

Formation of $(\text{CH}_4)_N$ van der Waals clusters by seeded supersonic expansion

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Abstract

The existence and the size of large methane van der Waals clusters $(\text{CH}_4)_N$, have been characterized for the first time. $(\text{CH}_4)_N$ van der Waals clusters were generated by the supersonic expansion of a gaseous mixture consisting of 90% H_2 and 10% CH_4 at nozzle temperatures of -30 and 27°C . Based on the buffer gas induced beam-broadening technique, the average sizes of $(\text{CH}_4)_N$ clusters were determined for all values of expansion at different stagnation pressures. For an identical stagnation pressure, the $(\text{CH}_4)_N$ cluster size produced by expansion at a nozzle temperature of -30°C were larger than these produced by expansion at nozzle temperature of 27°C , and cluster sizes of 120 molecules and 60 molecules have been measured for 10 bar stagnation pressure, respectively. In addition, we found $(\text{CH}_4)_N$ cluster formation did not occur by supersonic expansion of pure CH_4 gas at nozzle temperature of 27°C . These results reveal that the presence of H_2 permits the evacuation of the heat of condensation and, thus promotes the $(\text{CH}_4)_N$ cluster nucleation.

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1. Introduction

The field of clusters consisting of several to several thousands of atoms or molecules is particularly interesting, as these systems are intermediate between small molecules and bulk solids. From a fundamental point of view, they offer the opportunity to understand more precisely how atomic structure can lead to physical and chemical properties of macroscopic phase. Moreover, it is possible to produce clusters of atomic arrangements which do not exist in nature and which may consequently exhibit unusual properties. One of the challenges in this field is to produce clusters of any kind of materials in a wide range of sizes. This was achieved with the development of supersonic molecular beams [1–4]. To the present day, the phenomena of clustering and condensation continue to be objects of intensive research activity [5–11]. Methane is widely used for film deposition, because the decomposition of methane can grow diamond-like

carbon (DLC), amorphous carbon films, or carbon nanotubes. The decomposition of methane clusters on surfaces may create new pathways to fabricate nanomaterials. For that purpose, experimental work on producing large $(\text{CH}_4)_N$ van der Waals clusters has been carried out in order to study their formation by supersonic expansion.

In this paper, we demonstrate the formation of large $(\text{CH}_4)_N$ van der Waals clusters up to 120 molecules by the supersonic expansion of a gaseous mixture consisting of 90% H_2 and 10% CH_4 at nozzle temperatures of -30 and 27°C . The clusters have been characterized with the buffer gas induced beam broadening technique [12–14]. We also demonstrate that the formation of $(\text{CH}_4)_N$ clusters does not occur in a supersonic expansion of pure CH_4 gas at a nozzle temperature of 27°C . Results of the average sizes of $(\text{CH}_4)_N$ clusters versus stagnation pressure for both nozzle temperatures are given.

2. Experimental details

The experimental set-up applied to the studies reported here is shown schematically in Fig. 1. It is a slightly modified ver-

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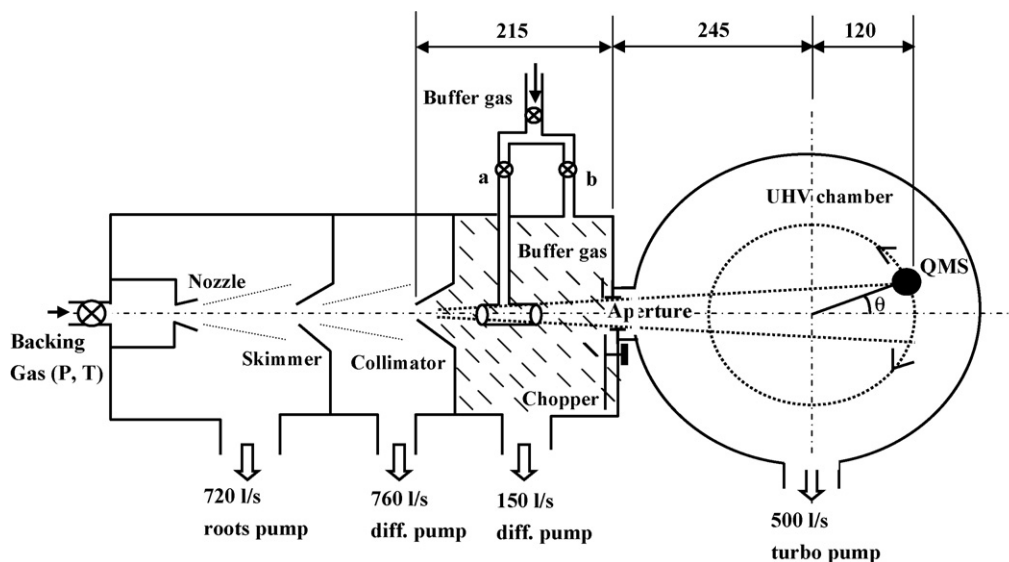


Fig. 1. Schematic representation of the experimental set-up; distances are indicated in mm.

sion of one described earlier [15]. The cluster beam is created by a Campargue-type beam generator through a conical nozzle with a diameter of $d=0.11$ mm, a half-angle of 5° , and a length of 10 mm. The conical nozzle is cooled down by an ethanol flow passing through an ethanol-dry ice mixture. After passing through three differentially pumped vacuum chambers, the cluster beam enters the ultrahigh vacuum (UHV) detection chamber with a base pressure of $\sim 10^{-10}$ Torr. The cluster size can be varied by changing the stagnation pressure and the nozzle temperature. The cluster beam is modulated at 173 Hz by a chopper placed in the third vacuum chamber to allow lock-in detection of the flux and time-of-flight (TOF) measurements.

