Cluster-ion Ejection from IR-preheated Liquid Water through Ion Pair Created by OH Vibrational Excitation

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Ions, $OH^-(H_2O)_n$, were found to be ejected from a liquid beam of water under irradiation of Mid- and Near-IR lasers resonant to the fundamental and the fourth harmonic ($v_{OH} = 4$) of the OH-stretching mode of liquid water, respectively. Dependence of the ion intensity on a delay time between the two lasers reveals that locally preheated water by the Mid-IR laser helps ejecting $OH^-(H_2O)_n$ to a vacuum through an ion pair ($H^+\cdots OH^-$) created by the Near-IR laser.

It has been reported that hydrated clusters and ions are ejected from a liquid beam of an aqueous solution by vibrational excitation of water molecules in the liquid beam.[1–5] Recently, we have measured an excitation function (excitation spectrum) by detecting $H_3O^+(H_2O)_n$ and $OH^-(H_2O)_n$ ejected from a liquid beam of pure water (liquid-water beam) under irradiation of a Mid-IR (MIR) laser resonant to the fundamental OH-stretching mode ($v_{OH} = 1$) of liquid water, as a function of the laser wavelength. It has been shown that (1) an ion pair ($H^+\cdots OH^-$) is created by vibrational four-photon excitation of local structures having less anharmonic OH potentials and (2) then split into two separate ions which are ejected to a vacuum with accompanying water molecules as $H_3O^+(H_2O)_n$ and $OH^-(H_2O)_n$.[4] In the present study, we elucidated the mechanism of the ion ejection from a liquid-water beam in such a manner that (1) the liquid water is preheated by irradiation of a MIR laser resonant to the fundamental OH-stretching mode ($v_{OH} = 1$) of the liquid water, (2) the ion pair ($H^+\cdots OH^-$) is prepared by illuminating a Near-IR (NIR) laser resonant to the fourth harmonic ($v_{OH} = 4$) with a delay time from the irradiation of the MIR laser, (3) the ion ejection is assisted by disintegration of the liquid water caused by the preheating.

Commercially available ultrapure water (Kanto Chemical) placed in a jar was purged with He gas, sacked into an on-line degasser for removing He gas and supplied to an nozzle with an aperture of 20 µm in diameter by a pump at a stagnation pressure of 20 atm. The water was allowed to spout in a form of a liquid beam with the flow rate of 0.2 mL/min through the nozzle into a source chamber, which was evacuated down to 10^{-4}–10^{-5} Torr.[4] After traveling a distance of ≈2 mm from the nozzle, the liquid beam was irradiated by two pulsed lasers at the same position on the liquid beam with varying a delay time of firing the two lasers; one laser is resonated to the fundamental OH-stretching mode ($v_{OH} = 1$) of liquid water (MIR laser, 3000–3800 cm^{-1}, 6–12 mJ/pulse) and the other to the fourth harmonic of the OH-stretching mode ($v_{OH} = 4$) (NIR laser, 13514 cm^{-1}, 1–3 mJ/pulse). The crossing point of the liquid beam with the lasers was located in the first acceleration region of a reflectron time-of-flight (TOF) mass spectrometer. Ions ejected from the liquid beam were accelerated perpendicularly to both the liquid and the laser beams by a pulsed electric field synchronized with a NIR laser pulse and mass-analyzed by the TOF mass spectrometer.

