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Preparation of Less Volatile Solute Molecules and Clusters in the Gas Phase through Selective Vibrational Excitation of Solvent in Liquid Beam of Solution

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Solute resorcinol molecules were isolated from a liquid beam of an aqueous resorcinol solution by employing selective vibrational excitation of solvent molecules in the solution under irradiation of an infrared (IR) laser. Resorcinol molecules and their clusters with solvent water molecules isolated in the gas phase were ionized by multiphoton excitation under irradiation of an ultraviolet (UV) laser, and ions thus produced were detected by mass spectrometry. The dependence of the ion intensities on the delay time from the IR to the UV excitation indicates that the neutral species are isolated in the gas phase through two different processes; one has a short characteristic time and the other a long characteristic time.

1. Introduction

As one of the efforts to explore a behavior of a molecule in a liquid medium, the molecule is isolated in the gas phase for scrutiny by use of the methods developed for studies of isolated molecules in the gas phase.[1−6] In this connection, we have developed a liquid beam technique in combination with UV laser (multiphoton ionization, MPI) and mass-spectrometric techniques.[7−15] Ions produced from solute molecules by MPI and ejected from the liquid beam are observed by mass spectrometry. Seemingly, the ions are found to be produced inside the liquid beam, and only the ions existing in a region much shallower than the electron escape depth are ejected into the gas phase by Coulomb repulsion. In this experimental configuration, the solute molecules are ionized by the UV laser and could react with the solvent molecules before they are ejected into vacuum. To isolate the solute molecules free from such complexity, we introduced a technique of resonant vibrational excitation of the solvent molecules by irradiation of an IR laser onto the liquid beam. It is expected that this selective excitation in conjunction with MPI facilitates isolation and detection of less volatile molecules vulnerable to heat treatment, etc., from the liquid beam in the gas phase.

In this paper, we report the development of this technique and application to isolation and detection of resorcinol from its aqueous solution, because resorcinol is highly soluble in water and has a low vapor pressure at room temperature. The mechanism of the isolation was investigated by UV laser (266 nm) ionization of species released after IR irradiation; IR-laser isolation−UV-laser ionization. The intensities of ions thus produced were measured by changing the delay time from the isolation to the ionization and/or the distance between the ionization region and the liquid beam.

2. Experimental Section

Figure 1 shows a schematic diagram of the experimental apparatus used in the present study, which consists of a liquid beam, IR and UV lasers, and a reflectron time-of-flight (TOF) mass spectrometer. A continuous liquid flow (liquid beam) was introduced downward into a vacuum chamber through an aperture with the diameter of 20 μm. The liquid was pressurized at 20 atm by a Shimadzu LC-6A pump designed for liquid chromatography, and the flow rate was maintained at 0.2 mL/min. A solution of resorcinol, m-$C_6H_4(OH)_2$, (Kanto Chemical Co., Inc.) in water (Kozakai Seiyaku Co., Ltd.) was used without further purification. The liquid beam was trapped on a surface cooled at 77 K at 10 cm downstream from the aperture. The chamber was further evacuated down to 10^{-5}−10^{-6} Torr by a 1200 L/s diffusion pump. Traveling a distance of 1 mm from the aperture, the liquid beam was crossed with the IR laser beam (the wavelength of 1.9 μm) at the first acceleration region of the TOF mass spectrometer. The IR laser is resonant with the first overtone of the OH vibration of solvent water molecules so that only the solvent molecules in the liquid beam are likely to be excited vibrationally by the IR laser. The IR laser beam was generated by focusing the fundamental (1.064 μm) of a Quanta-ray GCR-3 Nd:YAG laser into a Raman shifter filled with a 11 atm H_2 gas by a lens having a focusing length of 600 mm. The maximum output power (20 mJ/pulse) of the first Stokes line (1.9 μm) was attained with the input laser power of 400 mJ/pulse. The output of the 1.9 μm Stokes line was separated out of the fundamental of the Nd:YAG laser and other Raman lines by use of a wedge-shape $LiNbO_3$ prism, and was focused into a spot with a 1 mm diameter at the focusing point inside the liquid beam. The fourth harmonic of a Quanta-ray GCR-11 Nd:YAG laser (UV laser of 266 nm), was focused tightly into a spot with a diameter of 100 μm in diameter by a series of optical lenses with focal lengths of 250, −150, and 300 mm, and was illuminated outside the liquid beam. Neutral species, bare solute molecules, and clusters composed of solute and solvent molecules were produced in the gas phase by the IR-laser irradiation, and then were ionized through resonant two-photon excitation by the UV-laser irradiation. A Stanford Research Systems DG-535 digital delay pulse generator varied the timing of the UV laser irradiation delayed with respect to that of the IR-laser irradiation. Ions thus produced were accelerated by a pulsed electric field in the first acceleration

