five peaks reveals that water in the gel has a more networked structure consisting of weak hydrogen bonds compared with bulk water, and two types of bound water exist in the dried glassy PDMAA. At the temperatures below 37°C, the water molecules forming the hydration layer around the polymer chains evaporate, while at temperatures above 37°C, water molecules interacting with the polar groups of polymer chains evaporate.

Thermally responsive polymers in aqueous solutions display phase separation above lower critical solution temperature (LCST). To understand the role of water in the aggregation of the polymers, the water structure in the process of the aggregation was studied by temperature-dependent NIR spectroscopy.^[62] For the polymer poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA), the spectral feature of water molecules with two hydrogen bonds (S_2) was observed, the intensity of which goes up and then down with an inflection at 36°C. Therefore, S_2 plays an important role in forming the intermediate structure, serving as a bridge between polymer side chains to form the loose hydrophobic

structure. For the polymer poly(N-isopropylacrylamide) (PNIPAM),^[63] the water structure with three hydrogen bonds (S_3) was found to be crucial for the stabilization of the polymer. When urea was added in solutions as a denaturant, urea molecules reduce the content of S_3 by breaking the hydrogen bonds between water and polymer, resulting in the phase transition at a lower temperature.

The structures of water in the denaturation process of proteins including HSA, ovalbumin (OVA) and tau protein were studied by NIR spectroscopy with the help of chemometrics.^[64–66] The variation of water species with the structural changes of globular proteins OVA was investigated using temperature-dependent NIR spectra and Gaussian fitting.^[65] S_2 water shows a three-stage change with two inflections, which is consistent with the changes of protein structures. S_2 water was also found to play an important role in protein gelation. The interaction between water and OVA may be a driving force for forming the gel. The variation of hydration water during the aggregation of R2/wt induced by heparin was also studied by PCA and two-dimensional correlation spectroscopy.^[66] The spectral features of water with one (S_1) and two (S_2) hydrogen bonds around NH and CH groups of R2/wt were observed, and S_1 changes prior to free water molecules and S_2 . The result provides a possible mechanism for the aggregation, that is, the dehydration of NH groups initiates the change of the hydrogen-bonded network of the hydration water and then the water cage around CH group is destroyed before the formation of the fibrils.

For understanding the structure of water in confined environments, temperature-dependent NIR spectra of reverse micelles (RMs) containing bovine serum albumin (BSA), HSA, and OVA were analyzed.^[67] The spectral features of proteins and water with NHB, WHB, and SHB were observed from the CWT spectra. As shown in Figure 5a,b, the changes of WHB and SHB in BSA solution have obvious inflections, which are consistent with the structural change of protein. The result suggests that the changes of WHB and SHB can be used to indicate the denaturation of BSA. Observing the curves for RM containing proteins, there is no clear inflection, indicating that the protein is stabilized by the confined environment. Figure 5c shows a spectral component obtained by PCA of the CWT spectra for a sample of RM with BSA. A new peak at 6966 cm⁻¹ was observed. The peak may arise from the bridging water connecting NH in protein and S=O in the inner surface of RM. The bridging water only exists in RM with BSA and increases with the protein content. Therefore, the bridging water may be the reason for explaining the enhancement of the thermal stability of the protein.

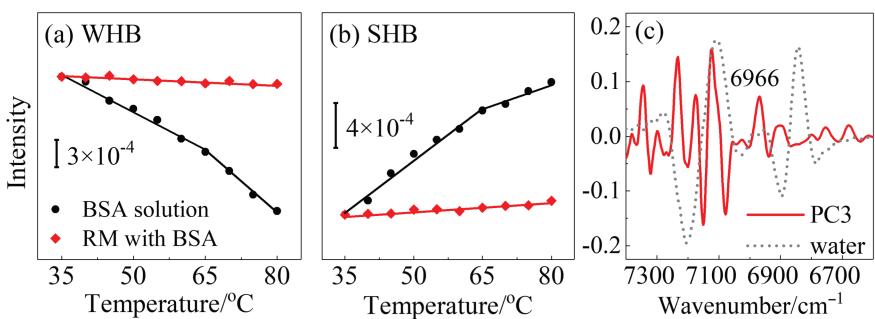


FIGURE 5 Variation of the spectral intensities with temperature for weakly hydrogen-bonded (WHB) (a) and strongly hydrogen-bonded (SHB) (b) water in the continuous wavelet transform (CWT) spectra of bovine serum albumin (BSA) solution and reverse micelle (RM) containing BSA. Panel (c) shows the third loading obtained by PCA for the CWT spectra of water, BSA solution, RM, and RM with BSA

5 | CONCLUSIONS

The combination of NIR and Raman spectroscopy provides abundant information of water structures. The spectral features of water structures with different hydrogen bonds were extracted with the help of chemometrics. Through the spectral changes of water, the structural changes and interactions of water with small molecules, proteins, and thermally responsive polymers can be obtained, providing an understanding for the functions of water in chemical and biological systems. Water is the most abundant molecule on the earth and participates in a variety of life activities. Nevertheless, its peculiar properties remain a mystery of nature to be unveiled. The complex and flexible structure of water, depending on not only water itself but also the microenvironment, plays a key role in the behavior of various systems. NIR and Raman spectroscopy has been proved to be a powerful tool for investigating water structures and interactions, through which the information of the surroundings can also be detected. The analysis of the complicated spectrum of water, however, is a hard task to provide enough information for the structures and interactions. Therefore, much effort is still needed, for example, the exploration of more analytical techniques and strategies like chemometrics, to acquire and extract the underlying information in the spectrum for providing more explanations to the mysterious nature of water.

ACKNOWLEDGEMENTS

This study was supported by the National Natural Science Foundation of China (no. 22174075), the Natural Science Foundation of Tianjin, China (20JCYBJC01480), the Frontiers Science Center for New Organic Matter, Nankai University (no. 63181206), the Fundamental Research Funds for the Central Universities, Nankai University (no. 63211019), and the Haihe Laboratory of Sustainable Chemical Transformations.

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How to cite this article: L. Han, Y. Sun, S. Wang, T. Su, W. Cai, X. Shao, *J Raman Spectrosc* **2022**, *53*(10), 1686. <https://doi.org/10.1002/jrs.6399>