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Identification of Free OH and its Implication on Structural Changes of Liquid Water

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The molecular structure of liquid water has been an outstanding issue for many years. The identification of free -OH holds the key in differentiating structure models for liquid water. By analyzing the relative changes of the intensity and depolarization ratio in temperature dependent Raman spectra, the occurrence of free -OH in liquid water is unambiguously determined. Furthermore, upon the increase of temperature from 5 °C to 85 °C, the structure of liquid water undergoes significant change, but the relative proportion of free -OH is considerably small and remains almost unchanged. This implies that the breaking of hydrogen bond from the tetrahedral structure prefers to occur at the site of the hydrogen acceptor. The energetic favoring of the structural change for liquid water is thus clearly revealed from experiments.

Key words: Water, Free -OH, Raman spectrum, Micro-structure

I. INTRODUCTION

The structure of liquid water has constantly been under debate owing to its complicated hydrogen bond (HB) network [1]. One of the controversies about the structure is the average number of HB per water molecule in liquid water. The commonly accepted structure model dominated by the tetrahedral four hydrogen bonds was challenged by a recent X-ray absorption spectroscopic study [2], from which the chain or ring structures with about two HBs was suggested to be the major species. The latter view has been found to be heavily dependent upon the data analysis [3], and is inconsistent with observations from other experiments including infrared and Raman spectroscopy [4, 5].

It is generally accepted that the structure of liquid water is different from that of ice and the broken HB structures should occur. Intuitively, one would expect that the broken HB structures could somehow be quantified by the existence of free -OH in liquid water. Actually it was shown that both X-ray absorption [6] and emission [7, 8] spectra are particularly sensitive to the species with free -OH, which gives distinct spectral features. But excessive theoretical fitting has artificially enlarged the fraction of free -OH [2]. At the other extreme, there is no direct experimental evidence yet for the existence of free -OH in pure liquid water from in-

frared and Raman spectroscopy [9, 10], the two mostly used techniques for the structural studies of liquid water, leading to the heated debate in literatures. In this work, we illustrate the first spectral fingerprint of free -OH in pure liquid water from high precision temperature dependent Raman spectra. It resolves the ongoing debate on this important issue.

Indirect evidence of free -OH has long been revealed in aqueous organic or inorganic mixtures. For instance, Giguère et al. observed a positive peak located at ∼3650 cm^{-1} in the difference Raman spectra between liquid water and hydrogen peroxide/water mixtures [11]. This peak was regarded as the sign of free -OH in liquid water based on the fact that it could be suppressed by the presence of hydrogen peroxide. By monitoring the excess IR spectra in the -OH stretching overtone region of aqueous methanol [12], a sharp negative peak located at 7110 cm^{-1} was assigned as the free -OH in liquid water. A negative peak at ∼3650 cm^{-1} in the attenuated total reflection infrared change spectra [13, 14] between the liquid water and aqueous salt mixtures was also assigned to the free -OH, considering the possible intermolecular interactions between ions and the free -OH. For pure liquid water, a distinct fingerprint of free -OH at ∼3650 cm^{-1} has not been identified in both infrared and Raman spectra [9, 10].

II. EXPERIMENTS

The liquid water was purified with a Millipore Simplicity 185 (18.2 MΩ·cm) from triple distilled water.

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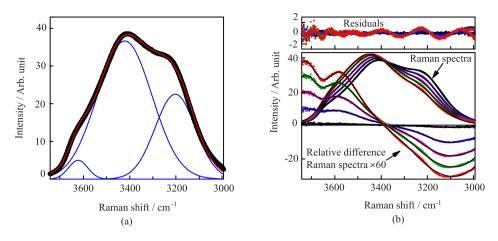
FIG. 1 (a) The Raman spectra and (b) their difference spectra ($I-I_5$) of liquid water in the -OH stretching region at temperatures of 5, 25, 45, 65, and 85 °C, respectively. The possible position of free -OH is marked in the figure.

