J. Phys. Chem. A **2002,** *106,* 12041−12044

Stimulated Raman Scattering of Liquid Water under the Strong Focusing Condition: Analysis of Local Hydration Network Environments in Dilute Ethanol Solutions

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Received: June 27, 2002

Stimulated Raman scattering (SRS) of OH stretching vibrations of water molecules is investigated when an intense pulsed beam is focused in liquid water. The SRS is emitted before the phase transition from liquid to plasma, and an enhanced vibrational spectrum is obtained at around 3400 cm^{-1}, the main peak of water in the liquid phase. Despite the strong and perturbing excitation condition, the temperature dependence of the forward SRS spectrum indicates that the SRS sensitively reflects the slight changes of the local hydrogen-bonding network environment in liquid water. The local network environments in dilute ethanol solutions (1−3 mol %) are investigated by utilizing the enhanced vibrational spectrum. Little change is observed in the peak shift of the SRS, indicating the that the perturbation is relatively small as compared to that induced by structure-breaking solutes such as KCl. There is, however, a clear decrease of the intensity on the higher frequency side of the SRS band in ethanol solutions. Although direct evidence is not observed for the well-known hypothesis that there is enhancement of the ordered icelike or clathratelike structures around hydrophobic groups, the SRS spectra indicate that reinforcement of the hydrogen-bonding network structure is induced by adding a small amount of ethanol molecules.

Introduction

Understanding the structure of hydrogen-bonding networks in water and aqueous solutions is crucial to elucidating not only the origins of the anomalous properties of water itself[1] but also the role of water molecules in many chemical and biological processes occurring in aqueous solutions. In particular, measurements of local structures of water adjacent to solutes are crucial to understand physical and chemical properties of many important aqueous systems such as water/alcohol binary solutions[2], clathrate hydrates around hydrophobic molecules,[3] and water molecules at hydrophobic fluid surfaces[4,5] and around biologically relevant molecules.[6] In general, vibrational spectra of water molecules are expected to provide detailed information on the microscopic environment of hydrogen-bonding networks. In particular, spectra in the OH stretching vibrations are believed to sensitively reflect the local structures and interactions of the hydrogen-bonding networks.[7]

Recently, we found transient enhancement of stimulated Raman scattering (SRS) of water molecules in the OH stretching region when a laser-induced plasma was formed by focusing an intense pulsed beam in water.[8] The SRS was emitted in both forward and backward directions with respect to the axis of the excitation beam. From the time-resolved measurement of the forward SRS spectrum, we found that the SRS was only emitted before the phase transition from liquid to plasma and its duration was about 40 ps (fill width at half-maximum (fwhm)) for a 12 ns excitation. A second spectroscopic study of the backward SRS verified that the SRS was initially induced by the interactions of water molecules between excess electrons formed in the liquid phase before the phase transition.[9]

In the present paper, we analyzed changes of spectroscopic features of the forward SRS while varying the bulk liquid temperature for the purpose of utilizing the enhancement phenomena for spectroscopic analysis of the local hydrogen-bonding network environment in liquid water. Even with the strong excitation condition, we found that the forward SRS sensitively reflected local changes of the hydrogen-bonding network environment. In addition, by utilizing the enhanced SRS spectra of the main peak in the OH stretching band at 3400 cm^{-1}, we investigated the local hydration environment in dilute ethanol solutions, which is still unclear at the molecular level and is an intriguing topic.[2]

Experimental Method

The experimental setup was as follows. The second harmonic of the pulsed Nd:YAG laser beam (EKSPLA2143B, wavelength 532 nm) was focused in water and aqueous solutions contained in a quartz cell. The pulse duration was 40 ps (fwhm), and the repetition rate was 10 Hz. The laser power was 1 mJ/pulse, and the focusing length of the focal lens was 100 mm; thus, the optical power density at the beam waist was estimated to be about 10^{13} W/cm^2 from the calculation for a Gaussian beam. The forward SRS was measured by a streak camera (Hamamatsu Photonics C4334) with a spectrometer (JASCO CT-25CS). The maximum time resolution was 15 ps, and the duration of the SRS was within at most 40 ps due to the pulse duration of the excitation beam. Thus, the signals were not time-resolved and they were accumulated on the time axis in the corresponding streak image. The SRS spectrum was accumulated 20 times in each measurement. The main difference between normal SRS experiments and ours was in the focusing condition. Usually, to avoid dielectric breakdown and to get sufficient interaction length, the laser beam is loosely focused by a focusing lens

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10.1021/jp021513q CCC: $22.00

