

Interaction of Excess Electrons with Water Molecules at the Early Stage of Laser-Induced Plasma Generation in Water

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Forward and backward stimulated Raman scattering (SRS) of OH stretching vibrations are measured when an intense 40 ps pulsed beam is focused into water. Characteristic features related to the interaction of OH groups with excess electrons generated by the strong laser irradiation are observed. The SRS spectra are indicative of the important role which excess electrons play in transient enhancement of the SRS at the initial stage of laser-induced plasma generation in water. The hydration structures around the excess electrons in water are also discussed.

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Laser-induced plasma (LIP) generation on or in condensed media has been extensively studied in various fields such as ultrafast x-ray pulse generation [1], material processing, and spectrochemical analysis [2]. Although the threshold of the beam intensity for the LIP generation has been well studied [3], its initial process in the picosecond region (i.e., after the beginning of laser irradiation and before the phase transition to the plasma state) is not clear. This is because the initial process is a complex phenomenon with various optical, electronic, and mechanical effects. In particular, the initial process of LIP generation in liquids is less well understood than that in solids because of the amorphous nature of the former.

Recently, we found that stimulated Raman scattering (SRS) of the OH stretching vibration was enhanced transiently in the early stage of LIP generation in water [4]. The average duration of the SRS was about 40 ps (FWHM) for a 12-ns excitation. The SRS was emitted before Rayleigh scattering of the pumping beam by plasma and plasma emission occurred [i.e., before the phase transition from liquid to plasma (gas) state]. However, the mechanism of the transient SRS enhancement is still not clear. The nanosecond-pulsed pumping beam used in the former study has an intensity fluctuation in the picosecond region. Thus, to obtain stable SRS signal and further information on the initial process of the LIP generation in water, much more controlled experiments in the picosecond region should be carried out.

In this paper, we studied the SRS of OH stretching vibrations when an intense 40-ps pulsed beam is focused into water. The intensity of the SRS is sensitive to the dielectric environment and the SRS spectrum in the OH stretching vibrational region is strongly related to the hydrogen-bonding structure [5]. Thus, it would be expected that the SRS is capable of giving detailed information on the initial process of LIP generation and the structural change of hydrogen-bonding network in the picosecond region. In this study, we also measured the backward SRS spectrum for the following reason. Excess

electrons, which are believed to be the initiator of plasma generation and growth, are generated when the power density of the pumping beam exceeds the threshold for their generation. Ordinarily, the optical power density at the beam waist is set to greatly exceed the threshold of plasma generation. Thus, it is expected that the region which has enough optical power density to generate the excess electrons widely extends both forward and backward from the beam waist of the pumping beam. However, since electrons strongly scatter the pumping beam, the effective generation and heating of excess electrons, which result in the LIP generation and growth, occur mainly in the backward region of the focal volume (i.e., the entering side of the pumping beam). Thus, it is expected that the backward SRS, which propagates in the backward region, reflects more sensitively changes of the dielectric environment and the structure of the hydrogen-bonding network in the initial process of LIP generation than the forward SRS. Consequently, we observed characteristic features which arose from the OH groups interacting with excess electrons in water in the backward SRS spectra. Using these characteristic features, we discuss the mechanism of transient SRS enhancement and the hydration structure surrounding the excess electrons in water.

A schematic illustration of LIP generation and forward and backward SRS emissions is shown in Fig. 1. The second harmonic of the pulsed Nd-YAG laser beam (EKSPLA2143B, wavelength 532 nm) was focused in water contained in a quartz cell. The quartz cell was 20 mm wide, 20 mm high, and 60 mm long in the optical axial direction. The laser power was 3.0 mJ per pulse and the pulse duration was 40 ps (FWHM). The repetition rate of the excitation laser pulse was 10 Hz and the beam diameter was 7 mm. The focal length of the focusing lens was 50 mm; thus the minimum beam waist in the focal region was estimated to be $3.5 \mu\text{m}$ from the calculation for a Gaussian beam of the same size, and the maximum optical power density was estimated as $2 \times 10^{14} \text{ W cm}^{-2}$. The SRS was emitted to both forward and backward

