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ARTICLES

Formation of Ca^+ $(EtOH)_m$ from Alcohol Solutions of $CaCl_2$

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A continuous liquid flow of a calcium chloride ($CaCl_2$) solution in ethanol (EtOH) in a vacuum (a liquid beam) was irradiated with a 266 nm laser, and ions ejected from the surface following multiphoton ionization via the CTTS (charge transfer to solvent) band of Cl^- were observed by a time-of-flight mass spectrometer. A variety of core ions (Ca^+, $CaOEt^+$, $CaOH^+$, $CaCl^+$, H^+, etc.) are formed by reactions involving Ca^{2+}, solvated electrons, and solvent molecules after the CTTS excitation by the laser irradiation and are ejected into vacuum with several accompanying alcohol molecules. The proposed mechanism is verified by the change of the ion intensity with introduction of an electron scavenger, $CHCl_3$, in the solution. The cluster ion, $Ca^+(EtOH)_m$, remains intact for $m < 3$, while it dissociates into $CaOEt^+(EtOH)_{m-1}$ for $m \geq 3$. This size-dependent dissociation is simply explained by the energetics.

1. Introduction

Since the first discovery of solvated electrons in a sodium-containing liquid ammonia, their fundamental features in various liquids have been unveiled gradually through intensive and systematic investigations for many years.[1−13] They are able to reduce selectively aromatic into unsaturated hydrocarbons in the presence of alcohol, which serves as a hydrogen donor.[14] In addition, a microscopic picture of reactions involving solvated electrons has been constructed by a variety of methods: pulse radiolysis, laser excitation, etc. In the radiolysis of liquid water, for example, solvated electrons generated are found to react simultaneously with produced species, H_3O^+ and OH, into H_2O + H and OH^- [15], respectively. Reactions of this kind have been reported in alcohol solutions, and typically alkoxide anions are produced.[15,16] The alkoxide formation is confirmed by studies on laser-induced electron transfer for ethoxide formation in ethanol containing solvated electrons.[17,18] Similar products are detected in reactions of solvated electrons in a variety of liquid solutions.[15] In general, solvated electrons in solutions contribute greatly to reduction of solute molecules as well as solvent molecules. Pulse radiolysis studies on an aqueous solution of a divalent salt, MX_2, have revealed that M^{2+} is reduced to M^+ by solvated electrons produced by the radiolysis.[15]

Evidently, solvated electrons in different local structures of a solution react very differently. In other words, the reactivity of the solvated electrons could be controlled by varying the local structure. In this respect, a cluster medium provides a unique opportunity for examining the influence of the local structure on the reactivity, since the local structure varies characteristically with the size and the structure of the cluster medium. It has been shown that in a cluster medium a metal atom, M, is ionized to be M^{2+} whose electron(s) liberated from M is delocalized in the medium; Sr in an ammonia cluster ion has the form $[Sr(NH_3)_m]^+$, where one electron is delocalized on $(NH_3)_m^-$.[19] A liquid surface also provides a specific local structure, where solvated electrons are not completely solvated with solvent molecules, but not many studies have been reported so far, probably because of difficulty of preparing a liquid surface in a vacuum. In this connection, the liquid beam technique is one of the most appropriate tools for dealing with such a problem,

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because it provides a clean liquid surface in a vacuum and facilitates the use of highly sensitive spectroscopic techniques employed in a vacuum.[20-27]

By using this technique, the following experiment is conceivable. A divalent ion, M^{2+}, on a solution surface interacts with solvated electrons produced by laser irradiation and its surrounding solvent molecules. The ionic species thus produced and ejected from the surface is characterized by a time-of-flight mass spectrometer. In the present paper, ions produced by irradiation of a UV laser on a liquid beam of a $CaCl_2$ solution in ethanol were measured by a time-of-flight mass spectrometer. The mechanism on a reaction of Ca^{2+} with solvated electrons in the vicinity of the solution surface was investigated by addition of an electron scavenger, $CHCl_3$.

2. Experimental Section

The apparatus employed in the experiment (a liquid beam and a time-of-flight mass spectrometer, etc.) has been described in detail previously.[20] An overview of the apparatus is described along with the details relevant to the present experiment. A continuous laminar liquid flow of an ethanol solution of $CaCl_2$ 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 Shimadzu LC-6A pump designed for a liquid chromatograph. The flow rate was maintained at 0.2 mL/min with a pressure of typically 20 atm inside the nozzle. The diameter of the liquid beam was measured to be 20 ± 1 μm by an optical diffraction method.[26] The velocity of the liquid beam was measured by use of an inductive detector detecting the photoions remaining in the liquid beam.[27] The velocity of the liquid beam thus measured agreed with the flow rate of the liquid. The results show that the liquid beam is a continuous laminar liquid flow with a diameter of $\sim$20 μm. The liquid beam surface is calculated to be cooled by $\sim$10 K at the region where the measurement is performed. The source chamber was evacuated down to 10^{-5}–10^{-6} Torr by a 1200 L s^{-1} diffusion pump and a cryopump cooled 77 K during injection of the liquid beam.