The experimental setup is similar to the one employed in our previous studies [15, 16]. The liquid water sample was kept in the 10 mm×10 mm quartz cell cuvette, which could be thermally controlled by a heating bath in the temperature range of 5 °C to 85 °C with a precision of 0.1 °C (THD-2006, Ningbo). All of the Raman spectra reported here were record with a triple monochromatic system (Acton Research, TriplePro) coupled to a liquid-nitrogen-cooled CCD detector (Princeton Instruments, Spec-10:100B). A cw laser (Coherent, Verdi-5W, 532 nm) was used as the light source (1.0 W power at the sample). During the experiments, the incident laser was linearly polarized by using a Glan-laser prism. The Raman signal was collected at back-scattering geometry relative to the incident laser beam with a pair of f=5 and 20 cm quartz lenses, and imaged onto the entrance slit of the monochromator for spectral dispersion. A Glan-laser prism was employed to choose the polarization of the Raman scattering light, and an optical depolarizer (scrambler) was put in between the Glan-laser prism and the entrance slit of the monochromator to remove any unwanted polarization effects from the gratings of the monochromator. The Raman spectra shown here were recorded with the polarization directions parallel (I_p) to the incident laser. The Raman depolarization ratios (ρ) were measured by varying the polarization direction of the scattering light with the Glan-laser prism. We recorded the spectra from 2994 cm^{-1} to 3744 cm^{-1}.

III. RESULTS AND DISCUSSION

A. Raman spectra of liquid water

We have measured high precision Raman spectra of liquid water at different temperatures. The obtained spectra in the -OH stretching region of liquid water at five temperatures from 5 °C to 85 °C with an interval of 20 °C are given in Fig.1(a). A noticeable temperature effect on the Raman spectra of liquid water is highlighted by the isosbestic point at 3380 cm^{-1}, at which the intensities are invariant. The isosbestic point in vibrational spectroscopy was traditionally regarded as the evidence of the equilibrium of two state microstructures in liquid water [17−19], but was recently argued to be arisen from the statistical thermal distribution of harmonic oscillators in a continuous distribution of structures [4, 20, 21]. In any cases, one would expect that the increase of temperature should disrupt the HB network and the free -OH should appear as a distinct peak at ∼3650 cm^{-1}. However, this cannot be directly seen from our Raman spectra, which is consistent with what was found in previous IR spectra of water from 29 °C to 95 °C [10], or Raman spectra at various temperatures at normal pressures [17, 18].

The invisibility of free -OH in IR/Raman spectra is not necessarily related to the absence of free -OH, but could be due to its low cross section [22, 23], or the spectral overlapping. One way to enhance the change of the spectral feature is to use the so-called difference Raman spectrum, which is the difference between the spectra at different temperatures. We have adopted this approach in our previous Raman study on the structure of liquid methanol [15]. Similar to the case of liquid water, the free -OH in liquid methanol was not directly observed in Raman spectra, but it is presented as a shoulder peak at ∼3660 cm^{-1} in the difference spectra. The difference Raman spectra of liquid water, with respect to the one at 5 °C, are given in Fig.1(b). The direct consequence of the temperature increase is the weakening of the hydrogen bonds, which should lead to the structure change in liquid water. The difference spectra shown in Fig.1(b) fit well with this notion. With respect to the isosbestic point at 3380 cm^{-1}, the intensity of the components with high vibrational frequency is gradually enhanced, which is compensated by the decrease of the low frequency components. However, from the difference spectra, we can not single out a distinct feature
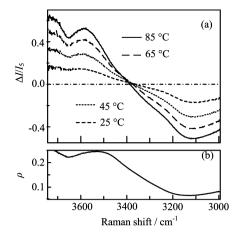
FIG. 2 (a) The relative difference Raman spectra ($\Delta I = I - I_5$) of liquid water under temperatures of 25, 45, 65, and 85 °C. (b) Depolarization ratio ρ dispersion of liquid water at 25 °C. The valley at ~3650 cm^{-1} in (a) and (b) has been clearly observed, indicating the existence of free -OH groups in liquid water.

corresponding to the free -OH at around 3650 cm^{-1}. This at least indicates that the free -OH in liquid water is much less than that in liquid methanol. Although the dominant structures in liquid methanol are short chains [15], the total number of free -OH is still quite limited due to the much less hydrogen bonds that a methanol possesses. In other words, the portion of free -OH in liquid water has to be rather small. One can thus understand why the free -OH is so difficult to be detected in liquid water by IR and Raman spectra.

B. Relative difference spectra of liquid water

To future search for the sign of free -OH, we have introduced here a relative difference spectrum, which is defined as $\Delta I/I = (I-I_5)/I_5$, *i.e.*, the relative difference with respect to the reference spectrum at 5 °C. From the numerical analysis point of view, the success of such a treatment heavily depends on the quality of the original spectral data, which are guaranteed by our high precise measurements. If the relative change of different spectral components is not uniform, there is a big chance to observe distinct spectral features corresponding to certain components.