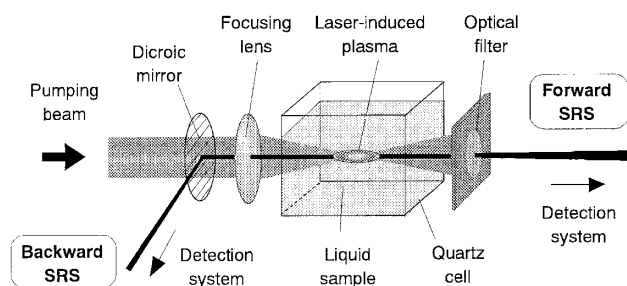


FIG. 1. Schematic illustration of LIP generation in water and enhanced SRS emissions in the forward and backward directions to the pumping beam.

directions with respect to the axis of the pumping beam. After eliminating the strong background of the pumping beam by an optical filter (cutoff wavelength 580 nm) or dichroic mirror, the SRSs in the forward and backward directions were measured by a streak camera (Hamamatsu Photonics C4334) coupled with a spectrometer (JASCO CT-25CS). The best time resolution of this system was 15 ps. We obtained the SRS signal without resolving the time course of the SRS spectrum because the SRS duration is too short (less than 40 ps) for the resolution of our detection system. All experiments were performed at room temperature (293 K) and ambient pressure (1 atm).

Figure 2 shows the SRS spectra in both directions. The Raman shift of the main peak in the forward SRS was 3400 cm^{-1} , which corresponded to the ordinary OH

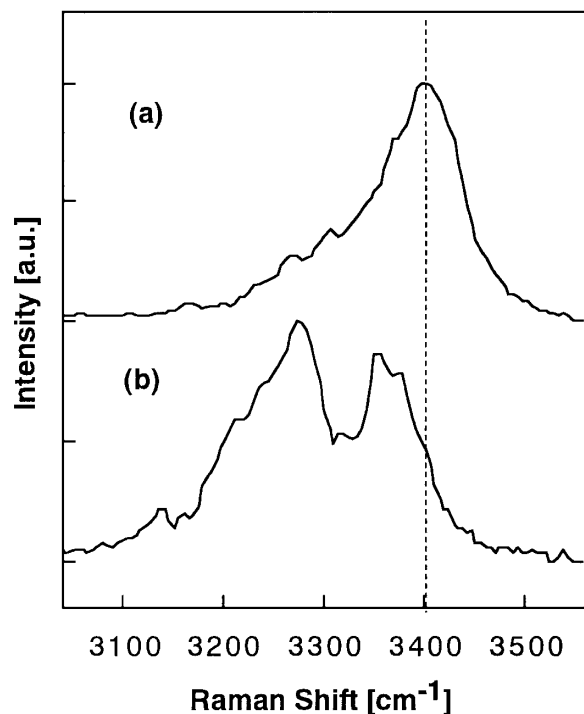


FIG. 2. SRS spectra in (a) the forward direction and (b) backward direction when the LIP was generated in water. The broken line in the figure indicates the Raman shift of water.

stretching vibration of water molecules in the liquid phase [6]. On the other hand, the backward SRS spectrum showed two characteristic peaks which were not observed in the forward one. The stronger peak appeared at 3270 cm^{-1} and the other at $3360\text{--}3380\text{ cm}^{-1}$. Since the ordinary OH stretching vibration in the liquid phase gives a peak centered at 3400 cm^{-1} as seen in the forward SRS, we considered that these two characteristic SRS peaks are derived from some specific interaction of OH groups which is usually not seen in water under normal conditions. At the very early stage ($< \text{several tens of picoseconds}$) of LIP generation, a large number of excess electrons (about $10^{20}/\text{cm}^3$) is generated as briefly mentioned above [7]. In addition, the Raman shifts of these characteristic peaks are found to be in good agreement with those of OH groups which interact with excess electrons in hydrated electron clusters [8]. From these results, the two characteristic peaks were assigned to the interaction of OH groups with excess electrons in water. In this spectrum, there are three interesting points. (1) The Raman shifts of the SRS peaks show good agreement with those observed in water hexamer anion $(\text{H}_2\text{O})_6^-$ [7]. Excess electrons in the liquid phase are believed to be trapped in a cavity space bounded by six water molecules in water [9,10]. This coincidence of the number of water molecules is consistent with the assignment that the characteristic peaks in the backward SRS are derived from the OH groups of water molecules interacting with the excess electrons in water. (2) Although there exist many other OH groups which participate in ordinary hydrogen bonds with other water molecules, the intensity of the two peaks appearing at 3270 cm^{-1} and $3360\text{--}3380\text{ cm}^{-1}$ dominates the spectrum. This indicates that the Raman cross section of OH groups interacting with excess electrons is considerably larger than that in ordinary hydrogen-bonding network in water. This feature provides important insight into the transient SRS enhancement during the initial process of LIP generation in water as discussed later. (3) The bandwidths of the two characteristic peaks are considerably broader than those observed in the water hexamer anion cluster $(\text{H}_2\text{O})_6^-$ (gas phase). This difference is usually seen between Raman spectra of the OH stretching vibration of water molecules in the liquid phase and in small clusters. In the liquid phase, unlike the gas or pseudo-gas-phase cluster, the environment of a water molecule varies widely due to the cooperative interaction with surrounding water molecules by hydrogen bonding. This cooperativity is characteristic and important for determining the structure and properties of water in the condensed phase. This wide variation of the cooperativity in the liquid phase results in broadening of Raman peaks of the OH stretching vibration [11]. Thus, this difference of the bandwidth is considered to be derived from strong cooperativity of OH groups in the liquid phase. It is worth noting that this feature is consistent with the result that the transient SRS