After traveling a distance of 5 mm from the nozzle, the liquid beam was crossed with the fourth harmonics of the Qanta-ray GCR-11 Nd:YAG laser (266 nm) in the first acceleration region of a reflecron TOF mass spectrometer. The laser power (400 μJ/pulse) was monitored by a LAS PM-200 energy meter. The laser was focused onto the liquid beam by a lens with a focal length of 450 mm.

The mass-to-charge ratios, m/z, of the ions produced in the gas phase were analyzed by the TOF mass spectrometer as follows. Ions ejected from the liquid beam were accelerated by a pulsed electric field in the first acceleration region in the direction perpendicular to both the liquid and the laser beams with a delay time from the moment of the photoionization. The delay time was set to be 1 μs in order to minimize the line widths of the mass peaks. The mass resolution was found to be typically 200 at $m/z = 200$. The ions were then steered and focused by a set of vertical and horizontal deflectors and an einzel lens. The reflectron provides a reversing field tilted by 2° off the cluster-ion beam axis. After traveling a 0.5 m field-free region, a train of spatially mass-selected ions were detected by a Murata EMS-6081B Ceratron electron multiplier. Signals from the multiplier were amplified and processed by a Yokogawa DL 1200E digital oscilloscope based on an NEC 9801 microcomputer. Commercially available ethanol and $CaCl_2$ ($>$99.5%) were used without any further purification.

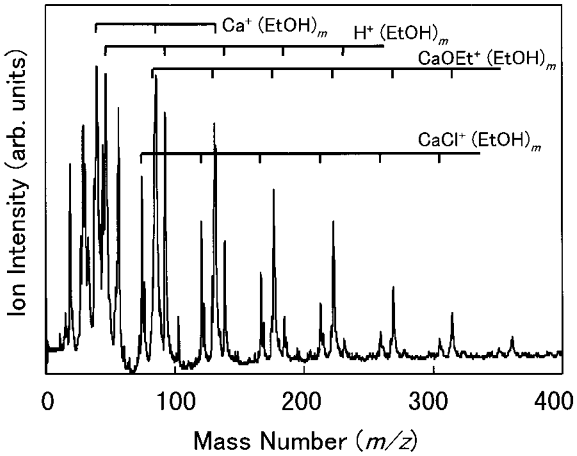


Figure 1. Mass spectrum of ions produced by irradiation of a 266 nm laser on a liquid beam of a 0.1 M $CaCl_2$ solution in ethanol.

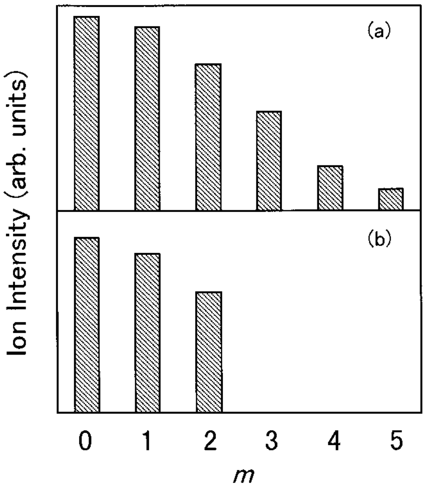


Figure 2. Cluster size distributions of $CaOEt^+(EtOH)_m$ (panel a) and $Ca^+(EtOH)_m$ (panel b).

3. Results

Figure 1 shows a mass spectrum of ions produced by irradiation of a 266 nm laser on a liquid beam of a 0.1 M $CaCl_2$ solution in ethanol. Peaks in the mass spectrum are assigned as $Ca^+(EtOH)_m$ ($m = 0$–2), $CaOEt^+(EtOH)_m$ ($m = 0$–6), $CaOH^+(EtOH)_m$ ($m = 0$–1), $CaCl^+(EtOH)_m$ ($m = 0$–6), and $H^+(EtOH)_m$ ($m = 1$–6). The mass assignment was confirmed by replacement of ethanol with methanol (MeOH) or n-propanol (n-PrOH). By this replacement, the mass of each cluster ion containing m ethyl groups (Et) was found to shift by $14m$; $m/z = 14$ corresponds to the mass difference between the methyl group and the ethyl group and the ethyl group and the n-propyl group. Figure 2 shows the cluster size distributions of $CaOEt^+(EtOH)_m$ (panel a) and $Ca^+(EtOH)_m$ (panel b). The intensities of $CaOEt^+(EtOH)_m$ and the other cluster ions appear to decrease monotonically with an increase in the number of the solvent molecules up to $m = 6$. On the other hand, $Ca^+(EtOH)_m$ gradually decreases in intensity until $m = 2$ and vanishes above it, as m increases. Similarly, the maximum number of the solvent molecules included in $Ca^+(ROH)_m$ was found to be 2 for both methanol and n-propanol. A drastic decrease in the intensity of $Mg^+(EtOH)_m$ is also observed between $m = 2$ and 3 for a 0.1 M $MgCl_2$ solution in ethanol.

