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Intracluster Ion–Molecule Reactions Within Methane Homoclusters

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Ion–molecule reactions within ionized methane clusters were investigated utilizing electron ionization mass spectrometry. A number of ionic reaction products were observed and interpreted as series of cluster ions of the form $(CH_4)_n \cdot X^+$ where $X = CH_4$, CH_5, C_2H_2, C_2H_3, C_2H_4, C_2H_5, C_2H_6 and C_2H_7 and $n \geqslant 0$. These cluster series, except for $X = C_2H_7$ and C_2H_6, are interpreted in terms of known bimolecular ionic reactions with both electron impact energy and pressure dependences. The two cluster ions with $X = C_2H_7$ and C_2H_6 demonstrate cluster reactions occurring easily in a solvated environment. The $C_3H_3{}^+$ and $C_3H_5{}^+$ ions show evidence of consecutive ionic reactions. Possible reaction paths are discussed and compared with previous work using photoionization of methane clusters and high-pressure mass spectrometry. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: intracluster ion–molecule reaction; methane cluster; electron impact; cluster reaction; consecutive ionic reaction

INTRODUCTION

Gas-phase clusters, consisting from two to several thousand atoms and molecules, have attracted a great deal of attention in recent years.[1–4] These weakly bound species provide a better understanding of the property differences of isolated and bulk molecules. The ion–molecule reaction is suitable for this purpose since mass spectrometry has proven to be a powerful tool in the investigation of van der Waals clusters.[5–8] Although most intracluster ionic reactions can be understood in terms of known bimolecular gas-phase reactions, some unique 'cluster reactions' have also been found to occur in a solvated environment.

Ion–molecule reactions of gaseous methane have been studied extensively using various experimental techniques.[9–17] In these studies, it has been found that the ionic reaction becomes complex as the source pressure increases. This complexity is known to come from the consecutive and termolecular reactions under high-collision conditions, and to be responsible for the formation of polymers by the high-energy irradiation to solid methane.[18] On the other hand, the cluster, being a microscopic solution, requires a study of the intracluster ion–molecule reaction in order to understand the ionic polymerization mechanism. In this regard, a study has been reported on an intracluster ionic reaction of a methane cluster using the photoionization technique at 10–25 eV synchrotron radiation.[19] This energy is, however, insufficient to produce the primary ions of $CH_2{}^+$, CH^+ and C^+, important to the polymerization reaction.

Methane is one of the most widely used chemical ionizing agents because of the moderately low proton affinity of the conjugate bases of $CH_5{}^+$ and $C_2H_5{}^+$, corresponding to the major product ions in the gas phase.[20] This property can also be applied to the mixed methane cluster system where the ionic products from methane molecules act as a proton source or hydride acceptor to ionize the partner molecule. This ionization process is different from that of conventional methods and makes it possible to ionize mildly and to prepare species with unique characters. Jung *et al.*[21] used this approach to unveil the mechanism of internal ion–molecule reactions of CF_3H clusters. In order to characterize this new ionization process in full, information on the reactions within methane homoclusters is necessary.

In this work, we studied the ion–molecule reactions within ionized methane homoclusters using an electron ionization (EI) technique. Many ionic reaction products have been observed and possible reaction paths are discussed based on the results of the dependence of ion abundance on EI energy and stagnation pressure.

EXPERIMENTAL

The molecular beam and quadrupole mass spectrometer used in this study have been described in detail elsewhere.[21] A neutral cluster pulse beam is generated and skimmed and then introduced into the ionizer of the mass spectrometer. One of the molecules within the

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Table 1. Product ion sequences observed in the mass spectrum of methane clusters

Series	$(CH_4)_n \cdot X^+$	Abundance	Analogous ion reaction[b]
a	$(CH_4)_n \cdot CH_4^+$	s	No reaction
b	$(CH_4)_n \cdot CH_5^+$	s	$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$
c	$(CH_4)_n \cdot C_2H_2^+$	vw	$CH^+ + CH_4 \rightarrow C_2H_2^+ + H_2 + H$
d	$(CH_4)_n \cdot C_2H_3^+$	vw	$CH_2^+ + CH_4 \rightarrow C_2H_3^+ + H_2 + H$
e	$(CH_4)_n \cdot C_2H_4^+$	w	$CH_2^+ + CH_4 \rightarrow C_2H_4^+ + H_2$
f	$(CH_4)_n \cdot C_2H_5^+$	m	$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$
g	$(CH_4)_n \cdot C_2H_6^+$	w	Not found
h	$(CH_4)_n \cdot C_2H_7^+$	m	Not found

[a] The ion abundance is denoted by s, strong; m, medium; w, weak; vw, very weak.

[b] Analogous ion–molecule reactions observed in the gas phase are adopted from Refs 9–12.

cluster is ionized by 20–60 eV EI energy and then initiated the intracluster ion–molecule reactions. The resulting product ions are scanned by a quadrupole mass spectrometer.

Methane (Matheson) was used without further purification. Care was taken to obtain the optimal conditions for clustering, 10% methane seeded in helium and a stagnation pressure of 6–9 atm. The formation of mixed clusters, e.g. $(CH_4)_n \cdot (H_2O)_m$, due to impurities was reduced by baking the sampling chamber and the valve and by passing the reactant through a dry-ice–acetone trap.