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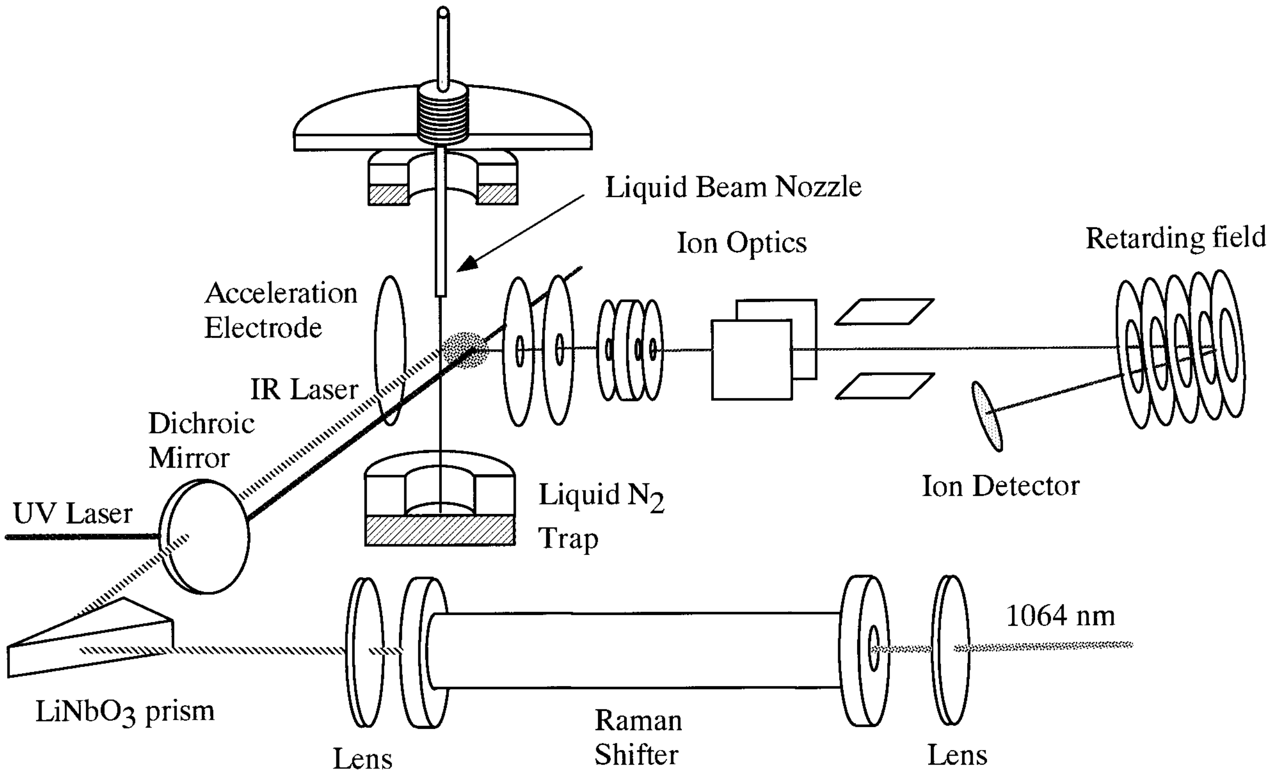

Figure 1. Schematic diagram of a liquid beam and a reflectron TOF mass spectrometer used in the present study. The liquid beam is crossed with an IR laser at 1 mm downstream from the nozzle. Neutral species isolated in the gas phase are ionized by a UV laser and mass-analyzed by a TOF mass spectrometer.

region of the time-of-flight (TOF) mass spectrometer, in the direction perpendicular to both the liquid and the laser beams. The ions were then steered and focused by a set of vertical and horizontal deflectors and an einzel lens. After traveling in a 1-m field-free region, the ions were reversed by the reflectron tilted by 2° off the beam axis and were detected by a Murata EMS-6081B Ceratron electron multiplier. Signals from the multiplier were amplified by a homemade 100 MHz preamplifier and processed by a Yokogawa DL 1200E digital oscilloscope. The mass resolution, $m/\Delta m$, was found to be more than 85 at $m = 200$ in the present experimental condition.

