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Quantum Effects on Global Structure of Liquid Water

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The structure difference between light and heavy liquid water has been systematically investigated by high precision Raman spectroscopy over the temperature range of 5−85 °C. Distinct difference between the Raman spectral profiles of two different liquid waters is clearly observed. By analyzing the temperature-dependent Raman spectral contour using global fitting procedure, it is found that the micro-structure of heavy water is more ordered than that of light water at the same temperature, and the structure difference between the light and heavy water decreases with the increase of the temperature. The temperature offset, an indicator for the structure difference, is determined to vary from 28 °C to 18 °C for the low-to-high temperature. It indicates that quantum effect is significantly not only at low temperature, but also at room temperature. The interaction energy among water molecules has also been estimated from van't Hoff's relationship. The detailed structural information should help to develop reliable force fields for molecular modeling of liquid water.

Key words: Light and heavy water, Quantum effect, Raman spectra, Structure, Temperature offset

I. INTRODUCTION

The nuclear motion is a key factor for correctly modeling the local structure of liquid water [1] due to the involvement of quantum effect. It has been shown that the local structure of quantum water is less structured than that of classical water [2]. Such a quantum effect can be best illustrated by the structure difference between light and heavy liquid water, which has been extensively explored by theoretical simulations [2−7] and experimental measurements [8−17]. Naturally, the heavy water due to the much weakened quantum effect should be more structured in comparison with the light water. It can thus be anticipated that the structure of light water at a low temperature (T_L) could be similar to the structure of the heavy water at a high temperature (T_H). The temperature difference between T_H and T_L is denoted as the temperature offset (TO).

In recent years, the majority of the experimental techniques employed is related to high-energy sources, such as the X-ray diffraction [8−11, 13, 16], neutron diffraction [16], X-ray Raman spectroscopy [14], and Compton scattering [15]. It has been shown that different experimental measurements could give quite different TO for liquid water. A value of 5.5 °C for TO was first obtained from X-ray diffraction measurements [8, 9]. But

a recent X-ray Raman measurement [14] demonstrated that the structure of heavy water at 22 °C could be closer to that of light water at 2 °C, i.e. the TO has a value of 20 °C, although the spectral difference is generally quite small below the room temperature. Quantum molecular simulations suggested that the difference revealed by the neutron diffraction experiments might not be solely resulted from the quantum effects [5]. However, no consensus has been reached so far.

The structure of liquid water have also been examined by the nondestructive Raman spectroscopy [18−23], from which two contrasting models were emerged. One is related to the conventional discrete model, or two-state model [18−21], in which the liquid water is composed by some discrete species with different numbers of hydrogen bonds. This model has also been favored by several recent experiments using X-ray emission [24], near-edge X-ray absorption [25], X-ray, and neutron scattering [26]. The alternational model is of course the continumm model, in which the local structure of the water molecule experiences a continuum change over the time. It is mostly supported by Monte Carlo simulations and Raman spectroscopy [22, 23]. Regardless of the structure models, the temperature dependent Raman spectra [18−23] of liquid water have shown that the contour of the Raman spectra in the -OH/-OD stretching region is very sensitive to the micro-structure of liquid water. This thus implies that the structure difference could be well reflected by the changes in this spectral region. However, to our best knowledge, there

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     127

is no systematic comparison between the contours in this spectral region for light and heavy liquid water. It should be mentioned that from the van't Hoff analysis of recent temperature dependent Raman spectra of light water [22], the enthalpy change ΔH of the light water is found to be smaller than that of the heavy water. It indicates that the hydrogen bonds in light water should be weaker than those in the heavy water, but such a comparison does not directly reveal the micro-structure difference between the light and heavy water.

In this work, we have carried out a systematic study on temperature dependent high precision Raman spectra of light and heavy liquid water over a wide temperature region, from 5 °C to 85 °C. Significant difference in spectral profiles of two systems has been clearly observed. By carefully comparing the Raman band contours, the temperature offsets have been accurately determined. The enthalpy change at different temperature has also been obtained from van't Hoff analysis. It resolves the debate on the exact structure difference in light and heavy liquid water and provides detailed structural information that will help to construct better models for molecular dynamics simulations.