RESULTS

A typical mass spectrum of methane (10% CH_4 seeded in 9 atm He and at 60 eV EI) is illustrated in Fig. 1. The mass number of the observed peaks is represented by the equation $m = k + 16n$ ($n \geqslant 0$ and $k = 16, 17, 26, 27, 28, 29, 30$ and 31) and interpreted as sequences of cluster ions of the form $(CH_4)_n \cdot X^+$, where X is a fragment or an ionic reaction product. The chemical formula of the core part X is unambiguously identified from the highly monoisotropic character of carbon and hydrogen atoms. These assignments are summarized in Table 1 together with their analogous ion–molecule reactions observed in the gas phase. Two other peaks, $m = 39$ and 41 (see Fig. 1), are also observed with perceptible intensity and assigned to the $C_3H_3^+$ and $C_3H_5^+$, respectively.

Relative cross-sections for the production of the ions observed in the monomer region from EI of methane homoclusters were measured for the electron energy range 18–45 eV. These ionization curves with ascending order of appearance potentials from CH_4^+, CH_3^+, CH_2^+, CH^+ to C^+ agree well with the previous results[22,23] obtained from a methane molecule, which suggests that the formation of the primary ions is not greatly perturbed by a solvated environment or that the relative amount of clusters to methane monomer is very small. Figures 2 and 3 show the relative ionization cross-sections for cluster ions in the dimer and trimer regions, respectively. Based on the abundance variation as a function of EI energy, the cluster ions are separated into several groups illustrated by the dotted lines (see Figs 2 and 3), notwithstanding slight discrepancies. Some cluster series *a* (X = CH_4) and *b*(X = CH_5) are known to be formed from the parent ion in the cluster[19] and in the gas phase,[9–12] the group of these two series with the lowest appearance potential results from the primary ion of CH_4^+, generated promptly by an inelastic interaction between an energetic electron and a methane molecule within clusters. Similarly, other series and the two ions $C_3H_3^+$ and $C_3H_5^+$ are also separated

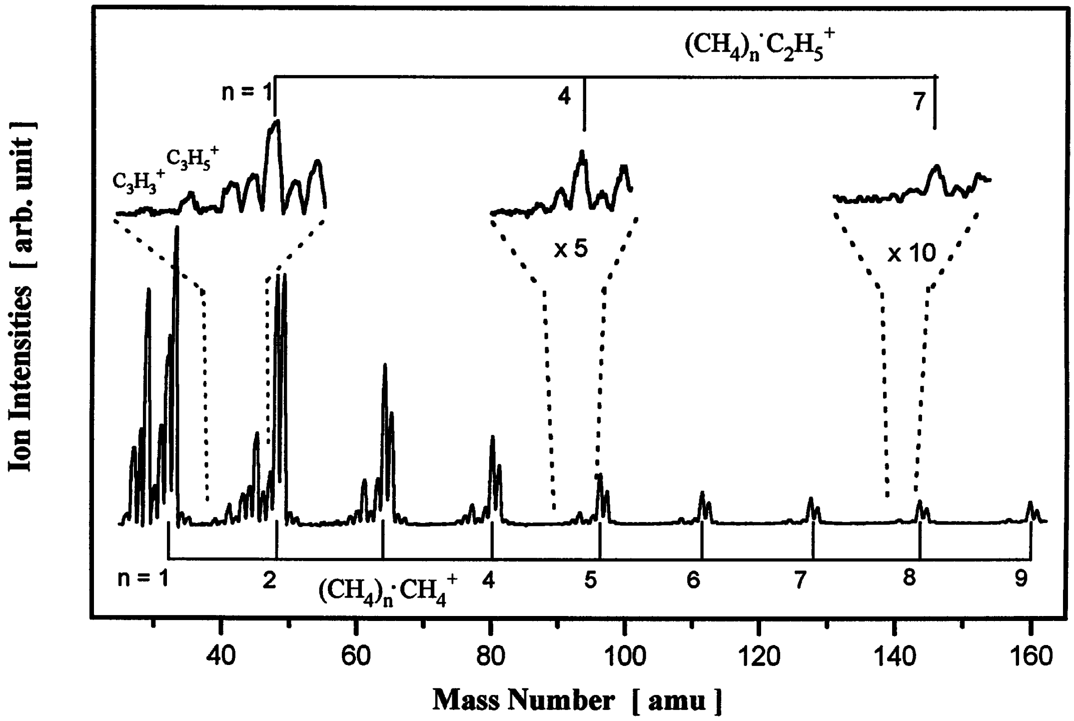

Figure 1. Electron impact mass spectrum of clusters formed by an expansion of 10% methane seeded in 9 atm He at 60 eV.