Figure 3 shows the mass spectra of ions produced by irradiation of a 266 nm laser on a 0.1 M $CaCl_2$ solution in ethanol (panel a) and a 0.1 M $CaCl_2$ solution in a mixture of 3

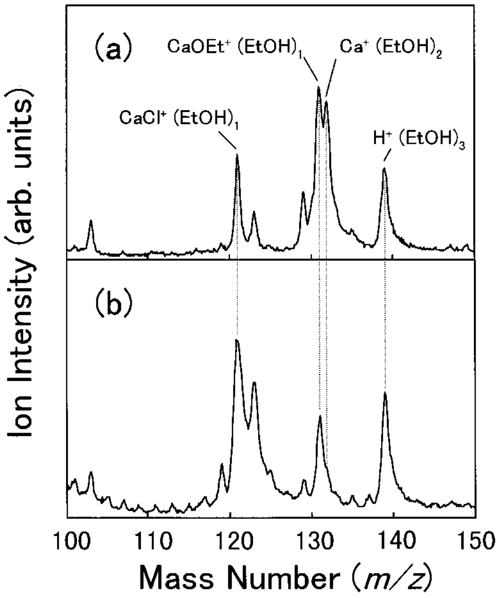


Figure 3. Mass spectra of ions produced by irradiation of a 266 nm laser on a 0.1 M $CaCl_2$ solution in ethanol (panel a) and a 0.1 M $CaCl_2$ and 3 M chloroform ($CHCl_3$) solution in ethanol (panel b).

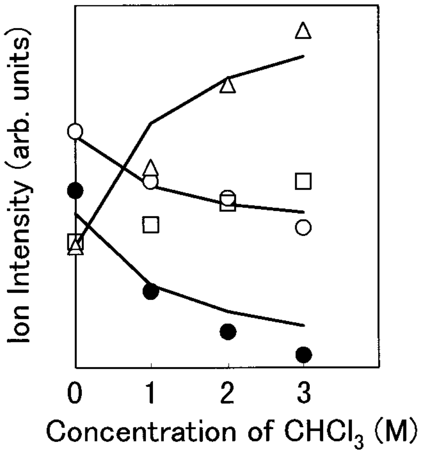


Figure 4. The intensities of $Ca^+ (EtOH)_2$ (●), $CaOEt^+ (EtOH)_1$ (○), $CaCl^+ (EtOH)_1$ (△), and $H^+ (EtOH)_3$ (□) as a function of the concentration of $CHCl_3$ in the 0.1 M $CaCl_2$ solution in ethanol. The solid curve represents the prediction based on the model calculation.

M chloroform ($CHCl_3$) in ethanol (panel b) in the range between $m/z = 100$ and 150. By addition of $CHCl_3$, the peak of $Ca^+(EtOH)_2$ vanishes and the peak of $CaOEt^+(EtOH)_1$ slightly decreases in intensity while the peaks of $CaCl^+ (EtOH)_1$ and $H^+ (EtOH)_3$ apparently increase in intensity.

Figure 4 shows the intensities of $Ca^+(EtOH)_2$, $CaOEt^+(EtOH)_1$, $CaCl^+(EtOH)_1$, and $H^+(EtOH)_3$ as a function of the concentration of $CHCl_3$ in the 0.1 M $CaCl_2$ solution in ethanol. The peak of $Ca^+(EtOH)_2$ and that of $CaOEt^+(EtOH)_1$, or the peak of $CaCl^+(EtOH)_1$ and that of the neighboring peak, overlap each other. Therefore, the intensities of these ions are obtained by deconvolution of the overlapping peaks, on the assumption that the shape of $Ca^+(EtOH)_2$, $CaOEt^+(EtOH)_1$, and $CaCl^+(EtOH)_1$ peaks is the same as that of $H^+(EtOH)_3$ peak, which is free from peak overlapping. The intensities of $Ca^+(EtOH)_2$ and $CaOEt^+(EtOH)_1$ decrease, and those of $CaCl^+(EtOH)_1$ and $H^+(EtOH)_3$ increase as the concentration of $CHCl_3$ increases.

4. Discussion

4.1. Coulomb Ejection Scheme. A solute molecule, $CaCl_2$, in the ethanol solution is dissociated into $CaCl^+$ and Cl^- and further into Ca^{2+} and $2Cl^-$. There is a UV absorption band (the absorption maximum at 185 nm) associated with electron transfer from Cl^- to the solvent, which is known as CTTS (charge transfer to solvent) band.[29] Even at the wavelength of the excitation laser (266 nm), the absorption coefficient is sufficiently large (more than 0.06 $mol^{-1}\ dm^3\ cm^{-1}$) so that Cl^- is excited into the CTTS state by irradiation of the 266 nm laser and releases one electron as a solvated electron, e_s^-. Then, this solvated electron is ejected into vacuum as a free electron by absorbing one more photon in the same pulse duration. These processes are expressed as

$$Cl^-(sol) + h\nu \rightarrow Cl^{-CTTS}(sol) \rightarrow Cl\ (sol) + e_s^-\ (sol) \quad (1)$$

$$e_s^-\ (sol) + h\nu \rightarrow e_f^- \quad (2)$$

where e_f^- is a free electron and (sol) represents solution. A time-resolved study on photodetachment dynamics of I^- in solution has recently been performed by Kloopfer et al.[30] An electron freed from I^- excited in the CTTS state is trapped in the solvent within 200 fs. Recombination of the electron with a neutralized halogen atom (I) takes place in a ~25 ps time scale, but a sizable fraction of electrons survive beyond 400 ps.

