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Impact of Gas Backing Pressure and Geometry of Conical Nozzle on the Formation of Methane Clusters in Supersonic Jets

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We present an experimental investigation of the dependence of the production of large methane clusters on the cluster source conditions. The clusters were produced at room temperature through supersonic expansion of methane gas at the backing pressures P_0 ranging from 10 to 84 bar using five conical nozzles of different geometries. The cluster size was characterized by Rayleigh scattering measurements and calibrated with Coulomb explosion of the clusters at $P_0 = 44$ bar subjected to an ultraintense laser pulse. A quantitative evaluation of the performance of the conical nozzles against the nozzle geometry and the backing pressure was made by introducing a parameter δ. Differ from the idealized case where the performance of the conical nozzle can be described by the equivalent sonic nozzle of diameter d_{eq}, in the present work, the "effective equivalent sonic-nozzle diameter" of the conical nozzle defined by $d_{eq}^* = \delta d_{eq}$ is introduced. δ represents the deviation of the performance in cluster formation of the conical nozzles from that predicted on the basis of the concept of the equivalent diameter $d_{eq} = d/\tan\alpha$, with d being the throat diameter, and α the half-opening angle of the conical nozzle. Experimental results show that the cluster growth process will be restricted when the gas backing pressure P_0 is higher and/or $d/\tan\alpha$ of the conical nozzle becomes larger, resulting in smaller δ. From the experimental data, δ can be expressed by an empirical relation $\delta = A/[P_0^B(d/\tan\alpha)^{1.36}]$, where $A = 8.4$ and $B = 0.26$ for 24 bar $\leq P_0 \leq$ 54 bar (2.8 mm $< d/\tan\alpha <$ 4.5 mm), and $A = 72$ and $B = 0.80$ for 54 bar $\leq P_0 \leq$ 84 bar (2 mm $\leq d/\tan\alpha \leq$ 7 mm). For all the cases investigated in this work, δ was found to lie between about 0.2 and 1.0, and the average radii of the methane clusters were measured to be 1−7 nm, depending on the experimental conditions. For lack of the experimental data on methane cluster formation with sonic nozzles, the data from the "sonic-like" conical nozzles were applied. Consequently, the δ values provided in this work for the conical nozzles remain relative in nature.

Introduction

Recently, molecular clusters, such as hydrogen and methane clusters, have received considerable attention for they act as target media in the interaction of ultraintense femtosecond laser pulse with matter.[1−12] For the production of large size molecular clusters of these gas species in pulsed supersonic expansion, the gas stagnation pressures used were usually higher than 50 bar.[2−5,11,12] To reduce the load to the vacuum pumping capability, the conical nozzles prevail because they are proved superior to the sonic nozzles in cluster production.[13−15] With the idealized streamtube picture, the conical nozzle functions as a sonic nozzle with the equivalent sonic nozzle diameter $d_{eq} = K_{15}d/\tan\alpha$.[14,15] In this case, the conical nozzles may be termed equivalent (sonic) nozzles that produce just the same flow fields on the jet axis as the sonic nozzles that possess the diameters d_{eq}. Here K_{15} is a constant depending on gas species. The value of K_{15} is 0.74, and 0.87 for monatomic and diatomic gases, respectively. For polyatomic gases, such as CO_2 and CH_4, K_{15} is estimated to be about unity in a distance 30d from the nozzle throat according to refs 14 and 16. With this equivalent diameter concept, a mass flow reduction of $(K_{15}/\tan\alpha)^2$ is expected for the conical nozzle compared with the sonic nozzle, which has the same diameter.[15] However, a question may arise as to whether this idealized equivalent diameter concept of the conical nozzle would remain when the value of $d/\tan\alpha$ becomes larger or/and the backing pressure is higher? Attempts were made in this work to examine the situation by using five conical nozzles of different geometries ($d/\tan\alpha$ = 2−7 mm) and with the backing pressure of methane gas ranging from 10 up to 84 bar. The size of methane clusters produced in supersonic expansion was characterized by Rayleigh scattering measurements[1,4,12,17] and calibrated with Coulomb explosion of the clusters ionized by an intense femtosecond laser pulse.[4,12,18]

Unlike argon clusters produced under the relatively low backing pressure and with the small $d/\tan\alpha$ where the net performance of the conical nozzle may deviate slightly from that based on the idealized equivalent sonic nozzle diameter d_{eq},[15] the circumstances for the present investigation on methane clusters were greatly changed. The boundary layers effect, as found earlier for argon clusters,[13,19] is expected to play an important role in the present case since the total molecular densities in the flows[14] at a distance x in the central line from the nozzle throat are $n_{mol} = K_7(d_{eq}/x)^2$, already, about 2 orders of magnitude higher compared with those in refs 13 and 19−21. In particular, the higher molecular densities are accompanied with more severe constraint of the

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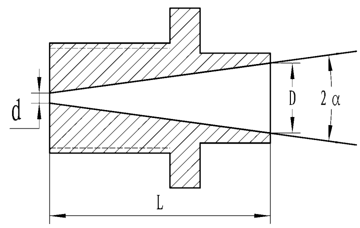

Figure 1. Schematic of the conical nozzle used in the present experiment.

flows by the inner surfaces of the conical nozzles. And, the ratio of specific heats γ of methane is a function of the stagnation temperature T_0 and the backing pressure P_0. At the constant stagnation temperature, with the backing pressure increased, $\gamma(P_0)$ will bring about an impact on the cluster growth process. It was found that the $P_0T_0^{(1.25\gamma-0.5)/(1-\gamma)}$ = const nearly isentropic relation (for a certain cluster size N) well fits the experimental results for Ar and N_2.[13] As indicated by our experimental results for high P_0 and large d/tan α, the idealized equivalent diameter d_{eq} is no longer adequate for the description of the performance of a conical nozzle. In this regard, we introduce the so-called "effective equivalent sonic-nozzle diameter" d_{eq}*, which is defined by $d_{eq}^* = \delta d_{eq} = \delta d/\tan\alpha$. The parameter δ is a function of the backing pressure P_0 and the nozzle geometry d/tan α, representing the deviation of the performance in cluster formation of the practical conical nozzles from that predicted on the basis of their idealized equivalent sonic nozzle diameters d_{eq} (δ = 1). The deviation reflects all the factors that influence cluster formation, especially the boundary layers effects. The values of δ of the conical nozzles used under different backing pressures can then be estimated from the experimentally measured data N of the $(CH_4)_N$ clusters (N is the number of molecules per cluster) by referring to the sonic-like nozzles of which the performance is defined to be idealized with δ being unity at low backing pressure. Consequently, characterized by δd_{eq}, the performance in cluster formation of the conical nozzles as a function of the nozzle geometry and the backing pressure can be studied in a quasi-quantitative way. Because the definition of $\delta = 1$ is made for some "sonic-like" conical nozzles under the somehow defined conditions, the values of δ are relative in nature in the present work.