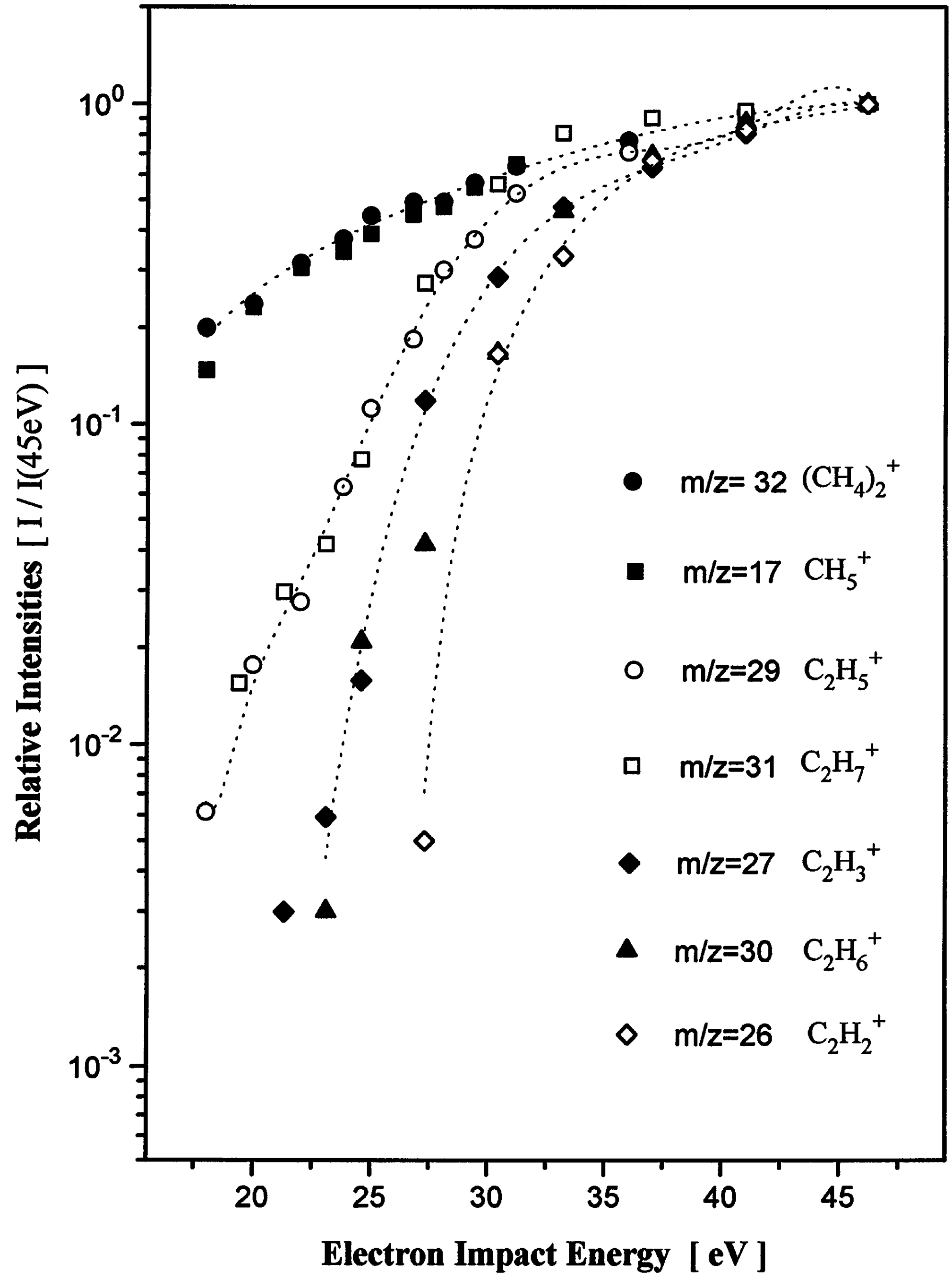

Figure 2. Relative ionization cross-sections for the ions produced in the dimer region as a function of EI energy.

Table 2. Sets of ions produced from intracluster ion–molecule reactions within methane homoclusters according to the primary ion

Primary ion	Cluster series and ions
CH_4^+	$(CH_4)_n \cdot CH_4^+$, $(CH_4)_n \cdot CH_5^+$
CH_3^+	$(CH_4)_n \cdot C_2H_5^+$, $(CH_4)_n \cdot C_2H_7^+$
CH_2^+	$(CH_4)_n \cdot C_2H_3^+$, $(CH_4)_n \cdot C_2H_4^+$ $(CH_4)_n \cdot C_2H_6^+$, $C_3H_5^+$
CH^+	$(CH_4)_n \cdot C_2H_2^+$, $C_3H_3^+$

into sets according to the primary ions formed by EI of methane as listed in Table 2.

The dependence of the ion abundance on the stagnation pressure is shown in Fig. 4. The ion abundances are well fitted to a linear line in a log–log plot. The parentage of the cluster ions can then be predicted from the slope of each line.[24,25] The slope of a product ion in a trimer region [Fig. 4(b)] is found to be larger than the corresponding value in a dimer region [Fig. 4(a)]. This tendency implies that the bulkier cluster ion is produced from the neutral methane with the larger cluster size.