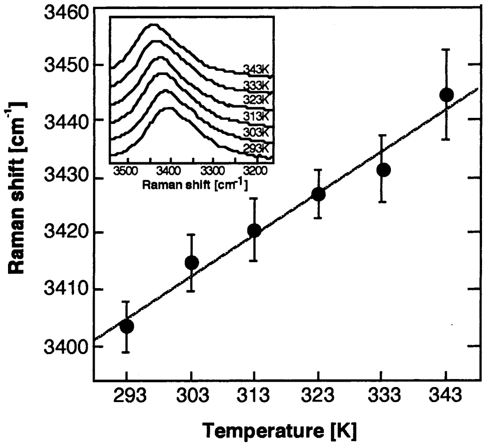

Figure 1. Temperature dependence of the peak position of the SRS spectrum. Peak position was measured at a single excitation event and the average of 20 shots was plotted at each temperature. The insert shows the corresponding SRS spectrum for each temperature.

with long focusing length (1−2 m). Instead, we adopted a strong focusing condition, which leads to the generation of many excess electrons (about 10^{20} number/cm^3) and plasma formation by a successive intense laser irradiation. The generated excess electrons at the beam waist of the excitation beam are considered to play an important role in inducing higher polarizability of the OH groups and enlarging the Raman cross-sections of water molecules.[9] Because excess electrons are more effectively extended in the backward region of the focal volume, the backward SRS spectrum is considered to be dominated by peaks attributed to the electron−OH groups interactions. On the other hand, in the forward region, effective growth of the excess electrons does not occur because the intensity of the excitation beam is remarkably reduced by the strong scattering due to many excess electrons in the backward region. Thus, the forward SRS spectrum, which is induced at the beam waist and grows in the forward region, is considered to mainly reflect the water molecules under normal environments based on its peak shift (3400 cm^{-1}) despite the strong and perturbing excitation condition.

Results and Discussion

To investigate whether the forward SRS sensitively reflects the slight change of the hydrogen-bonding network environments under ambient conditions, the temperature dependence of the SRS spectrum was measured while varying the temperature at first. It is generally thought that microscopic hydrogen-bonding network structure is altered by temperature changes. The more the temperature increases, the more breaking of the network structure proceeds. This environmental change increases the vibrational frequency of the OH stretching mode. Figure 1 shows the results. The temperature dependence of the peak shifts agrees with that observed in ordinary Raman spectra.[10] This result confirms that SRS spectra sensitively reflect the change of bulk liquid structure even under strong and perturbing excitation condition. In general, the intensity of the main peak increases more efficiently due to the stimulated (coherent) process in the SRS emission. This means that a stronger peak is more prominent, but the intensity of the weaker peak is reduced more, relatively speaking. In the ordinary Raman spectrum, a strong and broad shoulder peak at 3250 cm^{-1} is observed beside the main peak at 3400 cm^{-1} and it overlaps the main peak. However, in the SRS spectrum observed here, the main peak at 3400 cm^{-1} is selectively enhanced and this characteristic works favorably to investigate the slight change of the main Raman bands that represent the most probable hydrogen-bonding environment in liquid water.

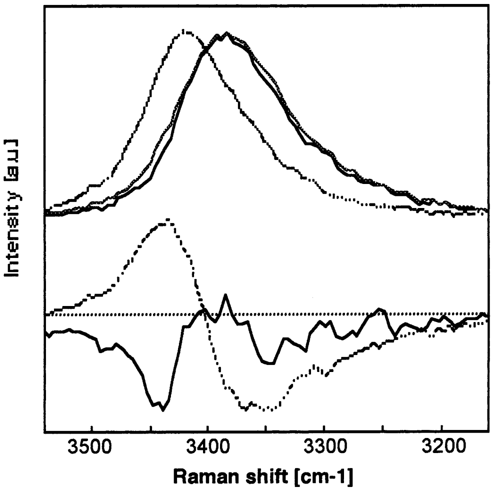

Figure 2. (a) Comparison of the SRS spectra in pure water (gray line), KCl 1 M solution (dotted line), and 2 mol % ethanol (about 5% in volume) solution (black line). To avoid shot-to-shot fluctuation of the signal intensity, the SRS signals were accumulated 20 times for each solution. Their intensities were normalized by the intensity at the peak position for convenience in comparing the peak shifts of these solutions. (b) Differential spectra of KCl (dotted line) and ethanol solution (black line) to pure water.