Experimental Section

The experiments were conducted on the basis of a vacuum chamber of 220 L in volume, which was pumped with two 3000 L/s oil diffusion pumps. The cluster source assembly consisting of a homemade solenoid pulse valve and a conical nozzle which is shown schematically in Figure 1, and the dimensions of five stainless steel conical nozzles used in this study are listed in Table 1. Methane clusters were produced in supersonic expansion of methane gas (99.999% in purity) into vacuum through the pulsed valve and the conical nozzle. The size of the clusters was characterized via Rayleigh scattering measurements. To do this, a 10 ns, 532 nm laser pulse with the energy of 1.8 μJ from a frequency-doubled Nd:YAG laser, intersected the gas flow with 90° angles about 3 mm from the nozzle exit. The laser beam was focused with a lens into the center of the gas flow, with the focus spot size being about 0.4 mm in diameter. The 90° scattered light, after an aperture of 5 mm in diameter, was collected with a lens and imaged onto a photomultiplier tube (PMT), which was covered with an interference filter centered at 532 nm. A digital oscilloscope (LeCroy 9350AL) was used for averaging and recording the signals from the PMT. All the data were averaged over 30 shots. The 532 nm laser output was monitored in situ by an energy meter to ensure that the laser pulse energy was kept unchanged throughout the whole period when the experiments were carried out. The Rayleigh scattering signals I_{RS} as a function of the gas backing pressure P_0 at room temperature T_0 (298 K) were recorded for the five conical nozzles. To maintain the vacuum, the repetition frequency of the pulsed valve varied from 1 to 0.05 Hz, depending on the experimental conditions. A crucial point of the experiments is that the pulsed valve should be fully open so that the steady state of the gas flow can be reached.[22,23] A time-resolved Rayleigh scattering experiment was conducted to examine the evolution and decay processes of the cluster flow. The occurrence of saturation of the scattered light signal is an indication that the steady state of the flow was established as a result of the complete opening of the pulsed valve. This statement is supported by total dose of the gas pulse measured in the experiment which will be given in the next section.

The calibration of the cluster size N of the Rayleigh scattering measurements of methane clusters $(CH_4)_N$ was made by fitting the experimental energy spectrum of protons and carbon ions, which were created from the Coulomb explosion of the methane clusters under the irradiation of an intense femtosecond laser pulse, with that formed from Coulomb explosion of the ionic methane clusters with a log-normal size distribution[4,12,18,19,24]

$$f(n) = \frac{1}{n\sigma\sqrt{2\pi}} \exp\left[-\frac{(\ln n - \mu)^2}{2\sigma^2}\right] \tag{1}$$

where μ and σ are the mean and standard deviation of the distribution of the natural logarithm of the size (n is the number of molecules in a cluster). These two parameters can be transformed into the average size N of the clusters in the distribution and the distribution width σ (fwhm). Assuming that the cluster size of peak abundance of the distribution is n_0, we have the relation $\mu = \ln n_0 + \sigma^2$. For a given n_0 and σ, the cluster size distribution is then defined. The average cluster size is given by $N = \int nf(n)\,dn/\int f(n)\,dn$. The charge state of the carbon ions in the ionized methane clusters $(C^{K+}H^{+}{}_4)_N$ is determined by the laser intensity and the radii of the clusters.[25,26] After the absolute size calibration made for one conical nozzle (0.36 mm/5.29° nozzle) at a defined backing pressure P_0 = 44 bar, the sizes of the clusters produced with the other conical nozzles at P_0 = 44 bar can be determined by comparison of the corresponding Rayleigh scattering signals I_{RS} through

$$I_{RS} \propto N n_{mol} D \eta \tag{2}$$

or

$$I_{RS} \propto N(d/\tan\alpha)^2 D\eta \tag{2'}$$

because the Rayleigh scattering measurements were carried out under the otherwise identical experimental conditions for all the nozzles.[4,27] Here, η is the condensation degree (i.e., the fraction of molecules under the cluster phase) and the total molecular densities in the gas flows are given to be $n_{mol} \propto (d/\tan\alpha)^2 P_0$. The accuracy of the transfer of the size calibration from the no. 3 nozzle to the others at the fixed P_0 = 44 bar will be associated with any possible backing pressure and nozzle geometry dependence of the ratio of n_{mol}, and η. The total molecular density n_{meas} measured in this work by interferometry

TABLE 1: Dimensions of the Five Conical Nozzles Used in the Present Investigation, and the Power Scaling of the Rayleigh Scattered Light Intensity I_{RS} versus the Methane Backing Pressure P_0, $I_{RS} \propto P_0^{\beta}$

nozzles	d (mm)	D (mm)	L (mm)	α (deg)	d/tan α (mm)	P_0 (bar)	β	I_{RS} (84 bar)
no. 1	0.30	5.2	17.5	7.97	2.14	10–54	4.50	11000
						54–84	2.64	
no. 2	0.27	3.6	17.5	5.43	2.84	12–44	4.01	11000
						44–84	2.68	
no. 3	0.36	3.6	17.5	5.29	3.89	9–44	4.00	16000
						44–84	2.70	
no. 4	0.59	5.2	17.5	7.50	4.48	14–54	3.90	29000
						54–84	2.82	
no. 5	0.62	3.7	17.5	5.03	7.04	44–54	3.69	15500 (64 bar)
						54–64	2.70	