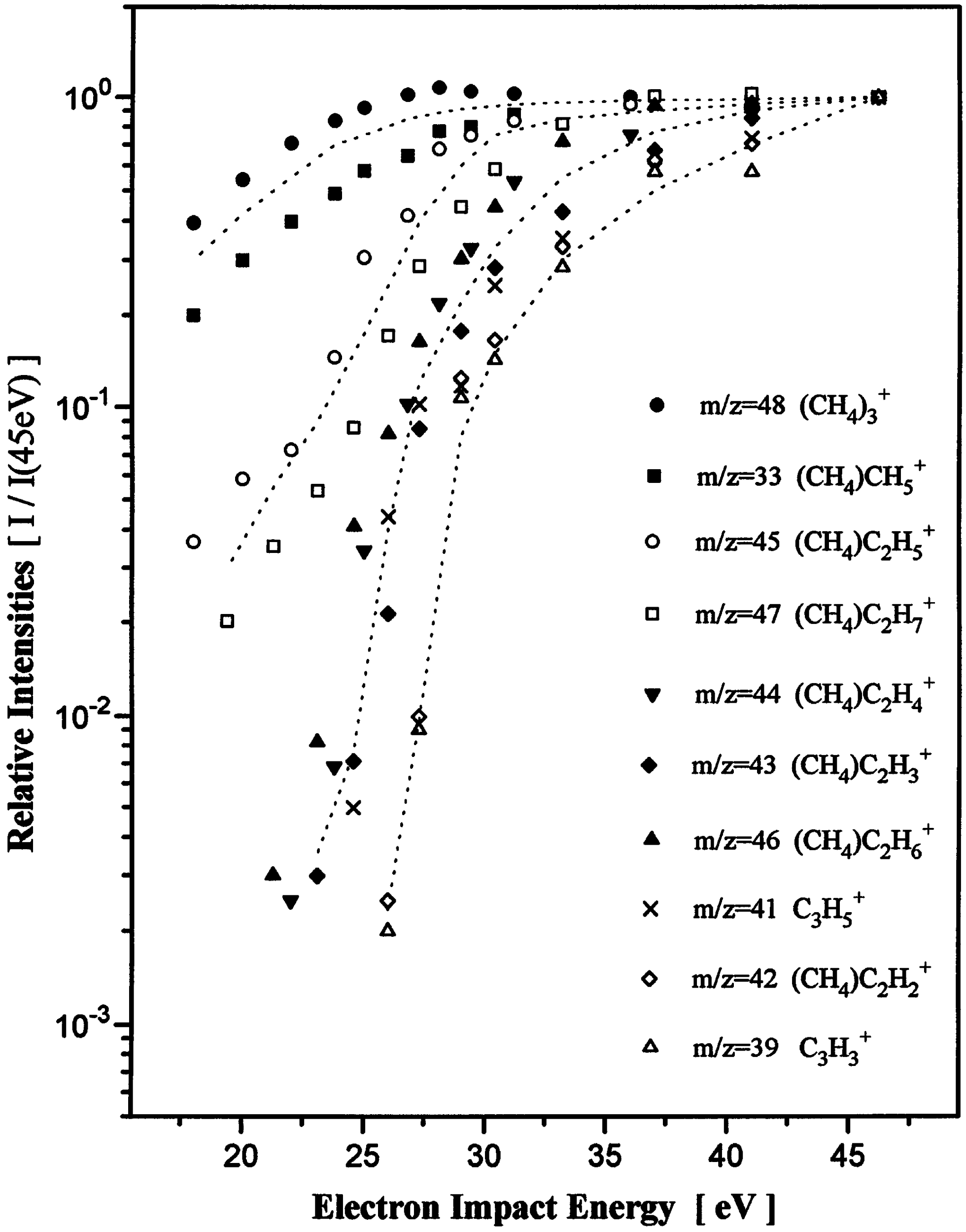

Figure 3. Relative ionization cross-sections for the ions produced in the trimer region as a function of EI energy.

The sensitivity to pressure change for each series is also different: strong for the series *g* and *h*, medium for the series *c*–*f* and weak for the series *a* and *b*. The two series *g* and *h* ($X = C_2H_6$ and C_2H_7) with the steepest gradient are likely to be produced more favorably in a solvated environment than the other series. The series *a* and *b* are observed to have nearly identical slopes at the same cluster size, which implies that the $(CH_4)_n \cdot CH_5^+$ cations mainly result from the $(CH_4)_n \cdot (CH_4—CH_4^+)$ species by loss of the CH_3 radical, without extensive evaporation of a neutral parent molecule.

The abundance distributions of $(CH_4)_n \cdot CH_5^+$ and $(CH_4)_n \cdot C_2H_7^+$ are displayed in Fig. 5(a) and (b), respectively, as a function of cluster size *n* at various EI energies. Considering the general intensity decrease as a cluster size increases, the anomalously intense peaks at the cluster size $n = 2$ in these two distributions reflect its thermodynamic stability. The stability of the $(CH_4)_2 \cdot CH_5^+$ ion has been confirmed experimentally[16,27] and theoretically.[28] It is known that the stable structure of the $(CH_4)_2 \cdot CH_5^+$ ion has two acidic H atoms participating in a three-center, two-electron bond of the core ion CH_5^+ are favorably solvated by two methane molecules.

DISCUSSION

The ionization of a methane molecule requires a timescale of 10 fs via the EI process, while its detection by a mass spectrometer takes microseconds. The excited parent cluster ion, $[(CH_4)_n^+]^*$, then has enough time to release its excess energy accumulated via the EI before the detection process. This stabilization is achieved by multi-path reactions such as monomer evaporation,