Next, to verify that the SRS reflects local structure changes of hydrogen-bonding network of aqueous solutions, we also measured the SRS spectra of 1 M KCl (about 2 mol %) and 2 mol % (about 5% in volume) ethanol solution. KCl is well-known as a structure-breaking solute, and it is expected to increase the number of strongly distorted and weakened hydrogen bonds, leading to the frequency shift of the OH stretching vibration to the higher side. On the other hand, the description of local environment water molecules surrounding ethanol molecules is still somewhat controversial at the molecular level, especially in dilute solutions. The water structure around the ethanol molecules has been investigated by many kinds of spectroscopic techniques from the viewpoint of hydrophobic hydrations. Previously, a normal Raman spectroscopic study,[11] neutron scattering measurements,[12] and small-angle X-ray scattering (SAXS) experiments[13] indicated that the network structure around ethanol molecules is not significantly perturbed in dilute ethanol solutions. On the other hand, infrared absorption spectroscopy,[14] low-frequency Raman measurements,[15] X-ray diffraction measurements, and mass spectra of water−ethanol clusters generated from dilute solutions[14,16] suggest that the self-association of ethanol molecules takes place accompanied by some degree of structural change of surrounding water even in the dilute ethanol solutions. Although the SRS observed here gives only the enhanced spectra around 3400 cm^{-1}, it is expected to sensitively reflect a slight change of the hydrogen-bonding network environment induced by the addition of a small amount of ethanol molecules. It should be noted that the contribution to the SRS intensity from the OH groups of methanol molecules at 3250 cm^{-1} is negligible here and this SRS characteristic enables us to obtain the information on the change of the hydrogen-bonded water network selectively.[17]

The SRS spectra of KCl and ethanol solution are shown in Figure 2. In the KCl solution, the Raman frequency of the SRS peak is significantly upshifted as expected. This feature indicates that the average strength of the hydrogen-bonding network is considerably weakened. This feature is consistent with previous

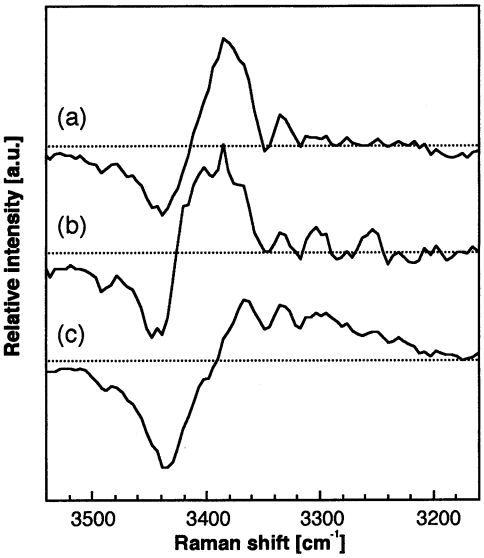

Figure 3. Difference spectra of ethanol solutions with (a) 1, (b) 2, and (c) 3 mol %. Each spectrum represents the accumulation of 20 SRS signals, and the intensity of each spectrum was normalized by integrated intensity in the wavelength range from 3000 to 3550 cm^{-1}. Each spectrum was obtained by subtracting the SRS spectra of pure water normalized in the same way.

conventional Raman measurements in terms of the frequency shift of the main peak.[18] This result also confirms that the SRS spectra surely reflect the local change of the hydrogen-bonding environment even under strong excitation conditions. To the contrary, the Raman frequency of the SRS peak of the ethanol solution (2 mol %) shows little change as compared to that of the KCl solution. This result indicates that the considerable part of the hydrogen-bonding network environment is not changed as compared to that in KCl solution. Thus, the little change in the frequency shift seems to be in accordance with those previous conventional Raman and neutron diffraction measurements.[11−13] However, the interesting point of our observation is that there seems to be a small but clear decrease of bandwidth, especially in the higher wavelength region as compared to that of pure water (Figure 2b).