exhibited a linear dependence on P_0 in the pressure range 44−74 bar, while a linear dependence of the molecular density n_{num} on P_0 from numerical calculations was reported for argon when a conical nozzle (0.62 mm/4.5°) was used under gas backing pressures of 20, 40, and 60 bar.[27] The values of n_{meas} and n_{num} are close to those estimated through $n_{mol} = K_7(d_{eq}/x)^2 n_0$, indicating that d/tan α in eq 2 is a suitable parameter for the geometric description of the conical nozzles used in the two works, and $(d/\tan \alpha)^2$ is an adequate representation of the total molecular densities n_{mol} in the flows at a defined P_0. In the previous studies, d/tan α is usually used as a single parameter in the estimation of sizes of clusters produced at high backing pressures.[3−5,27] The data of η reported by Dorchies et al.[27] for argon clusters through numerical simulations for a conical nozzle (0.62 mm/4.5°) at the backing pressure from 20 to 60 bar show that η increases within 20%, suggesting that η could be approximately treated as a constant in the size calibration transfer where P_0 is kept constant (44 bar). This approximation may be supported by the experimental data in ref 28. Then, eq 2 has been simplified to

$$I_{RS} \propto N(d/\tan \alpha)^2 D \tag{3}$$

From the Rayleigh scattering measurements, the average cluster size can be estimated simply by

$$N \propto P_0^{\beta-1} \tag{4}$$

based on the experimentally obtained results $I_{RS} \propto P_0^{\beta}$ (see the next section) in view of $I_{RS} \propto P_0 N$ for an individual conical nozzle.[4] As a consequence, all the cluster sizes N characterized by the Rayleigh scattering measurements for the conical nozzles under different backing pressures can be determined.

Results

At first, a time-resolved Rayleigh scattering measurement was performed and verified that the pulsed valve was completely open as indicated by the occurrence of a plateau of the scatter light intensity I_{RS}, as shown in Figure 2. It was supported by the measured number of molecules of the pulsed methane gas jets, which are given to be 1.76, 2.09, 2.66, 3.37, 4.14, 5.65, and 9.21(±0.05) × 10^{19} per shot at the backing pressures 19, 24, 34, 44, 54, 64, and 74 bar, correspondingly. The number of molecules of a pulsed methane gas jet can be estimated by the product of the gas flow rate through the exit area of the conical nozzle and the opening time of the pulsed valve Δt_{open}. The calculated results for P_0 = 19−74 bar are close to the data of 1−1.5 ms (fwhm) measured experimentally, showing that the value was fully open during the experiment. The characterization of cluster size by Rayleigh scattering was then performed under the conditions that the establishment of the steady state of the flow was ensured. The Rayleigh scattering signals I_{RS} as a function of the methane backing pressure P_0 at room temperature are given in Table 2 and shown in Figure 3a for the five conical nozzles. The curves in Figure 3a were characterized to follow a power dependence, with the scattered light intensity I_{RS} versus the backing pressure P_0 as $I_{RS} \propto P_0^{\beta}$, and the data are summarized in Table 1. It is noted that the $I_{RS} \sim P_0^{\beta}$ curves illustrate a gradual decline of the power β with the backing pressure increased. The variation of power β can be treated by roughly dividing the curves into two parts. Given in Figure 3b is an example, taken for one nozzle for clarity. The power β of the curves in the low-pressure regime is characterized with a larger value of 3.9−4.5, and in the high-pressure regime, β is somewhat smaller, which lies between 2.6 and 2.8 for the five nozzles. However, the unexpected poor performance of the 0.62 mm/5.03° nozzle in low pressures ($P_0 \leq$ 39 bar) is puzzling, and the pumping capacity is responsible for the missing of the data with this nozzle for P_0 > 64 bar.

Now, after the absolute size calibration with a Coulomb explosion scheme (see the next section for details) for the no. 3 nozzle, the sizes of methane clusters produced with these nozzles at different backing pressures can be determined by referring to eqs 3 and 4 and the data in Table 1, which were obtained under the otherwise identical experimental conditions. The cluster sizes N as a function of P_0 for different

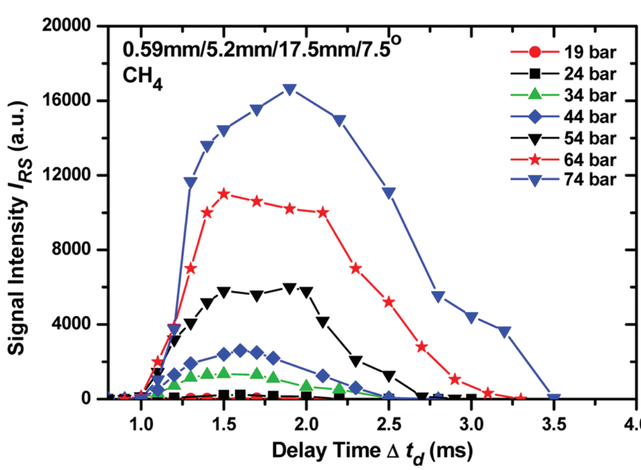

Figure 2. Typical time-resolved spectra of Rayleigh scattered light intensity I_{RS} as a function of the delay time of the probing 532 nm laser beam, which was delayed with respect to the triggering of the pulsed valve, are displayed. The occurrence of the plateau of the intensity indicates that the steady state of the methane gas flow was reached. The experiment was performed with the 0.59 mm/7.50° conical nozzle at the backing pressures ranging from 19 to 74 bar. The opening time of the pulsed valve Δt_{open} (fwhm) is about 1−1.5 ms for the different backing pressures.