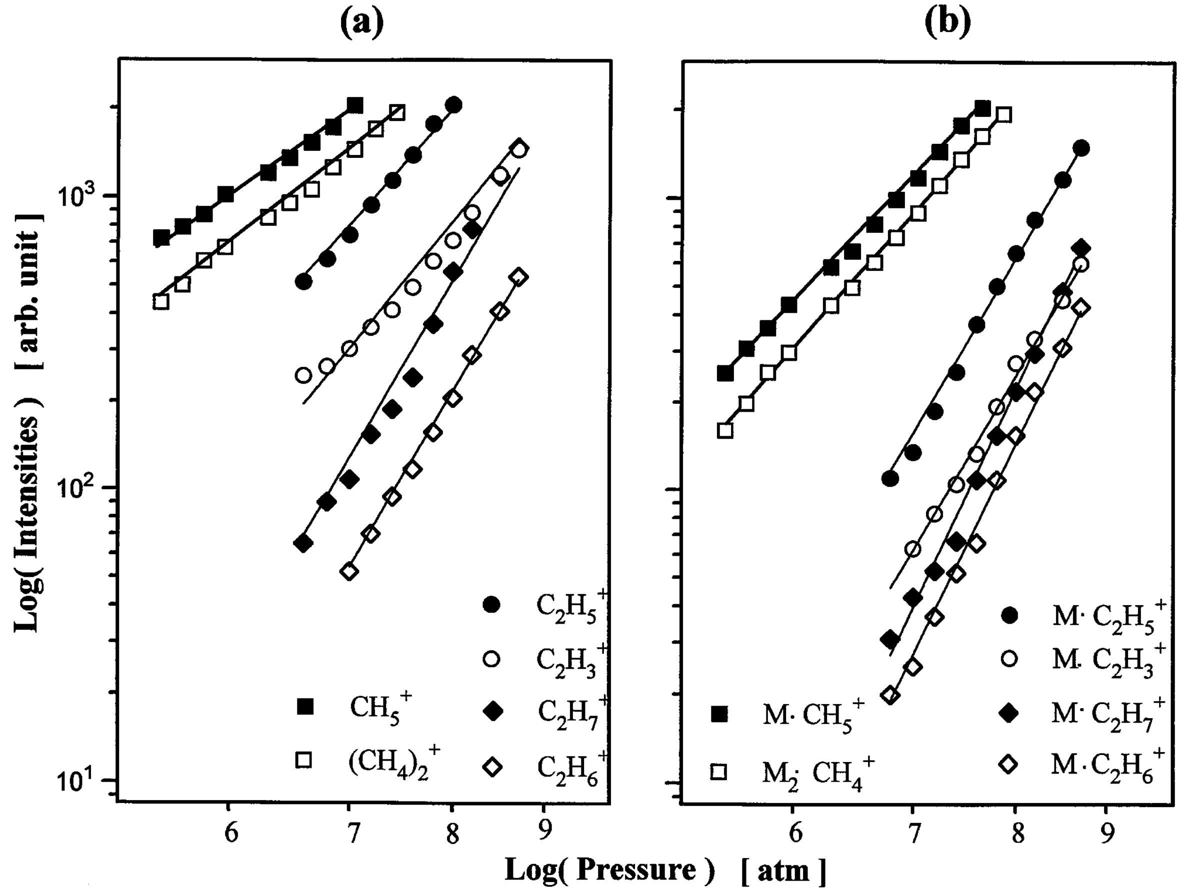

Figure 4. Pressure dependence for the cluster ions (series *a*, *b*, *d*, *f*, *g* and *h*) in the region of (a) a dimer and (b) a trimer at 60 eV electron energy. M represents a methane molecule.