The relative difference Raman spectra of liquid water are illustrated in Fig.2(a). It is interesting to see that with respect to the difference spectra, the negative peak is red shifted gradually from 3190 cm^{-1} to 3110 cm^{-1}, while the positive peak is blue shifted from 3550 cm^{-1} to 3585 cm^{-1}. This indicates that different components of liquid water depend differently on the increase of temperature. Most importantly, the relative difference Raman spectra exhibit a spectral dip at around 3650 cm^{-1}, in particularly at higher temperatures. At 85 °C, the local minimum is centered at 3650 cm^{-1} with

the full width at half maximum (FWHM) ~60 cm^{-1}. These numbers are consistent with those obtained in the difference Raman spectra between liquid water and hydrogen peroxide/water mixtures [11], and also in the difference infrared spectra between liquid water and aqueous salts [13, 14, 23]. The solvent molecules are known to strongly interact with the free -OH in liquid water, resulting in the distinct feature in the difference spectra. Together with the previous studies, one can conclude that the valley shown in Fig.2(a) is the direct evidence of free -OH in liquid water. The local minimum observed for the free -OH clearly suggests that the relative increase of free -OH upon heating is slower than other components. Another important parameter in Raman spectroscopy is the depolarization ratio, which is also sensitive to the surrounding of the molecules [15]. Figure 2(b) gives the measured Raman depolarization ratio of liquid water at 25 °C. A valley located at ~3650 cm^{-1} is also nicely presented, indicating that this spectral feature does correspond to a specific structure. This valley was unfortunately not observed in previous studies of depolarization ratio for pure water [24].

C. Proportion of free -OH

To evaluate the proportion of free -OH in liquid water, the relative intensities of free -OH are extracted from the spectral fittings to the original, the difference, as well as the relative difference spectra, tentatively using three spectral components centralized around the three spectral features in Fig.2(a). We use global fitting procedure to decompose these spectra and relative difference spectra, in the decomposition three Gaussian peaks were employed (Fig.3(a)). For clarity, the comparison between the experimental and fitting results for the original and the relative difference Raman spectra at difference temperatures from 5 °C to 85 °C with an interval of 20 °C, is shown in Fig.3, a perfect agreement has been achieved. Such a fitting procedure is quite robust, as demonstrated in Fig.1 and Fig.2(a), in which the fitted and the experimental spectra are almost identical.

It is found from the fitting that the center of the free -OH feature is not exactly at 3650 cm^{-1}, but red-shifted to ~3620 cm^{-1} upon heating. The estimated intensity fraction of free -OH over the entire OH stretching region is illustrated in Fig.4. It is around 3.4% over the entire temperature range. The relative change is quite small, less than 0.4% from 5 °C to 85 °C. It thus confirms two important hypotheses: the free -OH in water takes up a small proportion and increases with temperature slower than other components. This is consistent with the results of X-ray absorption measurements, which shows that the pre-edge, corresponding to the free -OH, is almost temperature independent [3].
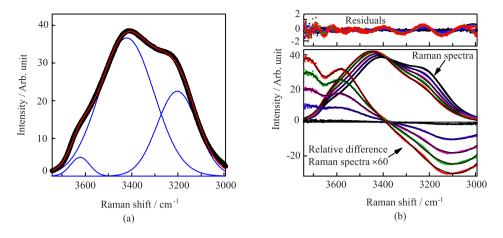
FIG. 3 (a) The fitting result and three decomposition peaks for the Raman spectra of water at 5 °C. (b) The fitting and the residual curves of the Raman spectra and the relative difference Raman spectra of water at 5 °C (black), 25 °C (blue), 45 °C (purple), 65 °C (green), and 85 °C (red).
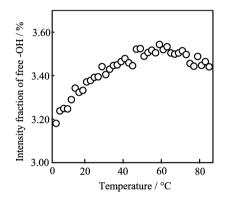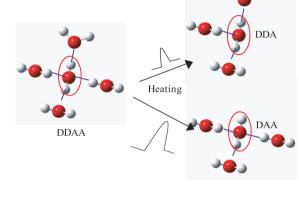

FIG. 4 Estimated intensity fraction of free -OH over the entire OH stretching region in liquid water from spectral fittings to experiments at different temperatures.

Scheme 1 Schematic illustration of the local structural changes of liquid water upon heating. A four-hydrogen-bonds structure with two hydrogen donors and two hydrogen acceptors (DDAA) can be converted to three-hydrogen-bonded species with two hydrogen donors and one hydrogen acceptor (DDA) or with one donor and two acceptors (DAA).