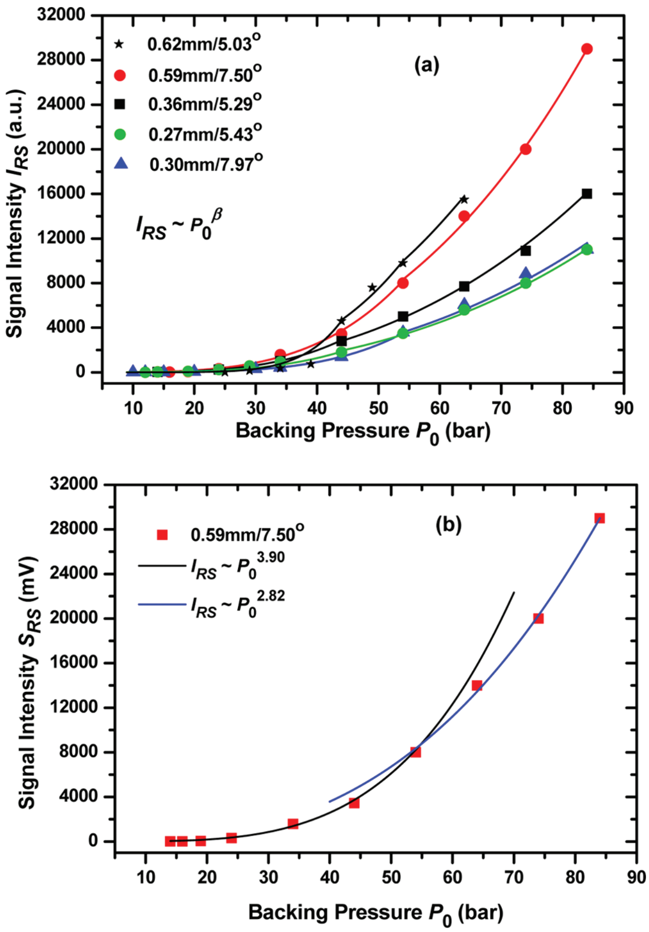

Figure 3. (a) Curves of Rayleigh scattered light intensity I_{RS} versus backing pressure P_0 for methane clusters produced with the five conical nozzles indicated a $I_{RS} \propto P_0^{\beta}$. (b) One curve, which is related to the 0.59 mm/7.50° nozzle, is separated from (a) to display, in a clear way, the variation of β (3.90−2.82 as indicated) taken to be an example for the five curves that have the similar feature.

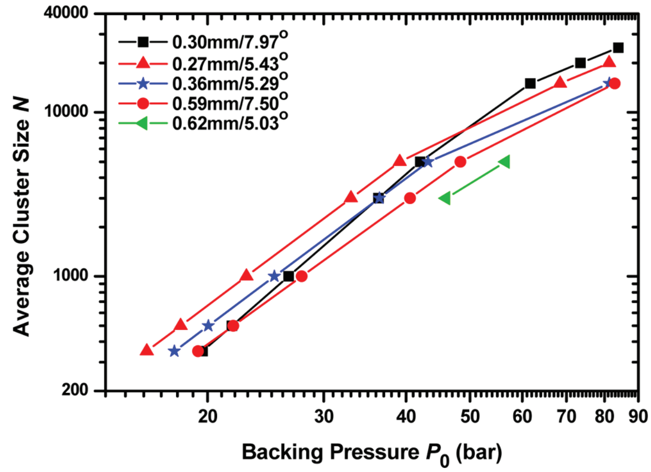

Figure 4. Average size N of methane clusters versus the backing pressure P_0 for the five conical nozzles.

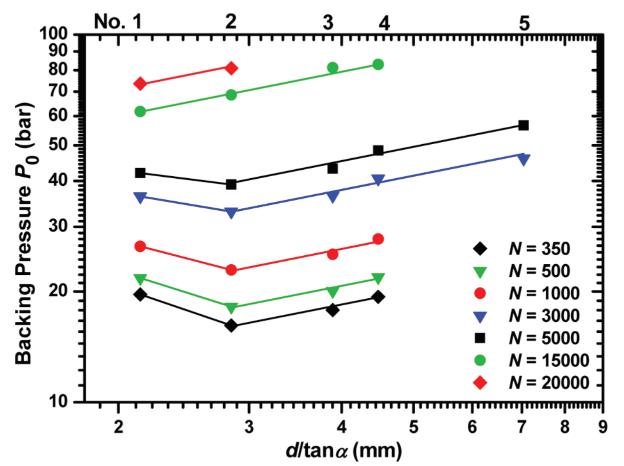

Figure 5. Shows the $P_0(d/\tan\alpha)^q$ = const relations at a defined size N of the methane clusters, with q varying with P_0 and d/tan α.

nozzles are presented in Figure 4, showing that the nozzles of the smaller d/tan α produce slightly larger clusters. At 84 bar, the largest clusters ($N = 2.5 \times 10^4$) were formed with the 0.30 mm/7.97° nozzle. The $P_0 d_{eq}{}^q$ = const relations for a certain N (N = 350, 500, 1000, 3000, 5000, 15000, and 20000) for the five nozzles are shown in Figure 5. The results in Figure 5 would be surprising as compared with the cases of argon clusters that showed the $P_0 d^{0.8}$ = const relation for a certain N, as well as of CO_2 clusters that followed the $P_0 d_{eq}{}^{0.6}$ = const relation.[13] In their study,[13] Hagena and Obert used several sonic nozzles with the diameters d being 0.15, 0.81, and 1.5 mm, and the backing pressures used for argon were less than 40 bar and for CO_2 were within 10 bar for $(N/Z)^*$ = 500. Nevertheless, much has been changed in the present work. It is shown in the left-bottom of Figure 5 that

TABLE 2: Experimentally Measured Rayleigh Scattered Light Intensity I_{RS} as a Function of the Gas Backing Pressure P_0 for the Five Conical Nozzles