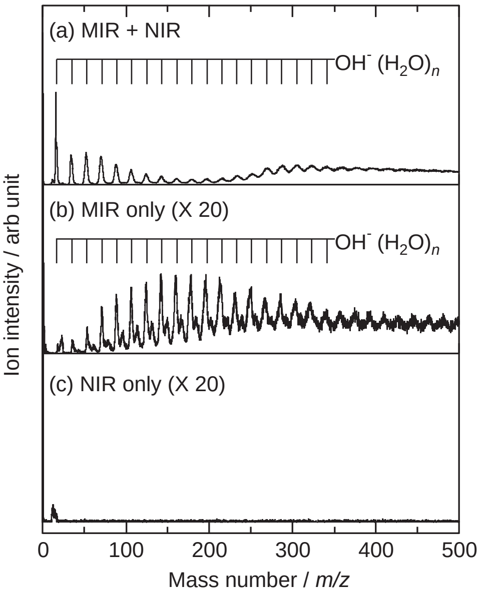

Figure 1. A mass spectrum of ions produced from a liquid-water beam by MIR-laser irradiation (3509 cm^{-1}, 12 mJ/pulse) followed by NIR-laser irradiation (13514 cm^{-1}, 3 mJ/pulse) with the delay time of 20 ns (panel a), by MIR-laser irradiation (panel b), an by NIR-laser irradiation (panel c). The ordinates of the panels b and c are magnified by 20 times while that of panel a remains unchanged.

Figure 1 shows a TOF-mass spectrum of negative ions ejected from a liquid-water beam under irradiation of a MIR laser (3509 cm^{-1}) followed by irradiation of a NIR laser (13514 cm^{-1}) with a delay time of 20 ns (panel a) and those obtained under mere irradiation of the MIR and the NIR laser (panels b and c, respectively). The main series of resolved peaks in the mass spectra are assigned to $OH^-(H_2O)_n$ ($n = 0$–26) (panels a and b). The intensity at higher mass numbers is assignable to $OH^-(H_2O)_n$ ($n = 0$–160), although the peaks are not resolved. As shown in panel b, one series of weak but discernible peaks are assigned to $HCO_3{}^-(H_2O)_n$ ($n = 0$–10), which result from carbon dioxide dissolved in the water. A weak broad peak assignable to free OH^- is only observed in a mass spectrum of ions produced by irradiation of the NIR laser (panel c).

Figure 2 shows the sum of the intensities of all of the ions ($OH^-(H_2O)_n$) ejected from a liquid-water beam under irradiation of the MIR laser and the NIR laser with the delay time of 20 ns and that under irradiation of the MIR laser, as a function of the wavenumber of the MIR laser in the range of 3000–

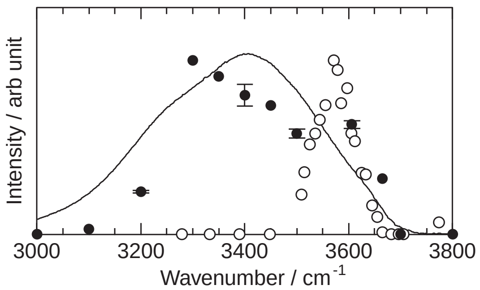

Figure 2. The sum of the intensities (●) of $OH^-(H_2O)_n$ produced from a liquid beam of water by irradiation of a MIR laser (3509 cm^{-1}, 12 mJ/pulse) and subsequent irradiation of a NIR laser (13,514 cm^{-1}, 2 mJ/pulse) with the delay time of 20 ns and the sum (○) by irradiation of the MIR laser (12 mJ/pulse), as a function of the wavenumber of the MIR laser. The solid curve represents an OH-vibrational absorption spectrum of liquid water. The spectra are normalized so that the peak of each spectrum has an equal intensity.

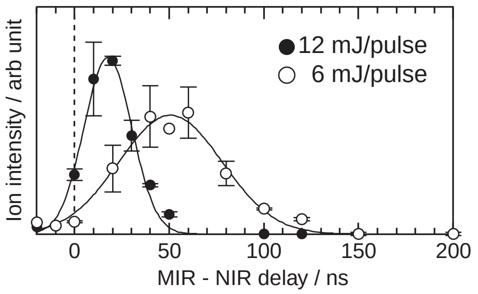

Figure 3. The sum of the intensities of $OH^-(H_2O)_n$ ($n =$ 0–160) produced by irradiation of a MIR laser (3509 cm^{-1}, 6 and 12 mJ/pulse) and a NIR laser (13,514 cm^{-1}, 2 mJ/pulse) onto a liquid-water beam as a function of the delay time from the MIR- to the NIR-laser pulses; both the lasers illuminate the same position. The power of the MIR laser was 12 mJ/pulse (●) and 6 mJ/pulse (○), and that of the NIR laser was 2 mJ/pulse for both cases. Solid curves are eye guides.