3. Results

Figure 2 shows TOF mass spectra of ions produced by irradiation of the laser beams onto a liquid beam of a 0.2 M resorcinol solution in water. Trace (a) shows the spectrum obtained with the IR laser being focused onto the liquid beam, while the UV laser illuminates a spot 0.4 mm outside the liquid beam. The powers of the IR and the UV lasers were 1 mJ/pulse and 100 μJ/pulse, respectively, along with the delay time of 0.2 μs. A series of ion peaks ($m/z = 110, 128, 146, 164...$) appears in the spectrum and is assigned to solvated resorcinol cluster ions, $C_6H_4(OH)_2^+(H_2O)_n (n = 1,2,3,...)$. Traces (b) and (c) show the spectra obtained by irradiation of either the IR or the UV laser under the conditions that trace (a) is obtained. As shown in traces (b) and (c), no ion is observed by irradiation of any single laser.[16−18] A small amount of $H^+(H_2O)_m$ observed is attributed to nonresonant ionization of water clusters existing in the gas phase (see traces (a) and (c)).

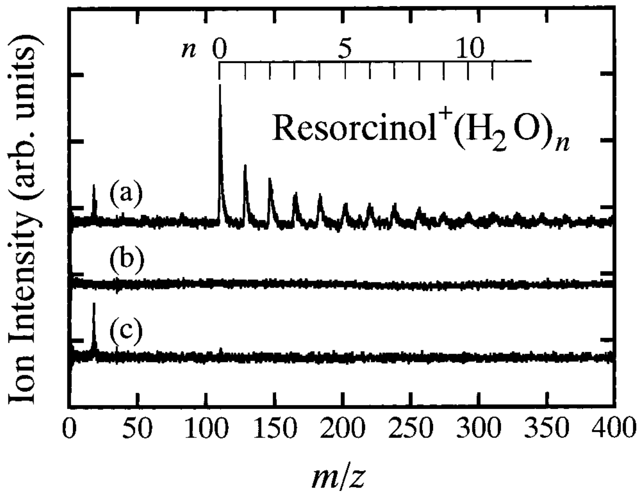

Figure 2. TOF mass spectra of ions produced by irradiation of IR and UV laser beams on a 0.2 M resorcinol solution in water. In trace (a), the IR laser was focused onto the liquid beam, and the UV laser illuminated 0.5 mm outside the liquid beam. Traces (b) and (c) show the spectra obtained by irradiation of either the IR or the UV laser with maintaining the laser and liquid beam arrangement employed for obtaining trace (a).

Figure 3 shows mass spectra at several different delay times. These mass spectra demonstrate that both the intensity and the size distribution of $C_6H_4(OH)_2^+(H_2O)_n$ change significantly with the delay time. No ion appears in the mass spectrum at 0 μs, because it takes more than 300 ns for the ejected clusters to arrive at the ionization region. Figure 4 shows the intensity of $C_6H_4(OH)_2^+$ and the total intensity of all the cluster ions, $C_6H_4(OH)_2^+(H_2O)_n$ ($n \geq 1$), as a function of the delay time (0−30 μs). In the delay times shorter than 3 μs (early-time domain), both the bare resorcinol ion, $C_6H_4(OH)_2^+$, and the cluster ions, $C_6H_4(OH)_2^+(H_2O)_n$, are observed, but in the delay times longer than 3 μs (late-time domain) only the bare resorcinol ion is observed. As the delay time increases, the total intensity of all the cluster ions observed reaches the maximum at 0.3 μs and decreases rapidly, while $C_6H_4(OH)_2^+$ has two maxima at 0.3 and 10 μs.

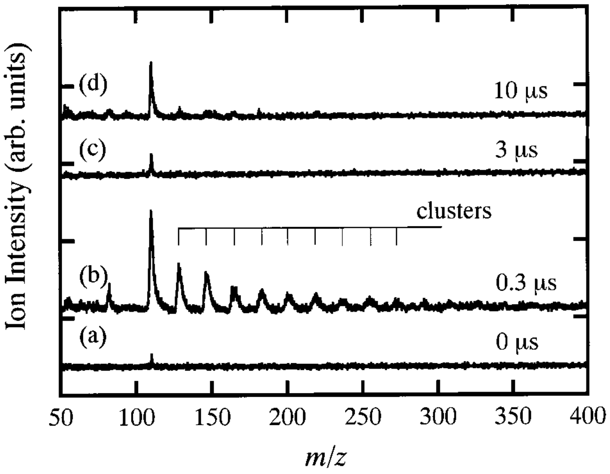

Figure 3. Mass spectra measured at various delay times from IR-laser to UV-laser irradiation. The delay times are 0, 0.3, 3, and 10 μs for traces (a), (b), (c), and (d), respectively. The observed cluster ions are assignable to $C_6H_4(OH)_2{}^+(H_2O)_n$ ($1 \leq n \leq 10$).