0.36 mm/5.29° Conical Nozzle											
P_0 (bar)	14	24	34	44	54	64	74	84			
I_{RS} (mV)	23	250	1000	2800	5000	7700	10900	16000			
0.59 mm/7.50° Conical Nozzle											
P_0 (bar)	14	16	19	24	34	44	54	64	74	84	
I_{RS} (mV)	5.5	14	55	315	1580	3440	8000	14000	20000	29000	
0.30 mm/7.97° Conical Nozzle											
P_0 (bar)	10	12	15	20	30	34	44	54	64	74	84
I_{RS} (mV)	3	5	11.5	48	296	426	1380	3580	6050	8800	11000
0.27 mm/5.43° Conical Nozzle											
P_0 (bar)	12	14	19	24	29	34	44	54	64	74	84
I_{RS} (mV)	2.8	21.5	88	240	560	920	1800	3500	5600	8000	11000
0.62 mm/5.03° Conical Nozzle											
P_0 (bar)	25	29	34	39	44	49	54	64			
I_{RS} (mV)	16.5	155	360	740	4600	7600	9800	15500			

a line drawn by connecting the two data points for the 0.30 mm/7.97° and the 0.27 mm/5.43° nozzles, which have the smaller $d/\tan\alpha$ among the five nozzles, follows a $P_0 d_{eq}{}^q$ = const relation. In this low pressure regime where the condensation just begins to occur, and these two conical nozzles are considered to function as "sonic-like" nozzles having the idealized equivalent diameters d_{eq}, q is found to be 0.65 for $N = 350$, close to the value of 0.6 for CO_2 where the sonic nozzles were used.[13] Figure 5 indicates that, with $d/\tan\alpha$ getting larger or the backing pressure increased, q varied substantially and became negative, implying that the idealized d_{eq} picture of the conical nozzles was completely broken.

The physical sense, if any, behind the observed negative q of the $P_0 d_{eq}{}^q$ = const relation, either with the backing pressure P_0 increased or/and with the larger $d/\tan\alpha$, is that the cluster growth in the flows was restricted. This can be understood through the $P_0(\delta d/\tan\alpha)^{0.65}$ = const (for a certain N) relation just by introducing the effective equivalent sonic nozzle diameter $d_{eq}{}^* = \delta d/\tan\alpha$. With the introduction of $d_{eq}{}^*$, the $P_0 d_{eq}{}^{*0.65}$ = const relation remains, meaning that the conical nozzles behavior in cluster formation like sonic nozzles that have the effective equivalent diameters of $\delta d/\tan\alpha$. Resembling the idealized concept where the conical nozzles are described by the equivalent sonic nozzles of diameters d_{eq},[15] in the present case, the conical nozzles are described by the effective equivalent sonic nozzles of δd_{eq} in throat diameters in cluster formation, but producing the gas flows with the total molecular densities $n_{mol} \propto P_0(d_{eq}/x)^2$ in the vicinity of the nozzle exit, with x being the distance from the nozzle throat along the axial line. The values of δ of the conical nozzles can be estimated by comparing the measured cluster sizes N with that produced by the idealized conical nozzles that have the equivalent sonic nozzle diameters d_{eq}. Taking the performance of the 0.30 mm/7.97° conical nozzle in the low backing pressure as an idealized case for reference for which δ is defined to be unity at $N = 350$, the average size of the methane clusters produced by the idealized conical nozzles with the equivalent sonic nozzle diameters d_{eq} can be given as

$$N_{id} = 1.84 \times 10^{-3}[(d/\tan\alpha)^{0.65}P_0]^{3.5} \quad (2\text{ mm} \le d/\tan\alpha \le 7\text{ mm},\ 10 \le P_0 \le 84\text{ bar}) \quad (5)$$

based on the experimental data. Meanwhile, the experimentally measured average sizes N of the methane clusters produced by the conical nozzles with the effective equivalent sonic-nozzle diameters $d_{eq}{}^*$ will be described by

$$N = 1.84 \times 10^{-3}[(\delta d/\tan\alpha)^{0.65}P_0]^{3.5} \quad (2\text{ mm} \le d/\tan\alpha \le 7\text{ mm},\ 10 \le P_0 \le 84\text{ bar}) \quad (6)$$

where d is in mm, α is in degrees, and P_0 is in bars.

From eqs 5 and 6, δ can be written as

$$\delta = \exp\left(\frac{\ln(N/N_{id})}{0.65 \times 3.5}\right) \quad (7)$$

On the basis of eqs 3 and 4 and the data given in Table 1 and after the cluster size calibration, the values of δ, which are a function of the backing pressure P_0 and the nozzle geometry $d/\tan\alpha$, can be calculated through eqs 5−7. The δ dependence on the nozzle geometry denoted by $d/\tan\alpha$ at the defined backing pressures P_0 (24, 34, 54, 64, and 84 bar) is demonstrated in Figure 6. It indicates that with the increase of $d/\tan\alpha$, δ drops down significantly at a fixed P_0, while the decrease of δ with the increasing P_0 for the individual conical nozzles is also manifested clearly. As a consequence, from the $\delta \sim d/\tan\alpha$ lines for the defined pressures shown in Figure 6, an empirical relation is found as

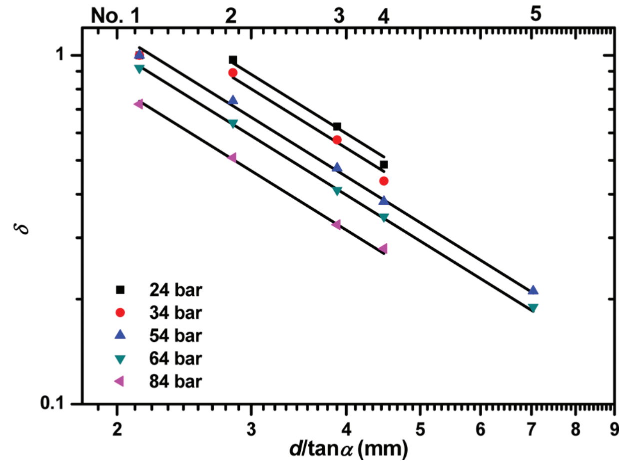

Figure 6. Power scaling of $\delta \propto (d/\tan\alpha)^{-1.36}$ at a defined backing pressure P_0 (24−84 bar as indicated) for the five conical nozzles that have $d/\tan\alpha$ ranging from about 2 to 7 mm.