II. EXPERIMENTS

The experimental setup is similar to that used in our previous studies [27, 28]. In this study, a back-scattering geometry was used to obtain the Raman spectra. All the spectra were obtained with a triple monochromator system (Acton Research, TriplePro) coupled to a liquid-nitrogen-cooled CCD detector (Princeton Instruments, Spec-10:100B). Liquid water was hold in a 10 mm×10 mm quartz cell cuvette, which was heated from 5±0.1 °C to 85±0.1 °C at an increment of 2 °C by a heating bath (THD-2006, Ningbo). A stable cw laser (Coherent, Verdi-5W, 532 nm) was employed as the excitation light source (∼1.0 W power at the sample). During the experiments, the incident laser was linearly polarized by using a Glan-laser prism, and its polarization was controlled vertically with a half-wave plate.

The Raman scattering light was collected with a pair of f=2.5 cm and 10 cm quartz lenses, and imaged into the entrance slit of the monochromator for spectral dispersion. Between the two lenses, a Glan-Taylor prism and an optical scrambler were inserted. The Glan-Taylor prism was used to select the scattering light with vertical polarization, and the scrambler was used to depolarize the polarized light in order to eliminate the polarization-dependent effect from the dispersion gratings.

The light water was purified with a Millipore Simplicity 185 (18.2 MΩ·cm) from triple distilled water, while the heavy water was purchased from Sigma-Aldrich without further purification. In this experiment, we focused our attentions on the spectral regions of -OH/-OD

stretching vibration, since they are most sensitive to the micro-structure of the liquid water [21, 22]. All the observed spectra were corrected following the Placzek equation [29]:

$$I(\nu) = I_{\mathrm{raw}}(\nu) \left[1 - \exp\left(-\frac{h\nu}{k_{\mathrm{B}}T} \right) \right] \frac{\nu}{(\nu_{\mathrm{L}} - \nu)^4} \quad (1)$$

where I_{raw} is the raw Raman spectral intensity, ν_{L} is the excitation laser frequency, ν is the frequency of Raman scattering light.

III. RESULTS AND DISCUSSION

A. Raman spectra of heavy and light liquid water at different temperatures

We have recorded the Raman spectra of water from 5 °C to 85 °C at a temperature interval of 2 °C, and for clarity we present the Raman spectra at -OH and -OD stretching vibrations with an interval of 10 °C in Fig.1. The isotopic effect is reflected by the different frequency scales. In our Raman spectra, the isosbestic point is observed at 2440 and 3380 cm^{-1} for heavy and light water respectively. It can be seen that for both systems, when the temperature is increased, the spectral component below the isosbestic point is decreased and the one above it is increased. This observation is similar to the previous temperature-dependent Raman spectra of liquid water [20−22].

This isosbestic point were traditionally regard as the evidence of two-state model of liquid water [18, 21], however some theoretical analysis [22, 23] on the Raman spectra challenged this notion. The isosbestic point could be reproduced by considering a single species in a fluctuating environment, which thus favored the continuum model. Recently the structure of liquid water with two different hydrogen bonding patterns was supported again by X-ray emission spectra [24], near-edge X-ray absorption spectra [25], and X-ray and neutron scattering [26].

In previous X-ray diffraction [8−11, 13, 16], neutron diffraction [16], and X-ray Raman studies, the structure difference could be characterized directly as the signal difference, *i.e.*,

$$\Delta S = S(\mathrm{D_2O}) - S(\mathrm{H_2O}) \quad (2)$$

where S is the signal, ΔS is the signal difference. The same approach can not be directly applied to Raman spectra of liquid water, due to the different frequency values involved in the two systems. As we know, the -OH stretching of light water is in the region from 2800 cm^{-1} to 3800 cm^{-1}, while the -OD stretching of heavy water is in the region from 2200 cm^{-1} to 2800 cm^{-1}. To visualize directly the contour shape difference of the Raman spectra of H$_2$O and D$_2$O, we have
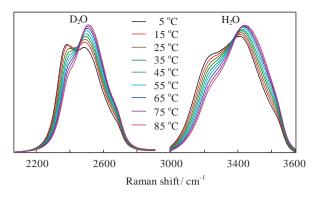
FIG. 1 Raman spectra of heavy and light water in the -OD and -OH stretching region at temperatures ranging from 5 °C to 85 °C.
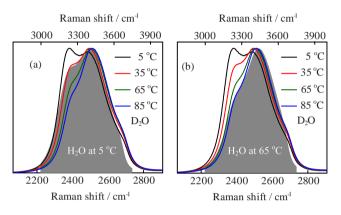

FIG. 2 (a) The comparison between Raman spectra of light water at 5 °C (shadow contour, top axis) and those of heavy water at 5 °C (black), 35 °C (red), 65 °C (green) and 85 °C (blue). (b) The comparison between Raman spectra of light water at 65 °C (shadow contour) and those of heavy water at the same temperatures.

normalized the maximum intensities of the Raman spectra and then put them together by recalibrating the frequency.