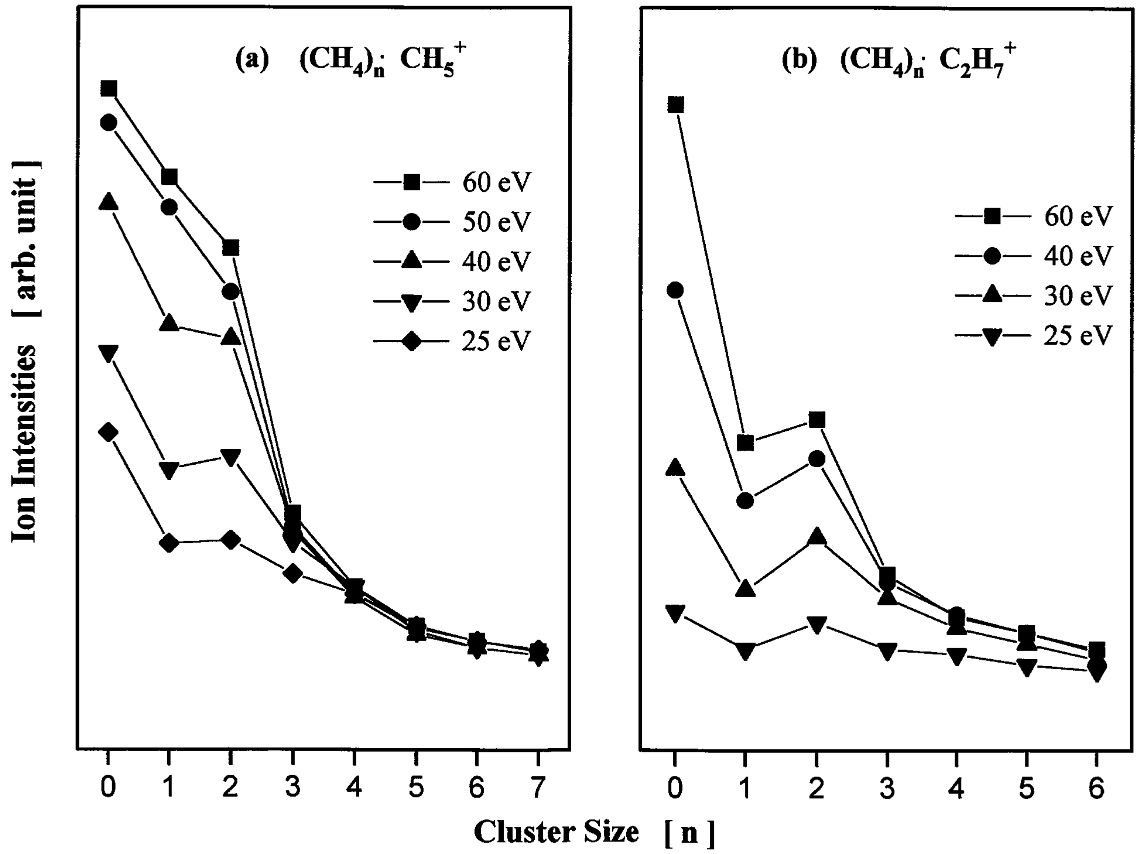

Figure 5. Abundance distributions of (a) $(CH_4)_n \cdot CH_5^+$ and (b) $(CH_4)_n \cdot C_2H_7^+$ ions as a function of cluster size, *n*, at different electron impact energies.

direct fragmentation, and intracluster ion reaction as described by the equation

$$[(CH_4)_n{}^+]^* \rightarrow (CH_4)_qX^+ + (n-q-2)CH_4 + Y \quad (1)$$

where X is the fragment or the reaction product and Y is the reaction fragment. The observed product ion series in Table 1 are interpreted as effects of the EI energy and stagnation pressure.

$(CH_4)_n \cdot CH_4{}^+$ and $(CH_4)_n \cdot CH_5{}^+$ series

These two series are the most abundant and their relative abundances are approximately 10 times higher than those of the rest of the series. From the ion abundance dependence on the EI energy, it is confirmed that these ions are formed from the $CH_4{}^+$ primary ion directly. The $(CH_4)_n \cdot CH_4{}^+$ series corresponds to the natural sequence stabilized by the monomer evaporation while the $(CH_4)_n \cdot CH_5{}^+$ series must be the product of the intracluster ion–molecule reaction between the parent ion and the molecule like the gas phase analogue with appreciable abundance:

$$CH_4{}^+ + CH_4 \rightarrow CH_5{}^+ + CH_3 \quad (2)$$

A recent cross-beam experiment has shown that three competing paths are involved in the reaction mechanism: proton stripping, hydride transfer and intermediate complex decomposition.[17] In the gas phase, the relative contribution of the complex decomposition has been found to be small ($\sim 10\%$) at collision energies of 0.67–2.3 eV and to increase slightly with decreasing collision energy. This mechanism becomes important in the cluster environment with a negligible collision energy.

As mentioned earlier, the pressure dependence study is consistent with the complex decomposition mechanism and further indicates that there is little or no monomer evaporation in the course of this reaction. It suggests that the primary parent ion is stabilized faster by monomer evaporation than the cluster reaction or that they have too small an excess energy for extensive evaporation to occur. The latter explanation is unreasonable on the grounds that there is sufficient EI energy and of the observation of their intensive peaks. Since reaction (2) is slightly exothermic with $\Delta H°$ (289 K) $= -4$ kcal mol^{-1} (1 kcal = 4.184 kJ) and the binding energy for a methane dimer ion is about 16 kcal mol^{-1},[16,17,19] the decomposition reaction of the dimer ion, $[CH_4—CH_4{}^+] \rightarrow CH_5{}^+ + CH_3$, requires an energy of 12 kcal mol^{-1}. Judging from this value and the observed ion abundances in the two series, the hot parent ions cool by tens of kcal mol^{-1} and then approximately half of the ions take part in the reaction. Consequently, the formation mechanism for these two series can be represented as follows:

$$[(CH_4)_n{}^+]^* \rightarrow (CH_4)_q{}^+ + (n-q)CH_4 \quad (3)$$

$$(CH_4)_{q-2} \cdot (CH_4—CH_4{}^+) \rightarrow (CH_4)_{q-2} \cdot (CH_3—CH_5{}^+) \rightarrow (CH_4)_{q-2} \cdot CH_5{}^+ + CH_3 \quad (4)$$

Considering that the intensity falloff as a function of cluster size is faster for the protonated series than for the parent, reaction (4) is quenched with cluster size. This suggests that a cluster environment provides unfavorable conditions for this reaction, probably owing to the hindrance to the CH_3 escape and/or the higher reaction barrier.

$(CH_4)_n \cdot X^+$ series ($X = C_2H_2$, C_2H_3, C_2H_4 and C_2H_5)