At the first place, electrons are ejected from a region in the vicinity of the liquid beam surface into the vacuum by the multiphoton excitation. Ions such as Ca^+, $CaOEt^+$, $CaCl^+$, and H^+ generated by various processes in the solution are ejected from the liquid surface by Coulomb repulsion exerted from the depleted region, with several accompanying ethanol molecules.[20-25] The nascent cluster ions ejected from the surface release several solvent molecules (evaporative cooling) as they travel in the gas phase; that is, the available energy accumulated during photoionization and ion ejection is dissipated by evaporating the solvent molecules. Our previous study on an NaI solution in ethanol has shown that a considerable amount of available energy is generated during a single laser pulse duration via electron detachment–geminate recombination cycles, where photodetachment of a solvated electron from I^- and geminate recombination of I with the solvated electron are repeated. This scheme shows that the sizes of the cluster ions tend to be reduced with an increase in the irradiation laser power by an increasing extent of evaporative cooling. This trend is actually observed. The formation of a nascent cluster ion and its evaporative cooling are expressed as

$$X^+\ (sol) \rightarrow X^+(EtOH)_n\ (g) \quad (3)$$

$$X^+(EtOH)_n\ (g) \rightarrow X^+(EtOH)_m\ (g) + (n - m)EtOH \quad (4)$$

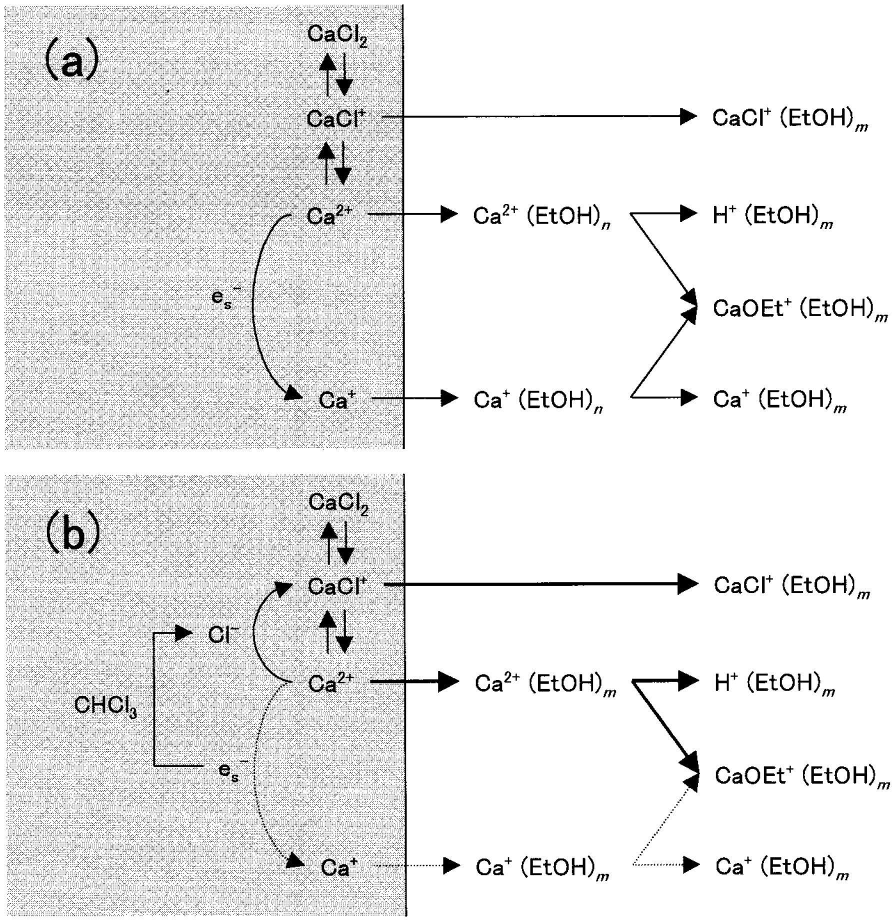
where X^+ represents an ion produced in the solution and (g) represents the gas phase.