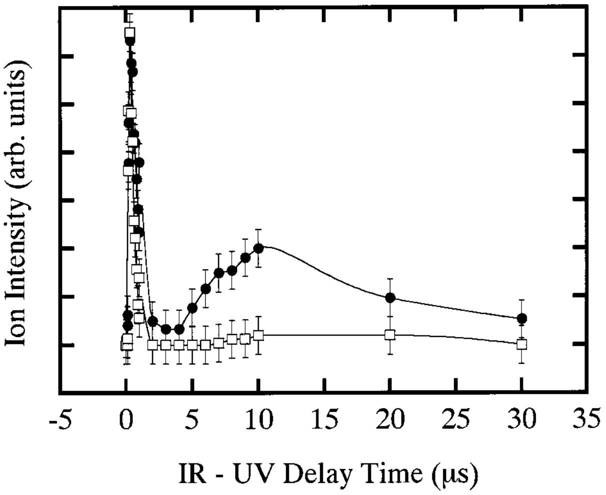

Figure 4. The intensity of $C_6H_4(OH)_2{}^+$ and the total intensity of $C_6H_4(OH)_2{}^+(H_2O)_n$($n \geq 1$) measured as a function of the IR−UV delay time (0−30 μs). Solid and open circles represent the intensity of $C_6H_4(OH)_2{}^+$ and the total intensity of $C_6H_4(OH)_2{}^+(H_2O)_n$ ($n \geq 1$), respectively. The sharp peak profile (early-time domain) and the broad peak profile (late-time domain) exhibit maxima at 0.3 and 10 μs, respectively.

4. Discussion

4.1. Isolation and Ionization. As described previously, $C_6H_4(OH)_2{}^+$ and $C_6H_4(OH)_2{}^+(H_2O)_n$ ($n = 1,2,3,...$) are produced, only when the IR laser irradiates the liquid beam of an aqueous solution of resorcinol and the UV laser does outside the liquid beam at a certain delay time after the IR laser irradiation. Although cluster ions such as $C_6H_4(OH)_2{}^+(H_2O)_n$ are produced by irradiation of a single UV laser directly onto the liquid beam, the cluster ions observed do not fall into this category, because the UV laser illuminates outside the liquid beam, so that there is no chance for molecules in the liquid beam to be ionized. These facts ensure that neutral clusters composed of resorcinol and water molecules are isolated in the gas phase by the IR laser, and then are ionized by the UV laser. Namely, a neutral cluster, $C_6H_4(OH)_2(H_2O)_m$, is isolated through selective vibrational excitation of solvent H_2O molecules by the IR laser irradiation, and is ionized to $C_6H_4(OH)_2{}^+(H_2O)_n$ by the UV laser irradiation. Several solvent H_2O molecules may evaporate after the ionization to release excess energy generated in the course of photoionization. In summary, $C_6H_4(OH)_2{}^+(H_2O)_n$ ($n \geq 1$) is produced as

$$C_6H_4(OH)_2(s) + h\nu_{IR} \rightarrow C_6H_4(OH)_2(H_2O)_m(g) \quad (1)$$

$$C_6H_4(OH)_2(H_2O)_m(g) + h\nu_{UV} \rightarrow C_6H_4(OH)_2{}^+(H_2O)_n(g) + (m - n)H_2O \quad (2)$$

where (s) and (g) represent species in the solution and in the gas phase, respectively. On the other hand, the precursor of $C_6H_4(OH)_2{}^+$ is a bare resorcinol molecule, $C_6H_4(OH)_2$, and/or a cluster with water molecules, $C_6H_4(OH)_2(H_2O)_k$. The mass-spectrometric measurements cannot alone definitely specify the number of H_2O molecules in the precursor. It is at least clear that the precursor contains a lower number of H_2O molecules than the precursor of $C_6H_4(OH)_2{}^+(H_2O)_n$ does.[19] As discussed above, a series of $C_6H_4(OH)_2{}^+(H_2O)_p$ ($0 \leq p \leq k$) is produced by photoionization of $C_6H_4(OH)_2(H_2O)_k$. Evidently, the bare resorcinol ion, $C_6H_4(OH)_2{}^+$, is produced differently from the cluster ions, since only the bare resorcinol ion is produced in the late-time domain (see Figure 3d). Under these circumstances, the absence of observed $C_6H_4(OH)_2{}^+$ ions solvated with water molecules leads us to suggest that the precursor of $C_6H_4(OH)_2{}^+$ is the bare molecule, $C_6H_4(OH)_2$.

