Formation and Detection of Large Neutral Clusters from Liquid Beam Surface by IR Laser Irradiation

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A continuous liquid flow of water in a vacuum (a liquid beam) was irradiated with an IR laser at 2.96 μm which is resonant to a vibration mode of liquid water related to the OH stretching vibration of H_2O. Large neutral water clusters, $(H_2O)_n$, were detected directly by a Daly-type detector without ionization. The velocity distribution determined from the flight-time distribution was found to be composed of fast and slow components, which are attributed to the water clusters ejected from the outermost region of the liquid surface and from the inside of the liquid, respectively.

Isolation of molecules from a solution to the gas phase is an important step for elucidating the behaviors of the molecules in the solution, because the molecules free of any ambient perturbation manifest the fundamental properties that the molecules themselves own. A variety of techniques has been developed for isolation of molecules in a solution. Electrospray is one of such techniques, by which molecules are introduced into a vacuum with a lower probability of decomposition. However, a sizeable portion of the isolated molecules are multiply charged, so that the intrinsic properties of the molecules are lost more or less.[1] Matrix-assisted laser desorption/ionization (MALDI) is an alternative method to isolate molecules in the matrix; the molecules thus isolated are readily ionized by photionization with laser irradiation.[2] In addition to these methods, molecules in a continuous liquid flow in a vacuum (liquid beam) are isolated by IR-laser desorption and subsequent IR-multiphoton ionization as demonstrated by Brutschy et al. (laser induced liquid beam ionization/desorption or LILBID).[3]

Recently, we have developed a method that molecules in a liquid beam are isolated from a beam of a liquid under irradiation of an IR laser having a wavelength resonant to a vibrational mode of the liquid.[4,5] In the present study, we applied this method to isolate water clusters from a liquid beam of water under irradiation of an intense IR laser having a wavelength resonant to a vibrational mode related to the OH stretching vibration of H_2O. The neutral water clusters were detected by collisional ionization on a metal surface, and the velocity distributions were measured. A bimodal velocity distribution observed was interpreted in terms of cluster ejection from different portions of the liquid beam.

A continuous laminar liquid flow (liquid beam) of a sample solution was introduced into a vacuum chamber from a nozzle having an aperture with 20 μm in diameter. A constant liquid flow was supplied by a pump designed for a liquid chromatograph. The flow rate was maintained at 0.2 mL/min. The source chamber was evacuated down to 10^{-5}–10^{-6} Torr by a 1200 L s^{-1} diffusion pump and a liquid N_2 trap in the presence of the liquid beam. Commercially available water (deionized and distilled) and aniline were used without further purification. After traveling a distance of 2 mm from the nozzle, the liquid beam was crossed with a 2.96-μm IR laser. The IR laser beam was generated by an INRAD IR – OPO system and was focused by a lens with a focal length of 775 mm. Neutral clusters ejected from the liquid beam under the IR laser irradiation were directly detected by a dynode-scintillator-photomultiplier detector (Daly multiplier). The neutral clusters were collimated by a 3 mm aperture which was placed at 25 mm apart from the liquid beam, and were allowed to collide with an aluminum surface mounted 1.65 m away from the liquid beam. Ionic species produced by the collision of the neutral clusters on the aluminum target floated up to ~ -20 kV against the ground were admitted onto the electrically grounded aluminized scintillator, and photons generated from the scintillator were detected by a photomultiplier. The detector is sensible to a neutral particle having the kinetic energy exceeding the work function of the aluminum target (4.28 eV) and the detection efficiency depends on the energy of the clusters. For instance, the size of a water cluster having a velocity of ~0.9, 1.5 and 2 km/s must exceed 56, 20 and 11, respectively. Actually, Even *et al* have reported that clusters with masses of more than 1000 *amu* ($n > 55$ for $(H_2O)_n$) in the molecular beam are ionized in collision with an aluminum surface at a velocity higher than 1 km/s.[6] The masses of the clusters were measured separately by a time-of-flight mass spectrometer, in combination with photoionization by a UV laser (270 nm),[4,5] where a trace amount of aniline was added to the liquid as a chromophor. The ions were detected by the same detector.

Figure 1 shows a flight-time distribution of neutral species produced by irradiation of a 2.96-μm IR laser on a liquid beam of

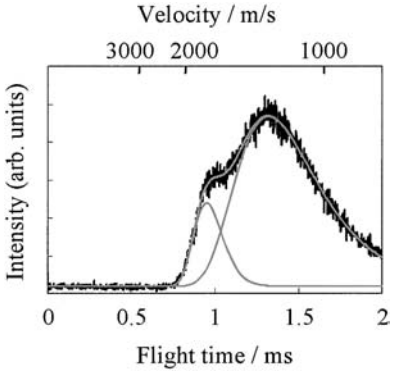

Figure 1. A flight-time distribution of neutral species produced by irradiation of an IR laser (5 mJ/pulse) on a liquid beam of water. Solid curves represent the flight-time distribution of fast and slow components.