4.2. Mechanism of Ion Formation in Solution. As described in the previous sections, the product cluster ions are categorized into five kinds, each of which contains Ca^+, $CaCl^+$, $CaOEt^+$, $CaOH^+$, or H^+ as the core ion. In the solution, Ca^{2+} and $CaCl^+$ are initially produced by dissociation of $CaCl_2$ dissolved in the solution. Then, Ca^{2+} is reduced to Ca^+ by solvated electrons, e_s^-, generated from Cl^- excited in the CTTS state by the laser irradiation:

$$e_s^- + Ca^{2+}\ (sol) \rightarrow Ca^+\ (sol) \quad (5)$$

The significant decrease of the $Ca^+ (EtOH)_m$ intensity by addition of an electron scavenger (see Figure 3) is consistent with that expected from the mechanism of the Ca^+ (sol)

SCHEME 1



formation (see reaction 5). On the other hand, the core ion, $CaOEt^+$, is produced by association of Ca^{2+} with EtO^- produced by the reaction of a solvated electron, e_s^-, with a solvent molecule in the solution as

$$e_s^- + EtOH\,(sol) \rightarrow EtO^-\,(sol) + H\,(sol) \qquad (6)$$

Formation of EtO^- by the reaction of e_s^- with EtOH is also supported by the resluts observed in an ethanol solution of sodium iodide (NaI).[23]

By the reactions of the initially present ions with the solvated electrons, Ca^{2+}, $CaCl^+$, $CaOEt^+$, and Ca^+ are formed in the solution and are ejected into the gas phase with accompanying solvent molecules; actually, $CaCl^+(EtOH)_m$, $CaOEt^+(EtOH)_m$, and $Ca^+(EtOH)_m$ are observed, but not $Ca^{2+}(EtOH)_m$. It is highly likely that a nascent $Ca^{2+}(EtOH)_n$ ejected from the liquid beam changes into $H^+(EtOH)_m$ and $CaOEt^+(EtOH)_m$ by intracluster charge transfer and subsequent Coulomb explosion on the basis of our previous study on a CaI_2 solution in ethanol.[25] The ion, $CaOEt^+$, is also produced by the decomposition of $Ca^+(EtOH)_m$, as discussed in section 4.3. In summary, three parallel mechanisms operate in the production of $CaOEt^+$ (see Scheme 1a): (1) association of Ca^{2+} and EtO^-; (2) intracluster charge transfer in Ca^{2+}; (3) intracluster hydrogen elimination in $Ca^+\,(EtOH)_m$. On the other hand, $H^+\,(EtOH)_m$ is produced by an intracluster charge-transfer reaction in parallel with $CaOEt^+(EtOH)_m$. In addition, $H^+\,(EtOH)_m$ is produced by nonresonant two-photon ionization of the solvent ethanol molecules. Previously, we have observed formation of $H^+(EtOH)_m$ under irradiation of a 266 nm laser onto pure ethanol.[24]

4.3. Formation of $Ca^+\,(EtOH)_m$. In relation to the formation of $Ca^+\,(EtOH)_m$, several studies have been reported so far. Sanekata and co-workers have studied a reaction of Mg^+ with water clusters[31] and discovered that $Mg^+(H_2O)_m$ with $1 \le m \le 5$ and $m \ge 15$ are produced predominantly, while $MgOH^+$-$(H_2O)_m$ are observed exclusively in the $6 \le m \le 14$ range. The switching of the dominant product ions at $m = 5$ is ascribed to the difference in the hydration energies of the M^+ and MOH^+ with an increase in the solvent water molecules. A similar phenomenon is observed in the reaction of Mg^+ with a methanol cluster; the size at which the switching occurs is reported to be 3 or 5. Stace and co-workers[32] observed a product switching from $Mg^+(CH_3OH)_m$ to $MgOCH_3{}^+(CH_3OH)_{m-1}$ at $m = 3$ by using a molecular beam pick-up source, while Lu and Yang[33] observed the switching at $m = 5$. Duncan and co-workers[34] have observed a product switching at $m = 5$ in the photodissociation experiment of $Mg^+(CH_3OH)_m$ produced by a pulsed nozzle expansion source, even though $MgOCH_3{}^+(CH_3OH)_m$ do not seem to be produced in the size range above $m = 5$. It is explained that the internal energy of the cluster ion produced from the nozzle expansion source is not high enough to exceed the barrier height for the production of $MgOCH_3{}^+(CH_3OH)_{m-1}$ from $Mg^+(CH_3OH)_m$. It follows that a critical size at which the product switch occurs depends not only on the energetics but also on experimental conditions, such as the cluster temperature.