$$\delta = A/[P_0{}^B(d/\tan\alpha)^{1.36}] \quad (8)$$

where $A = 72$ and $B = 0.80$ in the high pressure regime (54 bar $\le P_0 \le$ 84 bar, 2 mm $< d/\tan\alpha <$ 7 mm) and $A = 8.4$ and $B = 0.26$ in the low pressure regime (24 bar $\le P_0 <$ 54 bar, 2.8 mm $\le d/\tan\alpha \le$ 4.5 mm). Equation 8 describes properly the δ values given in Figure 6 for the no. 2, no. 3, and no. 4 nozzles. Indeed, the behavior of the no. 1 nozzle at low pressures seems unique for the reason that this nozzle is more likely "idealized" ($\delta = 1$) in this case as compared with the others. Yet its sonic nozzle-like characteristic at the low pressures provides a base for the evaluation of the sizes N_{id} of the clusters produced by the idealized conical nozzles. The large variation of the exponents of P_0 in eq 8, i.e., in the high pressure ($P_0 \ge$ 54 bar) and the low pressure ($P_0 <$ 54 bar) regimes is just a signature of the characteristics of the $I_{RS} \propto P_0{}^\beta$ curves where β drops abruptly in the high pressure regime after the break point (Figure 3). For the whole cases investigated, the δ values obtained are from 0.2 to 1.0, depending on the experimental conditions.

Discussion

Calibration of Cluster Size. The adequate calibration of the size of molecular clusters produced in high backing pressure remains to be a challenging subject.[1−5,11,12] In the present work, the absolute size calibration was made in a fitting procedure for the methane clusters produced with the 0.36 mm/5.29° nozzle at P_0 = 44 bar, which were irradiated by a 60 fs, 100 mJ laser pulse with an intensity of 2×10^{17} W/cm^2. The ions ejected from the Coulomb exploded ionic clusters $(C^{K+}H^+{}_4)_N$ were detected by a DMCP detector after a free-flight of 225 cm. Figure 7 presents the experimental time-of-flight spectrum (shown as an inset) of the protons and carbon ions, and the converted kinetic energy spectrum of the ions. It is known that hydrogen and carbon can be easily ionized to the charge states of H^+ and C^{4+} at the laser intensity of 1×10^{16} W/cm^2.[25] However, for methane clusters of a log-normal size distribution to be ionized to the charge state of $(C^{4+}H^+{}_4)_N$ when irradiated by an intense femtosecond laser pulse, the maximum cluster size N_{max}, which corresponds to the radius R_0 of the cluster sphere, is limited by the screening of the Coulomb potential created after the prompt inner and outer ionization of the

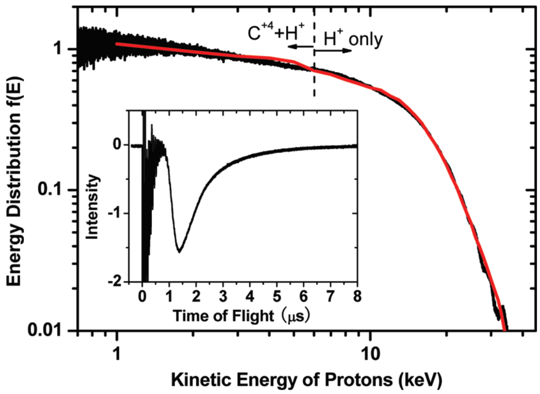

Figure 7. Energy spectrum of ions ejected from the explosion of $(CH_4)_N$ clusters irradiated by an intense laser pulse of an intensity of 2 × 10^{17}W/cm^2. The clusters were produced at the backing pressure of 44 bar. The time-of-flight spectrum of the ions is shown as an inset. The red solid line represents the energy spectrum of ions from the explosions of $(C^{4+}H^{+}{}_4)_N$ clusters which pertain to a log-normal distribution.

clusters. Referred to R_0, which can be termed the border radius, the clusters of smaller radii can be ionized to $(C^{4+}H^{+}{}_4)_N$ followed by full Coulomb explosion as a result of the complete removal of all of the electrons generated in the laser ionization process. R_0 is related to the laser parameters (wavelength λ, and intensity I) and the charge density n_+ of ions within the cluster through[26]

$$R_0^{(I)}\ (\mathrm{nm}) = 55.195\left(\frac{I/10^{18}\ \mathrm{W\ cm^{-2}}}{n_+/10^{22}\ \mathrm{cm^{-3}}}\right)^{1/2} \cdot \lambda\ (\mu\mathrm{m}) \qquad (9)$$

The charge density within the cluster is $n_+ = 8n_0$ for the ionic clusters $(C^{4+}H^{+}{}_4)_N$, where $n_0 = 1.6 \times 10^{22}$ cm^{-3} is the molecular density inside a cluster.[4,18] For the laser parameters used in this work, R_0 is estimated to be 5.5 nm, which corresponds to $N = 1.1 \times 10^4$ according to $r = 0.144(5N)^{1/3}$ (nm).[4,18] The red solid curve in Figure 7 shows a calculated energy spectrum of the ions resulted from Coulomb explosions of the $(C^{4+}H^{+}{}_4)_N$ clusters, which pertain to a log-normal distribution described in eq 1. The best fit of the calculated ion energy spectrum, which is variable with N and σ, with the experimental results (solid curve) leads to the determination of the average radius of 4.23 nm ($N = 5070$) and $\sigma = 0.70$ for the methane clusters at 44 bar with the no. 3 conical nozzle used. It is estimated that the vast majority (90%) of the clusters in a log-normal distribution (average radius of 4.2 nm and $\sigma = 0.70$) can be ionized to $(C^{4+}H^{+}{}_4)_N$ with the laser intensity used in this work. Thus, the calibrated cluster size may be slightly underestimated due to the existence of a small portion of clusters (10%) that have the larger radii than R_0. Attempts are made as to fit the experimental energy spectrum of the ions using other distributions, such as Gaussian, Rayleigh, and Maxwell−Boltzmann distributions, but resulting in χ^2 values about 5−10 times larger than those obtained in the log-normal fits.