To clarify the slight change in the bandwidth of the SRS spectra and to obtain further insight into the microscopic hydration environment of dilute ethanol solutions, we analyzed the change of the intensity distribution of the SRS spectra while varying the concentration of the ethanol molecules. It is well-known that the addition of a small amount of alcohol molecules induces volume contraction of the solutions.[19,20] The most remarkable decreases of the partial molar volume of ethanol have been observed from 0 to 3 mol %, independent of the temperature.[20] Detailed X-ray spectroscopic study also suggested that the self-association of ethanol molecules took place even in these dilute solutions.[14] Thus, we investigated the change of the intensity distribution of the SRS spectra in the range from 1 to 3 mol %. Figure 3 shows the difference SRS spectra of the 1−3 mol % ethanol solutions. We can observe the apparent intensity decrease in the higher wavelength region centered at 3440 cm^{-1}, even in the 1 mol % solution. This shape dip in intensity in the higher wavelength region is considered to be the main cause for the sharpening of the SRS peak of ethanol solutions. In contrast, the intensity ratio at around 3400 cm^{-1}, i.e., the main peak position of liquid water, is relatively increased. The sharp decrease on the higher frequency side indicates that some degree of reinforcement of hydrogen-bonding network structure takes place in dilute ethanol solution. If some enhancement of the “ordered” structure like ice or clathrate takes place, which is generally expected in hydrophobic hydration, a sharp increase at the corresponding lower frequency region is expected to be observed. On the lower frequency side (<3400 cm^{-1}), a slight increase of the SRS intensity also takes place over a wide wavelength region and this tendency becomes clearer with increasing the number of ethanol molecules. However, in the concentration range observed here, such a sharp increase is not detected on the lower frequency side. This result does not give evidence for the enhancement of the ordered icelike or clathratelike structure in the dilute ethanol solutions, which is generally expected in hydrophobic hydration. A previous IR study on the dilute ethanol solution reported that there was a decrease of gaslike quasi-free water molecules in dilute ethanol solutions from the relative decrease centered at 3600 cm^{-1}.[14] Although there is no comparable discussion focusing on the changes around the main peak at 3400 cm^{-1}, the decrease tendency in the ratio of weak hydrogen bonds observed here qualitatively accords with the result in the previous IR measurements. It should be noted, as referred to above, that the sharp decrease in the higher frequency side was clearly observed even in the 1 mol % ethanol solution as well as in more concentrated ones. From the viewpoint of hydrogen-bonding network environment, this result indicates that the strongly distorted and weak hydrogen bonds and/or defects in the hydrogen-bonding network are effectively reduced even by the introduction of a small amount of ethanol molecules.

Next, we consider the mechanism for the reinforcement effect on the hydrogen-bonding network induced by addition of a small amount of ethanol molecules. An ethanol molecule consists of a hydroxyl group and an apolar ethyl group. A hydroxyl group can participate in and rearrange the original hydrogen-bonding network structure of water molecules. On the other hand, it is considered that an ethyl group is small enough to exist in the cavity of hydrogen-bonding network structure. The SRS spectra indicate that no remarkable change derived form the hydrophobic hydration take place in the observed concentration range. Thus, we can consider that the most of the ethyl groups are located in the cavities of the hydrogen-bonded water network in dilute ethanol solution. From a viewpoint of structural change, a previously reported X-ray radial distribution function of an O−O pair exhibited the decrease of “linear” hydrogen bonds (LHB) at 2.85 Å and the appearance of the new peaks at 3.3 Å. These changes are quite similar to those observed in highly pressurized pure water where interstitial water molecules are increased.[14] The X-ray measurement indicates that some degree of rearrangement of the original hydrogen-bonding network takes place in dilute ethanol solutions. The X-ray measurement suggests that the reinforcement of the hydrogen-bonding network is achieved without recourse to the icelike LHB-based configuration. From a vibrational spectroscopic point of view, a bifurcated hydrogen bond (BHB)[21] and a cyclic trimer ring including another type of bifurcated hydrogen bond[22] are also considered to give a OH stretching band around 3400 cm^{-1} or less.[23] Although LHB is somewhat distorted in these BHB and cyclic trimer ring hydrogen bonds, they can also produce stable hydrogen-bonded network structures. As mentioned above, the sharp decrease on the higher frequency side indicates that some degree of reinforcement of hydrogen-bonding network structure surely takes place in dilute ethanol solution. Thus, as a mechanism of the enhancement of the network structure, we can consider that the hydroxyl groups are inserted into the defects and/or strongly distorted parts in the original hydrogen-bonding network and flexibly form stable network structures such as BHB or trimer ring, i.e., without recourse to icelike, volume-consuming configuration. Such a flexible reinforcement of local hydrogen-bonding network structure without utilizing tetrahedral, volume-consuming configuration may also contribute to the volume contraction that is remarkably observed in dilute ethanol solutions.

Summary

We investigated the forward SRS of liquid water under the strong focusing condition. The temperature dependence of the SRS indicated that it sensitively reflected the local change of hydrogen-bonding network environments under ambient conditions. We also applied the SRS to analyze the hydration structure in dilute ethanol solutions, focusing on the spectral change of the main peak around 3400 cm^{-1}. Although no remarkable shift of the peak frequency was observed, a sharp decrease on the higher frequency side and relative increase at the peak and in the lower frequency region was observed. These changes in the intensity distribution of the SRS spectra did not give direct evidence for the increase of the ordered icelike or clathrate structure, which is expected to be enhanced in hydrophobic hydration. However, the sharp decrease in the intensity distribution in the higher frequency region indicated that some reinforcement effect on the hydrogen-bonding network was induced by addition of a small amount of ethanol molecules. The participation of the hydroxyl groups of ethanol molecules into the original hydrogen-bonded water network is suggested to contribute to the reduction of defects and strongly distorted, weak hydrogen bonds in the original network, by forming additional hydrogen bonds or rearranging the network structure to a more stable one without recourse to the normal, ordered icelike tetrahedral configuration.

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