Taking these reports into consideration, one concludes that the product switching of $Ca^+(EtOH)_m$ into $CaOEt^+(EtOH)_{m-1}$ at $m = 2$ arises from the energetics that the formation energies of $Ca^+(EtOH)_m$ are higher than those of $CaOEt^+(EtOH)_{m-1}$ in the $m \le 2$ range and lower otherwise. In the $m \ge 3$ range, the following reaction proceeds:

$$Ca^+(EtOH)_m\ (g) \rightarrow CaOEt^+(EtOH)_{m-1}\ (g) + H\ (g)\ (m \geq 3) \quad (7)$$

This cluster ion, Ca^+ $(EtOH)_m$, was not observed by irradiation of a 220 nm laser onto the CaI_2 solution in ethanol.[25] Under the irradiation of the 220 nm laser, the CTTS band of I^- is resonantly pumped, and therefore, a lower laser power is necessary and in return suppresses excess heating of the solution. It follows that dissociation of the nascent cluster ion, $Ca^+(EtOH)_n$, into $CaOEt^+(EtOH)_k$ proceeds much faster than loss of solvent molecules from it in the $m < 3$ range. In the 266 nm excitation, a higher laser power is required for the production of a sufficient amount of ions because of a smaller absorption cross section at 266 nm (a longer wavelength tail of the CTTS band) and causes the solution to heat as a result. Then, the nascent cluster ion, $Ca^+(EtOH)_n$, loses its solvent molecules to form stable ions, $Ca^+(EtOH)_1$ and/or $Ca^+(EtOH)_2$. It is also likely that the product switching occurs at a larger size for a cluster ion containing a lower internal energy, as is the case of the same cluster ions produced by a pulsed nozzle expansion source, where the product switching occurs at the size of 5.

4.4. Scavenging of Solvated Electron by $CHCl_3$. With increase in the concentration of $CHCl_3$ in the CaI_2 ethanol solution, the intensities of $Ca^+(EtOH)_2$ and $CaOEt^+(EtOH)_1$ decrease, while those of $CaCl^+(EtOH)_1$ and $H^+(EtOH)_3$ increase. This finding is explained by efficient scavenging of solvated electrons by $CHCl_3$ and formation of Cl^- and $CHCl_2$. Namely, a less amount of Ca^+ and $CaOEt^+$ is produced in a higher concentration of $CHCl_3$, because of a less amount of solvated electrons available to Ca^{2+} and EtOH. This electron scavenging reaction of $CHCl_3$ is schematically depicted in Scheme 1b, where the thick line shows the reaction accelerated and the dotted line the reaction decelerated by addition of $CHCl_3$.

The dependence of the ion intensities on the $CHCl_3$ concentration is estimated by assuming the following reactions:

(1) reactions of solvated electrons

$$e_s^- + Ca^{2+}\ (sol) \rightarrow Ca^+\ (sol), \quad k_1 \quad (8)$$

$$e_s^- + EtOH \rightarrow EtO^- + H, \quad k_2 \quad (9)$$

$$CHCl_3 + e_s^- \rightarrow Cl^- + CHCl_2, \quad k_3 \quad (10)$$

(2) reactions of Ca^{2+} (sol)

$$Ca^{2+}\ (sol) + EtO^- \rightarrow CaOEt^+, \quad k_4 \quad (11)$$

$$Ca^{2+}\ (sol) + Cl^- \rightarrow CaCl^+, \quad k_5 \quad (12)$$

where k_n ($n = 1-5$) represents the rate constants for reactions 8−12, respectively. Studies on radiolysis of liquid ethanol give a k_2 of $\sim 10^4\ M^{-1}\ s^{-1}$ and a k_1 and k_5 of $\sim 10^{10}\ M^{-1}\ s^{-1}$.[15] Hence, Ca^{2+} reduction by a solvated electron (reaction 8) into Ca^+ proceeds much faster than EtOH reduction (reaction 9). In the present system, $CaOEt^+$ must be produced with a significantly higher efficiency by reactions 8 and 9 than reactions 9 and 11, in contrast to the system studied in our previous report.[25] The increase in $CaCl^+$ by addition of $CHCl_3$ indicates that Cl^- produced from $CHCl_3$ (reaction 10) reacts with Ca^{2+} to form $CaCl^+$. In other words, the intensity of $CaCl^+$ can be used as a propersity of the Cl^- abundance. Then, the rate equations are given as

$$\frac{d[Ca^+]}{dt} = k_1[Ca^{2+}][e_s^-] \quad (13)$$

$$\frac{d[Cl^-]}{dt} = \frac{d[CaCl^+]}{dt} = k_3[CHCl_3][e_s^-] \quad (14)$$

$$\frac{d[e_s^-]}{dt} = -k_1[Ca^{2+}][e_s^-] - k_3[CHCl_3][e_s^-] \quad (15)$$

The concentrations of Ca^{2+} and $CHCl_3$ are regarded to be unchanged throughout the reactions ($[Ca^{2+}] = [Ca^{2+}]_0$, $[CHCl_3] = [CHCl_3]_0$), since the concentrations of Ca^{2+} and $CHCl_3$ dominate that of the solvated electrons. The rate equations (equations 13−15) are solved as

$$[Ca^+] = \frac{k_1[Ca^{2+}]_0}{A}[e_s^-]_0(1 - e^{-At}) \quad (16)$$

$$[CaCl^+] = [CaCl^+]_0 + \frac{k_3[CHCl_3]}{A}[e_s^-]_0(1 - e^{-At}) \quad (17)$$