δ Parameter. From the definition of $\delta = d_{eq}^*/d_{eq}$, δ is a measure of the performance of the conical nozzle which is based on d_{eq}^*, against that in the idealized case where the conical nozzle functions as a sonic nozzle of the diameter d_{eq}. Here, d_{eq}^* denotes the diameter of a sonic nozzle such that the average size of the clusters generated in free jet expansion with this d_{eq}^* diameter sonic nozzle is equivalent to that of the clusters in the disturbed flow produced by the conical nozzle (d/tan α) in the nonidealized case where the boundary layers effects should be taken into account. The estimation of δ given in eq 7 includes two elements, i.e., N_{id} and the measured N. For the evaluation of N_{id}, the performance of sonic nozzles is necessarily needed to give a $N_{sonic} = a(d^qP_0)^u$ scaling, as that which predicts the argon cluster size.[15] Because of the lack of such a scaling for methane at the present, we have to rely on the "sonic-like" conical nozzles. N_{id}, the average size of the methane clusters produced with the idealized conical nozzles, which have the equivalent sonic nozzle diameters d_{eq}, is estimated through eq 5 on the basis of the performance of the two sonic-like conical nozzles which gives $q = 0.65$ and $u = \beta - 1 = 3.5$. Consequently, the experimentally measured average size $N(P_0,d/\tan\alpha)$ of the clusters, which reflects all the factors that influence the cluster formation, can be described with the effective equivalent sonic-nozzle diameters d_{eq}^* based on the performance of the sonic-like conical nozzles. In this regard, δ and the effective equivalent sonic-nozzle diameters $d_{eq}^* = \delta d/\tan\alpha$ represent the performance of the practical conical nozzles. Compared with the previous investigation on clustering of polyatomic molecules CO_2 made by Hagena and Obert with sonic nozzles at relatively low gas backing pressures,[13] the substantial change of the experimental conditions in this work has led to two observations: (a) a remarkable decrease of β found in the Rayleigh scattering measurements $I_{RS} \propto P_0^{\beta}$, i.e., $N \propto P_0^{\beta-1}$, when P_0 was getting higher, and (b) the anomalous values of q for the $P_0d_{eq}^q$ = const relation (for a certain N), which varied as a function of the backing pressures P_0 and the nozzle geometry d/tan α, and eventually became negative when P_0 was higher or/and d/tan α was larger. With the introduction of the effective equivalent sonic-nozzle diameter d_{eq}^* for the conical nozzles, the above two phenomena can be understood in a correlated and semiquantitative way. As shown in eq 8, $\delta = 72/[P_0^{0.80}(d/\tan\alpha)^{1.36}]$ for $P_0 \geq 54$ bar implies that the performance of the conical nozzles was degraded when the gas flows were strongly constrained by the inner surfaces of the nozzles, and that the reduction of δ is closely related to the molecular densities in the gas flows,[14] $n_{mol} \propto P_0(d/\tan\alpha)^2$, especially, in the high pressure regime. The reduction of the effective equivalent sonic-nozzle diameters of the conical nozzles reflects the restriction of the cluster formation due to some effects including the boundary layers effects in particular and will result in the production of smaller clusters at a certain P_0. It seems puzzling that the average cluster size N comes down with d/tan α of the conical nozzles increased. For instance, referring to the present investigation, the size of the clusters produced with a 0.3 mm/6° conical nozzle will unbelievably reduce a little when it is replaced with a 0.4 mm/6° conical nozzle at a fixed high backing pressure, e.g., $P_0 = 60$ bar. It may be worth mentioning that the cluster density $n_{clus} = n_{mol}/N$ will be increased with N getting smaller. With the example above, a factor of 0.8 reduction of N for the 0.4 mm/6° conical nozzle corresponds to 2.2 times larger cluster density than the 0.3 mm/6° conical nozzle.

From eq 7, it can be seen that δ is independent of the absolute cluster size calibration, on the condition that N and N_{id} are determined under the otherwise identical experimental conditions and with the same size calibration. However, δ will be affected in the transfer of calibration size according to eqs 2 and 7 if η is changed for different conical nozzles at the defined $P_0 = 44$ bar. As mentioned above, the data for argon clusters in ref 27 suggest that η increases a little for P_0 varying from 20 to 60 bar. The same tendency is shown experimentally for xenon clusters in Figure 3 of ref 28 and the other works therein, but η(condensed fraction) shown there is indicated to be saturated with Γ^*; i.e., P_0, increased. These results may imply that, in the present work at $P_0 = 44$ bar, the value of η for methane

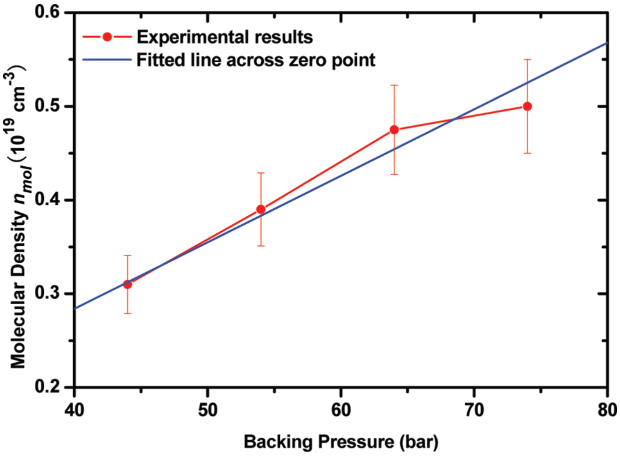

Figure 8. Total CH_4 molecular density n measured by interferometry plotted as a function of P_0, and the linear dependence of $n_{mol} \propto (d/\tan\alpha)^2 P_0$. In the experiment, the interferogram was formed 0.8 mm below the exit of the 0.36 mm/5.29° conical nozzle.

would increase a little with $d/\tan\alpha$ increased. This will result in a small increase of w for the $\delta \propto 1/(d/\tan\alpha)^w$ scaling. Meanwhile, the measurements of the total molecular densities n_{mol} in the flow using optical interferometry confirm that $n_{mol} = K_7(d_{eq}/x)^2 n_0$ is a good representation for the supersonic expansion with conical nozzles for methane[4] and argon.[27] Figure 8 shows our measured total molecular density n_{mol} of a methane flow using optical interferometry. A linear dependence of $n_{mol} \propto (d/\tan\alpha)^2 P_0$ found here for methane with P_0 varying from 40 to 74 bar and that for argon[27] at $P_0 = 20-60$ bar, provide support to the validity of eq 2′ on which the transfer of size calibration has been performed.