The formation of the ion cores of the cluster series *c* to *f* in Table 1 has been observed by the corresponding ion–molecule reactions in the gas phase.[9,12]

$$CH^+ + CH_4 \rightarrow C_2H_2{}^+ + H_2 + H \quad (5)$$

$$CH_2{}^+ + CH_4 \rightarrow C_2H_3{}^+ + H_2 + H \quad (6)$$

$$CH_2{}^+ + CH_4 \rightarrow C_2H_4{}^+ + H_2 \quad (7)$$

$$CH_3{}^+ + CH_4 \rightarrow C_2H_5{}^+ + H_2 \quad (8)$$

The reactant ions of reactions (5)–(8) are identical with the primary ions determined from the EI energy dependence of these series (see Table 2). These cluster series are interpreted as resulting from the corresponding intracluster reactions after the generation of the $CH_3{}^+$, $CH_2{}^+$ and CH^+ ions by the fragmentation of the parent ion. According to the photoionization study,[19] the $(CH_4)_n \cdot C_2H_4{}^+$ series has already been produced far below the threshold energy for $CH_2{}^+$ formation and has been assigned to come from the reaction $CH_4{}^+ + CH_4 \rightarrow C_2H_4{}^+ + 2H_2$. The disagreement in reaction path is understood from the difference in the magnitude of the excitation energy, i.e. whether the excitation energy is sufficient for $CH_2{}^+$ formation or not. The absence of the $(CH_4)_n \cdot C_2H_3{}^+$ series, which it is possible to form from the $CH_2{}^+$, in the photoionization study supports this explanation.

$(CH_4)_n \cdot C_2H_7{}^+$, $(CH_4)_n \cdot C_2H_6{}^+$ series

The protonated ethane ion, $C_2H_7{}^+$, has been directly observed when produced from other molecules and is known to be stable in its ground state. In spite of its stability, this ion has not been observed as an intermediate persistent complex in the gas reaction (8) owing to the released energy into the fast dissociation to $C_2H_5^+$ and H_2.[29] However, the ion has been reported in mass spectrometric studies on the solvated environment[9,10,19] where its excess energy can be taken away by third-body partners. We verified that the $(CH_4)_n \cdot C_2H_7{}^+$ cluster ions are produced from the $CH_3{}^+$ primary ion by measurement of the ionization cross-section. In addition, the slopes of their pressure dependences are found to be the highest together with those of the $(CH_4)_n \cdot C_2H_6{}^+$ ions. This prominent pressure dependence implies that the cluster ions are generated from the neutral precursor with a larger cluster size. These results suggest the mechanism

$$(CH_4)_n + e \rightarrow (CH_4)_m \cdot (CH_3{}^+—CH_4) + (n-m-2)CH_4 + H + 2e \quad (9a)$$

$$(CH_4)_m \cdot (CH_3{}^+—CH_4) \equiv (CH_4)_m \cdot [C_2H_7{}^+]^* \rightarrow (CH_4)_k \cdot C_2H_7{}^+ + (k-m)CH_4 \quad (9b)$$

Since the exothermicity of the reaction $CH_3^+ + CH_4 \rightarrow C_2H_7^+$ is large, ~ 37 kcal mol^{-1},[19] the additional excess energy deposited after the reaction will enhance the monomer evaporation. However, this mechanism alone cannot explain why reaction (9) has a more sensitive pressure dependence than reaction (7) with higher exothermicity. The sensitivity indicates that the excited core ion $[C_2H_7^+]^*$ in reaction (9b) undergoes considerable interaction with nearby methane molecules and that the excess energy flows into the methane molecules in the course of the reaction. This stabilization process and steric hindrance imposed by the neighboring molecules can restrict the $(CH_4)_n \cdot C_2H_7^+$ ion to dissociate into $(CH_4)_n \cdot C_2H_5^+$ and H_2.

If the core ion of this series is CH_3^+, whose stable structure is known to be planar and whose carbon atom is the most positive,[30] rather than $C_2H_7^+$, the $(CH_4)_2 \cdot CH_3^+$ ion with two methane molecules located up and down the plane will be more stable than that with three methane molecules. This prediction is, however, inconsistent with the fact that the ion distributions of $(CH_4)_n \cdot C_2H_7^+$ or $(CH_4)_{n+1} \cdot CH_3^+$ display enhanced stability at $n = 2$. The protonated ethane ion is reported to have two stable isomeric forms.[31] One (A) corresponds to the protonation to the C—C bond of ethane and the other (B) is a loose complex between the classical form of ethyl cation and a hydrogen molecule. If we consider the stability of the isomers only, the stable structure should be the cluster ion with two methane molecules up and down the plane defined by the three-center, two-electron bond of the A form. However, according to a molecular orbital study on the structure and the stability of the $(CH_4)_n \cdot CH_5^+$ ions,[28] the orientation of clustering of CH_4 is mainly affected by the spatial extension of some low-lying vacant orbitals and the steric hindrance. We propose the following for the stable structure of the $(CH_4)_2 \cdot C_2H_7^+$: the core ion has the B form and the two hydrogen atoms of the three-center bond gives the most favorable sites for the accommodation of the two CH_4 molecules as in the case of the $(CH_4)_2 \cdot CH_5^+$.

In the case of $X = C_2H_6$, the cluster ions have been ascertained to be formed from the CH_2^+ primary ion and to have a sensitive pressure dependence. Since the reaction $CH_2^+ + CH_4 \rightarrow C_2H_6^+$ has been observed at high pressure[12] and the exothermicity is 70 kcal mol^{-1} in the gas phase,[32] this series can also be interpreted as an ionic reaction favorable in the solvated environment between the CH_2^+ ion and neighboring CH_4 molecules, simultaneously stabilized by methane monomer evaporation as in reaction (9) for $(CH_4)_n \cdot C_2H_7^+$. These cluster reactions are observed to occur more easily than the analogue in the gas phase, which suggests that the cluster medium can be utilized to produce chemical species that are difficult to form in ordinary systems.