3800 cm^{-1} (excitation spectrum). The excitation spectrum obtained by irradiation of the MIR and the NIR lasers agrees fairly well in shape with an OH-vibrational absorption spectrum of liquid water, whereas the excitation spectrum measured by irradiation of the MIR laser is sharply peaked at 3600 cm^{-1}.[4]

Figure 3 shows the sum of the intensities of $OH^-(H_2O)_n$ ($n = 0$–160) ejected from a liquid-water beam under irradiation of the MIR laser and the NIR laser with varying the delay time from the MIR- to the NIR-laser pulses at two different powers of the MIR laser. The sum of the intensities peaks at the delay time of 20 ns when the power of the MIR laser is 12 mJ/pulse, while the peak shifts to the delay time of $\approx$50 ns when the power is lowered to 6 mJ/pulse. Any ions were hardly observed when the liquid-water beam was irradiated by the two lasers in reverse order.

Cluster ions, $OH^-(H_2O)_n$, are produced from a liquid-water beam under irradiation of the MIR laser and that of the NIR laser with a given delay time as follows: (1) the MIR laser serves to preheat the liquid water through resonant excitation of the OH-stretching vibration ($v_{OH} = 1$) of liquid water (see Figure 2) and subsequent transmission of vibrational energy to adjacent water molecules within $\approx$1 ps[6] (eq 1) and (2) the NIR laser serves to excite a water molecule in a hydrogen-bonded local network into an ion pair ($H^+\cdots OH^-$) which reacts further into H_3O^+ and OH^- due to a proton transfer from a neighboring water molecule (eqs 2 and 3).

$$H_2O\ (l) + h\nu_{MIR} \rightarrow H_2O\ (\text{preheated}), \tag{1}$$

$$H_2O\ (\text{preheated}) + h\nu_{NIR} \rightarrow (H_2O)_{m'}(H^+\cdots OH^-)(H_2O)_{n'}, \tag{2}$$

$$(H_2O)_{m'}(H^+\cdots OH^-)(H_2O)_{n'} \rightarrow H_3O^+(H_2O)_m + OH^-(H_2O)_n. \tag{3}$$

The preheating causes to create locally heated regions (hot spots) in the liquid water. After the irradiation of the MIR laser, the volume of the hot spots increases and finally makes the liquid water disintegrated within several tens ns.[5] Proton transfer (eq 2) is induced between hydrogen-bonded water molecules by excitation of the fourth harmonic of the OH-stretching vibration ($v_{OH} = 4$) of a water molecule before the disintegration as described in a later discussion. The energy of a NIR photon (13,514 cm^{-1}) is larger than that necessary for the proton transfer to proceed (12,500 cm^{-1}).[6] MIR multiphoton absorption does not contribute the production of the ions observed in panel a of Figure 1. The excitation spectrum for the production of $OH^-(H_2O)_n$ by irradiation of the MIR and the NIR lasers on a liquid-water beam agrees fairly well with the absorption spectrum of liquid water (Figure 2), whereas that produced by MIR multiphoton excitation (panel b of Figure 1) is sharply peaked at a high-wavenumber side of the absorption spectrum of liquid water.[4]

The delay-time dependence of the $OH^-(H_2O)_n$ intensity at a given laser power (see Figure 3) is explained by the following picture: (1) Splitting of an ion pair occurs in a region where hydrogen-bond networks are preserved, (2) this region happens to become a hot spot so that any separated ion pair is hardly recombined, and (3) the separated ions are ejected with accompanying water molecules to a vacuum. The delay time is interpreted as a characteristic time of creating the hot spots after illuminating the MIR laser. Naturally, the delay time is shortened at an increasing extent when the power of the MIR laser is increased, because the number of the hot spots increases with increasing the power of the MIR laser.

In conclusion, we elucidated the mechanism of ion ejection. The ion-ejection mechanism provides a basis for investigating local structures of liquid water by use of the infrared multiphoton ionization technique.

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