enhancement is observed before the phase transition from liquid to plasma.

First, we considered the mechanism of the transient SRS enhancement which occurs at the early stage of LIP generation and before phase transition from liquid to plasma. In studies of hydrated electron clusters, the OH groups interacting with excess electrons give strong resonant peaks [7]. Our results also show the same features. This is explained by the fact that a free electron is a very polarizable entity which induces a much larger polarizability of OH groups which bind to the electron by a hydrogen bond, resulting in enlargement of the IR absorption and/or Raman scattering cross section [7,12]. The SRS intensity depends on the Raman scattering cross section exponentially. Hence, we consider the large number of excess electrons generated in water at the early stage of LIP generation plays a key role for the transient SRS enhancement. The strong seed Raman light is generated in the focal volume by the interaction of OH groups binding to the excess electrons. Mixing of the seed light and the pumping beam induce the stimulated Raman scattering of the broad OH stretching vibration band of water. The seed Raman light grows toward, and then through, the surrounding bulk water region gaining in bandwidth and intensity. We consider that this is the generation and evolution mechanism of the transient strong SRS emission. The difference between forward and backward SRS spectra is also explained by the difference in the growth region of these SRS emissions. The generation and growth region of excess electrons extends mainly to the backward region as mentioned above. Thus, the backward SRS of the OH stretching vibration strongly reflects the interaction of the OH groups with the excess electrons. Regarding the short pulse duration of the SRS, once the following phase transition from liquid to the plasma (gas) has occurred, the phase matching condition for the SRS emission is strongly perturbed and the pumping beam is strongly scattered and cut off by the plasma. We consider that these are the main causes for the termination of SRS emission, which results in the short pulse duration of the SRS.

Second, we considered the hydration structure of water molecules surrounding the excess electrons in water. Since an individual water molecule does not bind excess electron, the localization of excess electron in water is believed to be a multibodied interaction [13]. In general, the Raman frequency of the OH stretching vibration decreases as the H atom of the OH group is held more strongly by hydrogen bonding. The SRS peak appearing at 3270 cm^{-1} is attributed to the OH groups which are more strongly bound to the excess electrons than those which give the peak at $3360\text{--}3380\text{ cm}^{-1}$. The appearance of two distinctive peaks indicates that there are at least two different interactions between OH groups and the excess electrons. Localization of excess electrons is accompanied by the breaking and rearrangement of the hydrogen-bonding network from the ordinary one. Since the hydrogen-bonding network is

more developed in heavy water than in ordinary water [14], we expected that comparison of the SRS spectra between water and heavy water would give additional information on the hydration structure around the excess electrons.