Two examples are given in Fig.2, in which the spectra of heavy water at 5, 35, 65, and 85 °C are compared respectively with light water at 5 and 65 °C. From Fig.2(a), it can be seen that the spectral contour shape of light water at 5 °C (shadow contour) is drastically different from the one of heavy water at 5 °C (black curve), showing significant quantum effect. It is noted that for the spectral component at low wavenumber region below the isosbestic point, the intensity of heavy water is much stronger than that of light water at 5 °C. This clearly shows that the local structure of heavy water is more ordered than that of light water at the same temperature, which agrees well with the previous results [8−11, 13, 14, 16]. One can immediately notice that the spectral contour shape of light water is quite close to that of the heavy water at 35 °C (red curve), implying that the TO should be around ∼30 °C at 5 °C. Such a value is somewhat similar to the value
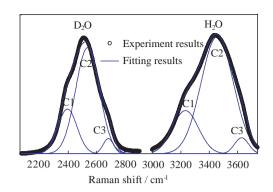

FIG. 3 Spectral fittings to the Raman spectra of heavy and light water at 85 °C with three Gaussian components. The black cycles are the experimental spectra and the blue curves are the decomposed fitting components.

of 20 °C for the light water at 2 °C obtained from previous X-ray Raman study [14]. However, for the Raman spectrum of the light water at 65 °C (shadow contour in Fig.2(b)), its spectral contour shape is similar to that of the heavy water at 85 °C (blue curve in Fig.2(a)), leading to a value of ∼20 °C for TO. These comparisons strongly suggest that TO is a temperature dependent parameter.

B. Temperature offsets

The direct comparison of the spectral contour shape certainly allows to obtain the temperature offsets as we illustrated above. The alternative approach is to use global spectral fitting procedure to quantitatively analyze the spectral contour shape of both systems. This would also provide some insights about the structural difference and its evaluation as the function of the temperature. In the global fitting procedures, three Gaussian peaks were employed to decompose each spectrum. The intensity parameters varied freely for both kinds of waters, and the Raman shift (v) and full width of half maximum (ω) of heavy water also varied freely, but for light water they are constrained by the relationship,

$$v(\mathrm{H_2O}) = cv(\mathrm{D_2O}) \qquad (3)$$
$$\omega(\mathrm{H_2O}) = c\omega(\mathrm{D_2O}) \qquad (4)$$

where c is a constant because of isotopic effect, it is also varied freely in the fitting procedures. For the sake of the clarity, only the fitting results for the Raman spectra of the light and heavy water at 85 °C are shown in Fig.3, which demonstrates a perfect agreement between the fitted and experimental spectra. Three components C1, C2, and C3 are employed in the fitting, which correspond to three hydrogen bonding situations with rich hydrogen bonds, less hydrogen bonds, and free -OD/-OH, respectively.

This global fitting procedure ensures that the contour shape could be simply represented by the intensity
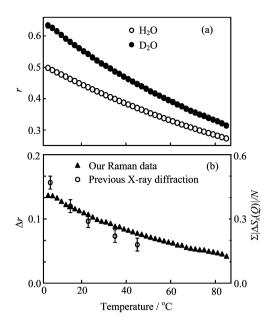
FIG. 4 (a) The ratio r of the intensity of C1 and C2 components at the temperature from 5 °C to 85 °C for heavy water and light water. (b) the temperature dependence of the intensity ratio difference Δr from our Raman, and the temperature dependence of the difference structure factor from previous X-ray diffraction [11].

ratio of the C1 and C2 components, $r=I_{C1}/I_{C2}$. The temperature dependent intensity ratio for both the light and heavy water is given in Fig.4(a). It is found that the ratio decreases with the increase of the temperature, implying that the hydrogen bonds among water molecules are destroyed when liquid water is heated up. It can also be seen that such a trend for the heavy water is faster than that of the light water, which is in agreement with previous results from Compton scattering [15]. At the same temperature, the intensity ratio for the heavy water is always larger than that for the light water. This indicates that the local structure of the heavy water is always more ordered than that of the light water. One might be able to illustrate the structure difference between the light and heavy water at the same temperature by the intensity ratio difference, $\Delta r=r(D_2O)-r(H_2O)$. As shown in Fig.4(b), the structure difference between the light and heavy water gets smaller at higher temperature, in consistent with the findings of previous X-ray diffraction [11]. In other words, the quantum effect becomes less pronounced when the temperature increases. However, it is interesting to see that even at a very high temperature (85 °C) the difference can still be clearly identified. This agrees with what was found in previous quantum molecular simulations [7].