$C_3H_3^+$ and $C_3H_5^+$ ions

These two ions with three carbon atoms cannot be produced from the ion–molecule reaction between a primary ion and a methane molecule. At least two consecutive ion reactions are demanded for it. Some pieces of evidence for the consecutive reactions have been reported in the mass pattern obtained by electron impact on CH_4 at a relatively high source pressure.[10] Our observation of the $C_3H_3^+$ and $C_3H_5^+$ products, therefore, demonstrates the occurrence of consecutive ion–molecule reactions within clusters. From the measurement for their relative ionization cross-sections, the $C_3H_3^+$ and $C_3H_5^+$ ions are found to have similar EI energy dependences to the CH^+ and CH_2^+ primary ions, respectively. These correlations are consistent with the previous results obtained in the gas phase.

These products are of interest in connection with the problem of the mechanism for polymer formation by high-energy irradiation of solid methane. Previous work provided evidence that the polymer is formed by an ionic process and its precursors are hydrogen-deficient ions produced from methane molecules, e.g. C^+, CH^+ and CH_2^+.[9,18] Considering the structure bonded with many methane molecules, the cluster medium is expected to provide a high reaction probability for the consecutive reaction. However, we do not observe their cluster series and larger hydrocarbon products induced by further consecutive reactions, which indicates that the formation of these two ions and succeeding reactions are suppressed in a solvated environment.

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REFERENCES

1. E. R. Berstein, *Atomic and Molecular Clusters*. Elsevier, New York, (1972).
2. A. W. Castleman, Jr and R. G. Keesee, *Chem. Rev.* **86**, 589 (1986).
3. J. A. Syage, *J. Phys. Chem.* **99**, 5772 (1995).
4. A. W. Castleman, Jr, W. B. Tzeng, S. Wei and S. Morgan, *J. Chem. Soc., Faraday Trans.* **86**, 2417 (1990).
5. J. F. Garvey, W. R. Peifer and M. T. Coolbaugh, *Acc. Chem. Res.* **24**, 48 (1991).
6. M. T. Coolbaugh and J. F. Garvey, *Chem. Soc. Rev.* **21**, 163 (1992).
7. B. Brutschy, *Chem. Rev.* **92**, 1567 (1992).
8. D. N. Shin, K. W. Jung and K.-H. Jung, *J. Am. Chem. Soc.* **114**, 6926 (1992).
9. F. H. Field and M. S. B. Munson, *J. Am. Chem. Soc.* **87**, 3289 (1965).
10. S. Wexler and N. Jesse, *J. Am. Chem. Soc.* **84**, 3425 (1962).
11. F. P. Abramson and J. H. Futrell, *J. Chem. Phys.* **45**, 1925 (1966).
12. F. H. Field, J. L. Franklin and M. S. B. Munson, *J. Am. Chem. Soc.* **85**, 3575 (1963).
13. G. A. W. Derwish, A. Galli, A. Giardini-Guidoni and G. G. Volpi, *J. Chem. Phys.* **40**, 5 (1964).
14. W. T. Huntress, Jr, *J. Chem. Phys.* **56**, 5111 (1972).
15. Z. Herman, P. Hierl, A. Lee and R. Wolfgang, *J. Chem. Phys.* **51**, 454 (1969).
16. K. Kamiya and K. Morokuma, *Chem. Phys. Lett.* **123**, 331 (1986).

17. Z. Herman, M. Henchman and B. Friedrich, *J. Chem. Phys.* **93**, 4916 (1990).
18. D. R. Davis and W. F. Libby, *Science* **144**, 991 (1964).
19. A. Ding, R. A. Cassidy, J. H. Futrell and L. Cordis, *J. Phys. Chem.* **91**, 2562 (1987).
20. M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.* **88**, 2621 (1966).
21. K. W. Jung, C. J. Choi, Y. S. Kim, K.-H. Jung and D. Kim, *Int. J. Mass Spectrom. Ion Processes* **135**, 119 (1994).
22. O. J. Orient and S. K. Srivastava, *J. Phys. B* **20**, 3923 (1987).
23. H. C. Straub, D. Lin, B. G. Lindsay, K. A. Smith and R. F. Stebbings, *J. Chem. Phys.* **106**, 4430 (1997).
24. U. Buck and H. Meyer, *Surf. Sci.* **156**, 275 (1985).
25. A. Amirav, U. Even and J. Jortner, *J. Chem. Phys.* **75**, 2489 (1981).
26. K. Hiraoka and P. Kebarle, *J. Am. Chem. Soc.* **97**, 4179 (1975).
27. K. Hiraoka and T. Mori, *Chem. Phys. Lett.* **161**, 111 (1989).
28. S. Yamabe, Y. Osamura and T. Minato, *J. Am. Chem. Soc.* **102**, 2268 (1980).
29. Z. Herman, P. Hierl, A. Lee and R. Wolfgang, *J. Chem. Phys.* **51**, 454 (1969).
30. L. D. Kispert, C. U. Pittman, Jr, D. L. Allison, T. B. Patterson Jr, C. W. Gilbert, Jr, C. F. Hains and J. Prather, *J. Am. Chem. Soc.* **94**, 5979 (1972).
31. K. Raghavachari, R. A. Whiteside, J. A. Pople and P. v. R. Schleyer, *J. Am. Chem. Soc.* **103**, 5649 (1981).
32. F. H. Field and J. L. Franklin, *Electron Impact Phenomena*, Academic Press, New York (1957).