We therefore measured the SRS spectra of heavy water under the same experimental conditions as in water. Figure 3 shows the forward and backward SRS spectra of heavy water. In the backward SRS spectrum, the characteristic peak at about 2380 cm^{-1} is observed which is the counterpart of the peak appearing at 3270 cm^{-1} in water. Since the Raman scattering cross section of the OD stretching vibration of heavy water is relatively smaller than that of water [14], the characteristic SRS peak at 2380 cm^{-1} is also observed in the forward direction without interference from the broad band of OD stretching vibration in the liquid phase at 2490 cm^{-1} under our focusing conditions. One remarkable difference in the backward SRS spectra between water and heavy water is that the OD stretching vibration peak, which corresponds to the peak which appeared at $3360\text{--}3380\text{ cm}^{-1}$ in water, is almost absent in heavy water under our experimental conditions. In heavy water, since the hydrogen bonding network is more developed than in water as mentioned above [15], more energy is needed to break and rearrange the ordinary hydrogen-bonding framework than in water. Thus, the corresponding hydration structure is considered to require a larger degree of rearrangement of the ordinary

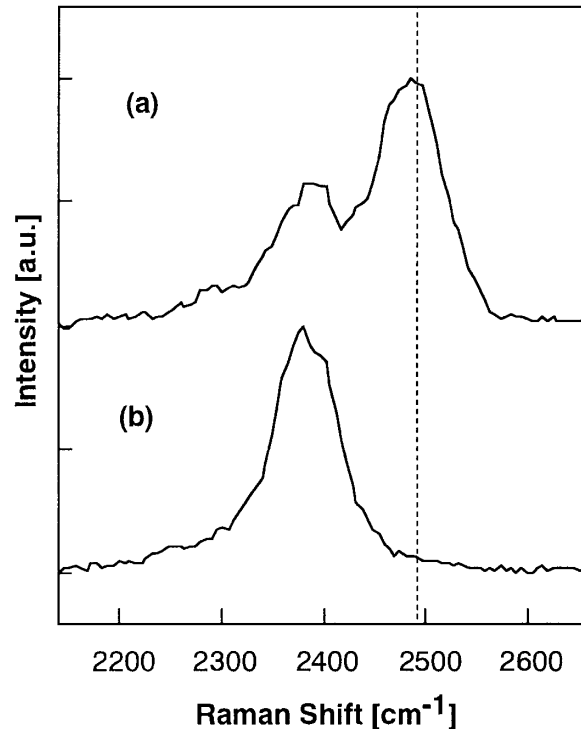


FIG. 3. SRS spectra in (a) the forward direction and (b) backward direction when the LIP was generated in heavy water. The broken line in the figure indicates the Raman shift of heavy water.

hydrogen-bonding framework to be formed than the structure which corresponds to the SRS peak at 3270 cm^{-1} . In addition, the higher Raman frequency of the SRS peaks at $3360\text{--}3380\text{ cm}^{-1}$ indicates that the interactions between OH groups and excess electrons in the former hydration structure are relatively weak compared to those in the latter which gives a SRS peak at 3270 cm^{-1} . Although further investigation is required for obtaining information on the detailed geometries of the hydration structures around the excess electrons in water, we can reasonably conclude that there are at least two distinctive hydration structures around excess electrons in water. One which corresponds to the SRS peak at 3270 cm^{-1} is capable of strongly binding the excess electron. The other which corresponds to the SRS peak at $3360\text{--}3380\text{ cm}^{-1}$ is capable of weakly binding the excess electron. It is worth mentioning that two distinctive structures which can bind excess electrons have been predicted theoretically in the water hexamer anion [9,13].

In conclusion, we focused a picosecond-pulsed beam with a sufficient power density to generate LIP into water and heavy water and observed the spectra of forward and backward SRS. Two characteristic peaks were observed in the backward SRS which were assigned to OH groups interacting with the excess electrons generated in water by the strong laser irradiation. The enhancement mechanism of the SRS at the early stage of LIP generation was discussed from the viewpoint of the enlargement of the polarizability of OH groups interacting with the excess electrons in water. The hydration structures around excess electrons were also discussed from comparison of the SRS spectra for water and heavy water. We inferred that there were at least two distinctive hydration structures which bind excess electrons in water. The ultrafast solvation dynamics of electrons in water has been extensively studied theoretically and experimentally in the visible region (see, for example, [16–19]). However, there are only a few investigations in the vibrational region such as the studies on hydrated electron clusters in the gas phase using photodetachment spectroscopy [8,20,21]. Thus, it is worth mentioning that the enhanced backward SRS spectrum in the vibrational region observed here allows us to measure directly the interaction of excess electrons with OH groups of water molecules and to obtain information on the hydration structure which binds excess electrons in the liquid phase. On the other hand, the enhanced forward SRS which propagates and reflects mainly ordinary bulk water surrounding the LIP generation region is also expected to give structural

information on water itself and water solutions. Further investigation and applications of these enhanced forward and backward SRS will be reported elsewhere [22].

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