The cause of the degradation of the performance of conical nozzles could be qualitatively interpreted by taking into account the boundary layers effects.[13,19,29,30] Although the boundary layers would become thicker with the higher P_0 and the larger $d/\tan\alpha$, because of the more severe constraint of the flows by the inner surface of the nozzles that was associated with the higher molecular densities in the gas flows, it is suggested that the major effects of the boundary layers may pertain to the disturbance of the supersonic free jet expansion,[13] consequently leading to the interference with the gas condensation process.

About the Hagena Parameter. The Hagena parameter Γ^*, which was developed for the estimation of argon cluster size,[14,15] was widely used with success.[19−21] It is speculated that the Hagena parameter Γ^* could be used for molecular clusters, for example, for the CO_2 and CH_4 clusters. Referring to the case of argon clusters,[14,15] the Hagena parameter Γ^* for the methane clusters may be given in the following form for sonic nozzles

$$\Gamma^* = K\frac{(d/\tan\alpha)^q}{T_0^{q'(\gamma)}}P_0 \qquad (10)$$

where K is the condensation parameter taken to be 2360 for methane,[1] and γ is the ratio of heat capacities c_p/c_v, being a function of P_0 and T_0 for methane.[31,32] At the constant temperature T_0, $T_0^{q'(\gamma)}$ will bring about a P_0^f factor to Γ^*, leading to $\Gamma^* \propto P_0^{1+f}$. Unfortunately, the $P_0T_0^{-q'(\gamma)}$ = const scaling is unknown for CH_4 currently. It is expected that the inclusion of the boundary layers effect[13,19,29] will provide a P_0^{-g} factor to Γ^*, leading to the relation $\beta - 1 = 1 + f - g$ for $N \propto P_0^{\beta-1} \propto \Gamma^{*\beta-1}$. When $P_0T_0^{-q'(\gamma)}$ = const and $\gamma(P_0,T_0)$ are known, the boundary layers effects, which are related to g, would be estimated after the experimental determination of the value of β. It is expected that the parameter Γ^* will differ greatly in quantity for argon and methane, largely due to the difference in γ for the two kinds of gas species, as well as the difference in the $P_0T_0^{-q'(\gamma)}$ = const. relations anticipated. Resembling the case for argon clusters in which the same Γ^* corresponds to the same cluster size, when the concept of the effective equivalent diameter d_{eq}^* is used for conical nozzles, then it is the same $\Gamma^{**}(\delta)$ that will result in the same cluster size for methane.

Finally, we wish to mention a separate Rayleigh scattering experiment made in this work in which cluster formation was conducted with the 0.36 mm/5.29° conical nozzle at $P_0 = 10-84$ bar for CH_4 and CD_4 under the otherwise identical conditions. Some similarities were revealed for the two gases, except that the cluster size with CD_4 was about 0.9 times smaller in radius than CH_4 at 84 bar. In this regard, the present results for CH_4 would be, if any, of interest for the research work on the nuclear fusion neutron production resulted from Coulomb explosions of $(CD_4)_N$ clusters subjected to femtosecond intense laser pulses.[3,4] Because the fusion neutron yields due to D−D collisions are closely related both to the average cluster size N and to the total molecular density in the flow n_{mol},[4,18] as shown in this work, $N \propto P_0^{1.7}(d/\tan\alpha)^{-0.82}$ for $P_0 \geq 54$ bar and $n_{mol} \propto P_0(d/\tan\alpha)^2$, a compromise in the design of the conical nozzle for a cluster source would be considered.

Conclusion

In conclusion, we demonstrated experimentally that the methane cluster formation in supersonic expansion will be restricted by the higher gas backing pressure P_0 and the larger $d/\tan\alpha$ of the conical nozzles, which are associated with the increased total molecular densities in the gas flows. To interpret the experimental findings (a) the power β of the $N \propto P_0^{\beta-1}$ scaling of the Rayleigh scattering measurements was decreased with the backing pressure P_0 increased and (b) the values of the exponent q of the $P_0 d_{eq}^q$ = const relation for a certain cluster size N varied and even became negative for higher P_0 and/or larger $d/\tan\alpha$, the effective equivalent diameters d_{eq}^* of the conical nozzles are introduced in the present work. On the basis of the model developed by Hagena and the modification of the idealized d_{eq} with δ, the performance of the conical nozzles as a function of the nozzle geometry denoted by $d/\tan\alpha$ and the backing pressure P_0 is investigated. Coupled with a cluster size calibration procedure, the Rayleigh scattering measurements using five conical nozzles have led to the establishment of an empirical relation $\delta = 72/[P_0^{0.80}(d/\tan\alpha)^{1.36}]$ for 54 bar $\leq P_0 \leq$ 84 bar and 2 mm $\leq d/\tan\alpha \leq$ 7 mm. In the low pressure regime (24 bar $\leq P_0 <$ 54 bar), however, eq 9 is applicable for the conical nozzles with 2.8 mm $< d/\tan\alpha <$ 4.5 mm. This implies that the effective equivalent diameters d_{eq}^* of the conical nozzles will be reduced as the molecular densities in the flows are becoming higher either with P_0 increased or/and with $d/\tan\alpha$ getting larger. It is noted that the impact of P_0 on the performance in cluster formation characterized by δ will be more significant in the high pressure regime. The decrease of δ is caused by all the effects that influence the cluster formation and growth in the gas jets, with the boundary layers effects playing a major role. With the aid of δ, of which the values are relative in nature, the performance of the conical nozzles can be evaluated quasi-quantitatively. The present investigation has shown that δ lies between 0.2 and 1, depending on the experimental conditions. It is expected that for smaller d, larger α, shorter L, and high-quality surfaces of the conical nozzles, the exponent w of $d/\tan\alpha$ for the $\delta \sim (d/\tan\alpha)^w$ scaling would come down.

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