When the intensity ratio, r, for the light water at one temperature T_L is the same as the ratio for the heavy water at another temperature T_H, the temperature difference (T_H-T_L) gives the TO. The TO as a function
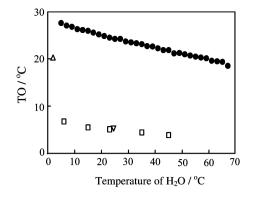
FIG. 5 The temperature offset (TO) between liquid D_2O and H_2O derived from our spontaneous Raman spectra (solid circle), and the TO from previous X-ray Raman [14] (upper triangle), X-ray diffraction (lower triangle [8] and square [11]) studies.

of the temperature T_L estimated from the global fitting procedure is summarized in Fig.5. The value decreases from 28 °C to 18 °C when the temperature of the light water goes down from 5 °C to 65 °C. As can be seen in Fig.5, the trend observed here agrees with that obtained from previous X-ray diffraction study [11], but with different absolute values. The single value for TO at $T_L=2$ °C from X-ray Raman measurements [14] is close to our data, but still about 10° to small.

C. van't Hoff analysis

The enthalpy change ΔH of the liquid water can be obtained from van't Hoff analysis [20−22] by the so-called van't Hoff plot, in which a linear relationship between the $1/T$ and the natural logarithm of the intensity ratio for the spectral components below and above the isosbestic point is often obtained. The slope of the linear function corresponds to the ΔH between the water molecules with more hydrogen bonds and the molecules with less hydrogen bonds.

Similar to previous procedure [22], here we also employ the integrated area of the spectral components to calculate the intensity ratio. The van't Hoff plots of light water and heavy water are listed in Fig.6 (a) and (b), respectively. If using a rough linear fitting, the ΔH in the light water is found to be 1.4 kcal/mol, the same as that obtained from previous Raman study and X-ray emission study [30]. The ΔH in the heavy water is calculated to be 1.6 kcal/mol, which is about 0.2 kcal/mol larger than that in the light water. This also agrees well with previous Raman study for hydrogen isotope diluted water [22]. However, because of the high quality of our Raman spectra, the van't Hoff plots in Fig.6 present obviously a non-linear relationship. It is noted that a similar non-linear behavior also recently observed in the supercooled water droplet [31]. We have found that one has to use at least two linear functions to fit the
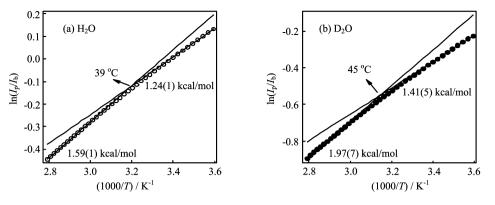
FIG. 6 van't Hoff plot for the Raman spectra of liquid light (a) and heavy (b) water. The ΔH can deduced from the slopes of the fitting lines.

plots as shown in Fig.6. For both systems, the ΔH at the high temperature region is larger than that at the low temperature region. This temperature-dependent ΔH might be related to the fact that hydrogen bond strength is temperature-dependent [32]. The cross point of the two lines is located at 39 °C for the light water, and 45 °C for the heavy water. As an educated guess, the temperature of 39 °C might be of biological relevance, since it is around the body-temperature of the human being. Above this temperature, the change of the hydrogen bonding network starts to accelerate, which might be the cause of the dehydration. The values obtained from our Raman spectra are certainly very useful for adjusting the parameters for molecular dynamics.

IV. CONCLUSION

In summary, the high precision Raman spectra of light and heavy liquid water have convincingly illustrated the quantum effects on the local structure of liquid water. It is shown that the structure of the light water is much less ordered than the heavy water, indicating that the quantum effect is more pronounced than often anticipated. Although the structure difference between two systems decreases with the increase of the temperature, it can be still clearly observed at high temperature of 85 °C. The temperature dependent temperature offset has been accurately determined, which is very different from what has been found from X-ray related experiments. Our results have shown that the ΔH is also temperature dependent, which can be at least estimated by two well-defined values for the low and the high temperature, respectively. The quantitative structural information derived from this study has significantly enriched our understanding the quantum effects in the liquid water, and can provide a good reference to improve the molecular simulations in general.

V. ACKNOWLEDGMENTS

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