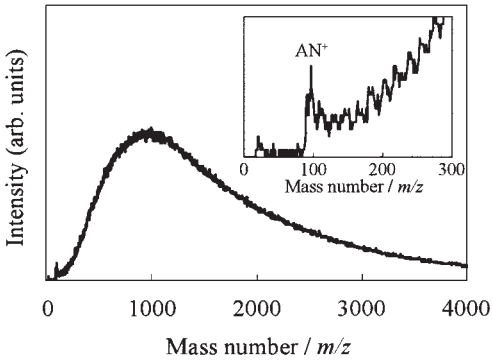

Figure 2. A mass spectrum of ions produced from a liquid beam of 0.01 M amiline aqueous solution by irradiation of an IR laser (wavelength of 2.96 μm) and a UV laser (wavelength of 270 nm). Powers of the IR and the UV lasers were 5 and 0.9 mJ/pulse, respectively.

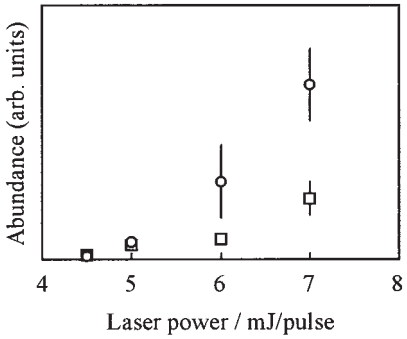

Figure 3. Abundances of fast (□) and slow (◯) components as a functiion of the incident IR laser power. The scale for the fast component is enlarged by a factor of 5.

water; the signal from the detector does not change with a retarding voltage up to 2 kV applied to the flight tube. The flight-time distribution gives the velocity distribution of the neutral species with velocities of 0.9–2 km/s. Figure 2 shows a mass spectrum of ions produced from a liquid beam of a 0.01 M aqueous solution of aniline. The observed species are assigned to hydrated aniline cluster ions, $AN^+ (H_2O)_n$ whose sizes, n, extend much larger than 56.

The neutral species actually detected are concluded to be large neutral water clusters, $(H_2O)_n$ ($n > 56$), because (1) water clusters having a velocity of 0.9 km/s and sizes larger than 56 can have more kinetic energy than the work function of the aluminum target and (2) a dominant amount of the cluster ions, $AN^+ (H_2O)_n$, possess sizes much larger than 56. In claim (2), one assumes that the size distribution of water clusters from a liquid beam of pure water is almost the same as that of water clusters containing one aniline molecule from a liquid beam of a diluted aqueous solution of aniline.

Figure 1 shows a bimodal velocity distribution consisting of fast and slow component. The abundances of the two components are evaluated from the flight-time distribution by deconvolution. (see solid curves in Figure 1). Figure 3 shows the abundances of the two components thus obtained as a function of the incident IR laser power. The abundances start to rise rapidly at a threshold laser power (~4 mJ/pulse) and increases with increase in the laser power. The high threshold value of the laser power implies that a neutral water cluster can only be released from the liquid surface when the incident IR laser power is high enough to rupture many hydrogen bonds, which hold the water cluster with the liquid surface.

It is conceivable that a water cluster is ejected from the outermost region or the inside of the liquid beam. In the former case, the cluster should possess a faster velocity (fast component) because it leave the surface with a much less extent of retardation by collision with ambient molecules. In the latter case, on the other hand, the cluster should possess a slower velocity (slow component) because of much more significant retardation of its velocity by collision with much dense ambient molecules. This scheme is supported by the laser-power dependence of the abundances of the fast and the slow components. The abundance of the slow component increase more significantly with increase in the laser power than the fast component as shown in Figure 3. This finding indicates that the more intense IR laser produces water clusters from the deeper region of the liquid, that is, slower water clusters are produced (the slow component).

In summary, neutral clusters, $(H_2O)_n$, with a wide size distribution are found to be produced by irradiation of a 2.96-μm IR laser onto a liquid beam of water, and a portion of large neutral clusters with $n > 56$ are detected directly by a Daly type detector without ionization. The detector provides a flight-time or a velocity distribution of neutral species arriving at it. The analysis of the bimodal flight-time distribution observed shows that the water clusters are ejected from the outermost region of the liquid surface providing the fast component of the bimodal velocity distribution and from the inside of the liquid providing the slow component.

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