$$[e_s^-] = [e_s^-]_0\, e^{-At} \quad (18)$$

where $A = k_1[Ca^{2+}]_0 + k_3[CHCl_3]_0$. All the reactions (reactions 8−12) proceed much faster than the ion ejection from the liquid beam surface, and hence, the ion concentrations just before the ejection are obtained by setting $t \rightarrow \infty$ in eqs 16−18 as

$$[Ca^+] = \frac{k_1[Ca^{2+}]}{k_1[Ca^{2+}]_0 + k_3[CHCl_3]_0}[e_s^-]_0 \quad (19)$$

$$[CaCl^+] = \frac{k_3[CHCl_3]}{k_1[Ca^{2+}]_0 + k_3[CHCl_3]_0}[e_s^-]_0 \quad (20)$$

$$[e_s^-] = 0 \quad (21)$$

Equations 19−21 give the concentrations of Ca^+ and $CaCl^+$ in the solution, whose concentrations are proportional to the abundance of the ions being ejected into the gas phase.[35] Thus, the abundance of the ions are given as

$$I(Ca^+) = c\frac{k_1[Ca^{2+}]_0(1 - R)}{A}[e_s^-]_0 \quad (22)$$

$$I(CaOEt^+) = c\frac{k_1[Ca^{2+}]_0 R}{A}[e_s^-]_0 \quad (23)$$

$$I(CaCl^+) = c[CaCl^+]_0 + c\frac{k_3[CHCl_3]}{A}[e_s^-]_0 \quad (24)$$

where $I(X^+)$ is the abundance of X^+ in the gas phase, c is a fraction of an ion in the solution which is ejected into the gas phase, R is a fraction of Ca^+ $(EtOH)_m$, which decays into $CaOEt^+(EtOH)_{m-1}$, and $A = k_1[Ca^{2+}]_0 + k_3[CHCl_3]_0$. The results show that $[Ca^+]$ and $[CaOEt^+]$ decrease and $[CaCl^+]$ increases with increase in the $CHCl_3$ concentration, and hence, Ca^+ $(EtOH)_m$ and $CaOEt^+$ $(EtOH)_m$ decrease and $CaCl^+$ $(EtOH)_m$ increases. The solid lines in Figure 4 show the least-squares fitting of the dependence of the ion intensities on the concentration of $CHCl_3$ by using eqs 22−24, where c, R, and $k_1[Ca^{2+}]/k_3$ are treated as the fitting parameters. The solid lines in Figure 4 reproduce the experimental values reasonably well when R and $k_1[Ca^{2+}]/k_3$ are set to 0.41 and 1.1 M, respectively. The dependence of the ion intensities on the $CHCl_3$ concentrations is reproduced well by this model calculation. The rate constant for the electron scavenging reaction of $CHCl_3$ is reported to be 3×10^{10} M^{-1} s^{-1} in an aqueous solution.[36] Assuming that the rate constant is the same in an ethanol solution, one obtains a $k_1[Ca^{2+}]$ of 3.3×10^{10} s^{-1}. As the rate constants for reactions of solvated electrons with divalent metal ion are known to be commonly 10^{12} M^{-1} s^{-1} in nonpolar solvents,[15] k_1 is considered to be on the order of 10^{12} M^{-1} s^{-1}. Therefore, $[Ca^{2+}]$ is calculated to be on the order of 10^{-2} M by using a $k_1[Ca^{2+}]$ of 3.3×10^{10} s^{-1}. This result indicates that about 10% of $CaCl_2$ dissociates into Ca^{2+} and $2Cl^-$ in the solution used.

In this model, H^+ $(EtOH)_m$ must not be influenced by addition of $CHCl_3$, but the $H^+(EtOH)_m$ intensity increases slightly with adding $CHCl_3$. This slight increase might arise from the assumption that the concentration of Ca^{2+} is unchanged during the whole reaction process.

5. Conclusion

Cluster ion formation induced by laser excitation of the CTTS band of $CaCl_2$ in an ethanol solution were studied by using liquid beam−multiphoton ionization mass spectrometry. The observed ions were $Ca^+(EtOH)_m$ ($m = 0-2$), $CaOEt^+(EtOH)_m$ ($m = 0-6$), $CaOH^+(EtOH)_m$ ($m = 0-1$), $CaCl^+(EtOH)_m$ ($m = 0-6$), and $H^+(EtOH)_m$ ($m = 1-6$). The intensity changes of these cluster ions with the concentration of $CHCl_3$ (electron scavenger) were measured and explained in terms of a series of reactions involving solvated electrons generated concurrently by the CTTS excitation. A product switch from $Ca^+(EtOH)_m$ to $CaOEt^+(EtOH)_{m-1}$ at $m = 3$ observed is ascribed by the energetics of these cluster ions.

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References and Notes

(1) Tachikawa, H.; Lund, A.; Ogasawara, M. *Can. J. Chem.* **1993**, *71*, 118.

(2) Fletcher, J. W.; Richards, P. J.; Sekkon, W. A. *Can. J. Chem.* **1970**, *48*, 1645.