4.2. Formation Processes of Molecules and Clusters. As shown in Figure 4, two different intensity-delay time profiles are observed, indicating two different ejection processes, which possess short and long characteristic times; an early-time domain for the production of solvated clusters, $C_6H_4(OH)_2(H_2O)_m$ ($0 \leq m \leq 10$), vs a late-time domain for the production of a bare resorcinol molecule, $C_6H_4(OH)_2$.

Our preliminary experiment shows that $C_6H_4(OH)_2(H_2O)_m$ in the early-time domain are generated shortly after the laser irradiation with having an average velocity of 1300 ± 100 ms^{-1}, while $C_6H_4(OH)_2$ in the late-time domain with having an almost thermal velocity (400 ± 300 ms^{-1}). As shown in Figure 4, the peak time (0.3 μs) of $C_6H_4(OH)_2{}^+(H_2O)_n$ in the early-time domain is predicted by the average velocity of $C_6H_4(OH)_2(H_2O)_m$ with considering the position of a UV laser spot, which is located 0.4 mm outside the liquid beam. The peak width of 500 ns in the early-time domain implies that ejection of the solvated clusters, $C_6H_4(OH)_2(H_2O)_m$, continues for less than 500 ns. Applying a similar argument for ejection in the late-time domain, one would then predict a peak time of 2 μs by assuming that the velocity of $C_6H_4(OH)_2$ follows the Maxwell−Boltzmann law at the local temperature of the beam estimated to be equal to 300 K with a most probable velocity of 200 ms^{-1}. Contrary to this prediction, the peak time in the late-time domain is observed to be at 10 μs. This difference with the prediction indicates that $C_6H_4(OH)_2$ in the late-time domain continues to evaporate with a thermal velocity from the liquid beam for more than 10 μs. The broad peak width in the late-time domain also implies that ejection of $C_6H_4(OH)_2$ continues for 10 μs. In summary, $C_6H_4(OH)_2(H_2O)_m$ in the early-time domain is liberated from the liquid surface right after the IR laser irradiation with a relatively high velocity, while in the late-time domain, $C_6H_4(OH)_2$ continues to be ejected for ~10 μs with an almost thermal velocity.

The nascent solvated clusters, $C_6H_4(OH)_2$ $(H_2O)_m$, produced in the early-time domain dissociate to dissipate the internal energy and become stable as they fly away from the liquid beam (evaporative cooling). According to our preliminary measurement on the change of the cluster-size distribution with the delay time and a distance between the liquid beam and the photoionization region, less than one water molecule seems to evaporate from the nascent clusters before ionization. This result indicates that the internal energies of the clusters are in the order of 10^{-1} eV. Namely, the clusters produced in the early-time domain are internally cold, while they have super-thermal velocities.[17] On the other hand, the bare resorcinol molecules produced in the late-time domain are regarded to be internally hot, but have a thermal velocity.

These two formation processes are related to equilibrium and nonequilibrium processes: When the IR laser illuminates a surface of the liquid beam, $C_6H_4(OH)_2(H_2O)_m$ are removed from it before establishment of thermal equilibrium. It seems that the clusters are removed outward at the liquid surface (boundary region) by a compression wave, resulting from vibrational excitation of the solvent molecules by the IR laser irradiation. Actually the clusters (in the early-time domain) gain a velocity (1300 ms^{-1}) as large as the velocity of sound in the solution. On the other hand, the bare molecules in the late-time domain result from evaporation of the solvent molecules in the vicinity of the solute molecules after the excitation energy is completely thermalized. Therefore, only the bare molecules, which have thermal translational energy, are isolated in the gas phase.

5. Conclusions

The method for preparation of less volatile molecules and their clusters in the gas phase was developed by selective vibrational excitation of solvent molecules in a liquid beam of a solution under irradiation of an IR laser. The neutral species thus isolated into the gas phase were ionized under irradiation of a UV laser, and identified by mass spectrometry. This novel method was successfully applied to a liquid beam of an aqueous solution of resorcinol. It is anticipated that this method is applied to large molecules, such as those of biological importance.

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