D. Local structure of liquid water

The identification of free -OH in liquid water is certainly exciting, but its implication is probably more important. The weak spectral features are a convincing sign of small fraction of free -OH in liquid water. This simply implies that it should be very difficult to find structures with two hydrogen bonds in liquid water, since they offer too many possible free -OH groups. In other words, the so-called ring and chain structures proposed by Wernet *et al.* [2] are definitely not supported by this work. Upon the increase of temperature, we do observe significant spectral changes, which should reflect the structural changes in liquid water. One could ask what kind of structural change that gives rise to the less favorable increase of free -OH. Scheme 1 gives the possible explanation. Apart from one hydrogen bond or two hydrogen bonds structures, there are three more local structures for a water molecule, namely the four hydrogen bonds tetrahedral structure with two hydrogen donors and two hydrogen acceptors (DDAA), the three

hydrogen bonds structure with two hydrogen donors and one hydrogen acceptor (DDA), and another three hydrogen bonds structure with one hydrogen donor and two hydrogen acceptors (DAA), respectively. It is noticed that both DDAA and DDA structures do not provide the free -OH group for the center water molecule, while only DAA structure possesses a free -OH group. The fact that the fraction of free -OH is almost temperature independent indicates that the fraction of DAA structure is less changed, or to say there is an equilibrium in the structural conversion between the DDAA and DDA species [3]. The increase of temperature has significant effect on the structure transformation from DDAA to DDA, as shown in Scheme 1. This implies that the energy barrier for structure converting from

DDAA to DDA is much lower than that from DDAA to DAA. Such a new finding is particularly useful for improving the force fields in molecular dynamics simulation studies.
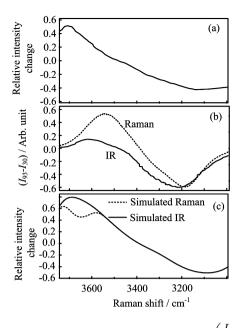
FIG. 5 (a) The relative difference IR spectra $\left(\dfrac{I_{93} - I_{30}}{I_{30}}\right)$ of liquid water at 30 and 93 °C [25]. (b) The difference IR spectra of liquid water at 30 and 93 °C [25], the difference Raman spectra of liquid water at temperatures of 5 and 85 °C. (c) The simulated relative difference IR and Raman spectra.

E. Comparison of IR and Raman spectra of liquid water

Similar to Raman spectra, IR spectra were also employed to study the structure of liquid water previously [5, 10, 25]. Recently the IR spectra of liquid water demonstrated there was not free OH in liquid water [5, 10]. Using previous IR spectra of liquid water at temperatures 30 and 93 °C [25], we can calculate the relative difference IR spectra. As shown in Fig.5(a), the relative difference IR spectrum is much different from our relative difference Raman spectra. In this spectrum, we do not observe the valley around 3620 cm^{-1} which is the direct evidence of free -OH in our Raman spectra. The disappearance of the valley could be understood by the intrinsic difference of the IR and Raman technology. The intrinsic properties of these two spectroscopic technologies could be reflected by the difference spectra. In the difference Raman spectra, shown in Fig.5(b), the integrated area of the positive and negative peak are almost the same, this demonstrated they are the same of the Raman scattering cross sections of the water molecules with various hydrogen bonds. However this situation is different for the IR spectra. In difference IR spectra, shown in Fig.5(b), the area of the positive peak located at weak hydrogen-bonding region is much smaller than that of the negative peak located at strong hydrogen-bonding region, which reflected the IR absorption ability of the water molecules connected with other molecules with weak hydrogen bonds is much

weaker than that of water molecules with strong hydrogen bonds. Employing the area ratio of the negative and positive peak in the difference IR spectra, we can simulate the relative difference IR spectra between 85 and 5 °C. In this simulation procedure, the number of the water molecules with same hydrogen bonding strength is the same in IR and Raman spectra, and the peak position and width is fixed with those in Raman spectra, only peak intensity is calibrated using the area ratio in difference IR spectra. The simulated relative difference IR and Raman spectra are shown in Fig.5(c). Same with the experiment result, the valley also disappeared in the simulated relative difference IR spectra. This comparison between IR and Raman spectra demonstrated the Raman spectroscopy was suitable to study the free -OH in liquid water.

IV. CONCLUSION

The high precision Raman spectra of liquid water have provided convincing evidence that the free -OH does exist in liquid water, but with small proportion. The dominant structures in liquid water are found to consist of DDAA and DDA species. The structural change in liquid water favors a specific channel to break the hydrogen-acceptor bond of a water molecule. These new structural information has enriched our basic understanding of liquid water and resolved the ongoing debate about the local structures of liquid water.

V. ACKNOWLEDGEMENTS

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