(3) Baxendale, J. H.; Wardman, P. J. *J. Chem, Soc., Faraday Trans. 1* **1973**, *69*, 584.

(4) Chase, W. J.; Hunt, J. W. *J. Phys. Chem.* **1975**, *79*, 2835.

(5) Kenney-Wallace, G. A.; Jonah, C. D. *Chem. Phys. Lett.* **1976**, *39*, 596.

(6) Wang, Y.; Crawford, M. K.; Eisenthal, K. B. *Chem. Phys. Lett.* **1980**, *74*, 160.

(7) Huppert, D.; Kenney-Wallace, G. A.; Rectzepis, P. M. *J. Chem. Phys.* **1981**, *75*, 2265.

(8) Kenney-Wallace, G. A.; Jonah, C. D. *J. Phys. Chem.* **1982**, *86*, 2572.

(9) Barat, F.; Gilles, L.; Hickel, B.; Lesigne, B. *J. Phys. Chem.* **1973**, *77*, 1711.

(10) Schwarz, H. A.; Gill, P. S. *J. Phys. Chem.* **1977**, *81*, 22.

(11) Milosavljevic, B. H.; Micic, O. I. *J. Phys. Chem.* **1978**, *82*, 1359.

(12) Maham, Y.; Freeman, G. R. *J. Phys. Chem.* **1988**, *92*, 1506.

(13) Shinsaka, K.; Hatano. Y *Nucl. Instrum. Methods* **1993**, *A327*, 7.

(14) Pine, S. H. *Organic Chemistry*, 5th ed.; McGraw-Hill Int.: New York, 1987.

(15) Faehataziz, Rodgers, M. A. J., Eds. *Radiation Chemistry*; VCH: New York, 1987.

(16) Fowles, P. *Trans. Faraday Soc.* **1971**, *67*, 428.

(17) Kenney-Wallace, G. A.; Hall, G. E.; Hunt, L. A.; Sarantidis, K. *J. Phys. Chem.* **1980**, *84*, 1145.

(18) Hunt, L. A.; James, F. C.; Kenney-Wallace, G. A. *J. Phys. Chem.* **1983**, *87*, 2981.

(19) Shen, M. H.; Farrar, J. M. *J. Phys. Chem.* **1989**, *93*, 4386.

(20) Mafuné, F.; Takeda, Y.; Nagata, T.; Kondow, T. *Chem, Phys. Lett.* **1992**, *119*, 615.

(21) Mafuné, F.; Takeda, Y.; Nagata, T.; Kondow, T. *Chem, Phys. Lett.* **1994**, *216*, 234.

(22) Mafuné, F.;. Kohno, J.; Nagata, T.; Kondow, T. *Chem, Phys. Lett.* **1994**, *218*, 7.

(23) Matsumura, H.; Mafuné, F.; Kondow, T. *J. Phys. Chem.* **1995**, *99*, 5861.

(24) Mafuné, F.; Kohno, J.; Kondow, T. *J. Phys. Chem.* **1996**, *100*, 10041.

(25) Kohno, J.; Mafuné, F.; Kondow, T. *J. Phys. Chem. A* **1999**, *103*, 1518.

(26) Horimoto, N.; Kohno, J.; Mafuné, F.; Kondow, T. In preparation.

(27) Kohno, J.; Mafuné, F.; Kondow, T. *J. Phys. Chem. A*, submitted.

(28) Faubel, M.; Schlemmer, S.; Toennies, J. P. *Z. Phys. D* **1988**, *10*, 269.

(29) Kloepfer, J. A.; Vilchiz, V. H.; Lenchenkov, V. A.; Bradforth, S. E. *Chem. Phys. Lett.* **1998**, *298*, 120.

(30) Blandamer, M. J.; Fox, M. F. *Chem. Rev.* **1970**, *70*, 59.

(31) Sanekata, M.; Misaizu, F.; Fuke, K.; Iwata, S.; Hashimoto, K. *J. Am. Chem. Soc.* **1995**, *117*, 747.

(32) Woodward, C. A.; Dobson, M. P.; Stace, A. J. *J. Phys. Chem. A* **1997**, *101*, 2279.

(33) Lu, W.; Yang, S. *J. Phys. Chem. A* **1998**, *102*, 825.

(34) France, M. R.; Pullins, S. H.; Duncan, M. A. *Chem. Phys.* **1998**, *239*, 447.

(35) During the laser irradiation, electron detachment−geminate recombination cycles take place; namely photodetachment of I^- and liberation of a solvated electron, and consecutive geminate recombination of I with the solvated electron. A much larger number of solvated electrons take part in the recombination cycle than that of electrons liberated from the surface, because most of the solvated electrons produced recombine with I atoms. Therefore, it is highly likely that the amount of the electrons liberated into vacuum does not change significantly by addition of $CHCl_3$. It is concluded, therefore, that the total amount of the ions observed is not influenced by the $CHCl_3$ addition.

(36) Hart, E. J.; Gordon, S.; Thomas, J. K. *J. Phys. Chem.* **1964**, *68*, 1271.