Argon buffer gas is introduced into the third chamber through a leak valve (b in Fig. 1) in order to check the existence of clusters and to measure their sizes in the next UHV chamber by gas induced beam-broadening technique. For an efficient scattering, the buffer gas is contained in a tube bounded on the entrance by the 0.5 mm diameter collimator which separate the two chambers and of a 3 mm diameter aperture. The total path length (L) of the beam through the tube containing the buffer gas is 215 mm. This third chamber is pumped by a 150 l s^{-1} pumping speed oil diffusion pump. The pressure in this third chamber could normally be kept below 10^{-6} mbar, but due to the introduction of the buffer gas, it is raised step by step up to 10^{-3} mbar and measured with a Penning ionization gauge.

Beam diagnostics are performed in the UHV chamber with a rotatable quadrupole mass spectrometer (QMS) and a lock-in amplifier. The angular resolution of the QMS is better than 0.05° (spatial resolution < 0.1 mm). The spatial resolution required for the beam characterization is obtained by using a rectangular (2 mm wide and 7 mm long) aperture on the head of the QMS. The QMS mass range extends to 200 amu and can consequently only detect monomers and quite small van der Waals complexes (dimers and trimers). Nevertheless, the clusters entering the ionization head of the QMS are fragmented into small particles by electron impact ionization. Consequently the particles which are

finally detected are not the clusters entering the QMS ionization head, but the very small fragments coming from cluster fragmentation on the ionizer meshes. As a result, the QMS is essentially sensitive to the flux of each gas. Hence the cluster composition can be readily obtained from comparison of the QMS signals measured at different masses. In order to obtain the angular distributions, the QMS signals are registered as a function of the QMS positions by taking into account the distance indicated in Fig. 1 and by assuming that the scattering process was taking place in the middle of the path through the buffer gas.

For the supersonic expansion presented here, we used either pure CH_4 gas or a gas mixture of 10% CH_4 diluted in 90% H_2 as the backing gas and the experiments have been run for different nozzle temperatures. Under cooled operation the conical nozzle was kept at a temperature of -30°C , and the backing gas was operated at stagnation pressures of 2.9, 3.9, 4.7, and 9.7 bar. Under room temperature operation the conical nozzle was kept at temperature of 27°C , and the backing gas was operated at stagnation pressures of 2.9, 7.2, and 10.7 bar. The pure CH_4 gas expansion was done only at a nozzle temperature of 27°C , and stagnation pressures of 5 and 10 bar.

3. Results and discussion

Fig. 2 shows a typical set of buffer gas broadening beam profiles for a CH_4 mass setting and a supersonic expansion of the gaseous mixture at a nozzle temperature of -30°C . The stagnation pressure was 4.7 bar, and five different values of the buffer gas pressure P_B were investigated. These angularly resolved flux distributions of CH_4 are quite similar to a Gaussian distribution even far out in the tails of the distribution.

The experimental beam profiles shown in Fig. 2 are normalized, and the normalized beam profiles are shown in Fig. 3 along with their best-fit Gaussian distributions (full curve). The data are scaled by the amplitudes of the fitting curves, to better visualize the broadening. The fits are quite satisfactory, even though the

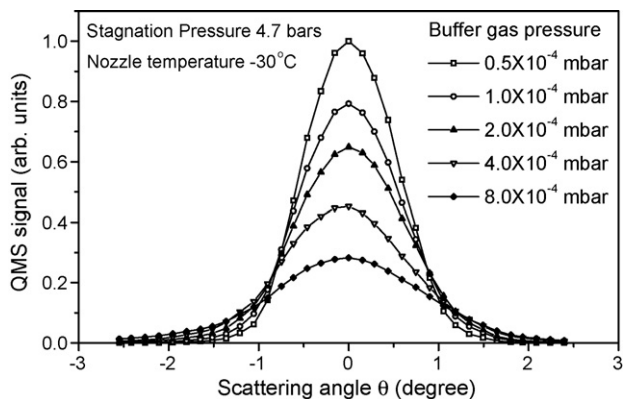


Fig. 2. Angular distributions recorded at stagnation pressure of 4.7 bar of a mixture 90% H₂ + 10% CH₄ and nozzle temperature of -30 °C. The lines joining the experimental data are guides for the eye.

intensities in the tails of the experimental distributions at high buffer gas pressure seem to be slightly underestimated. From the best-fit curves, the values of the full width at half maximum (FWHM) for the beam profiles for each buffer gas pressure are determined.

Since the full details on buffer gas induced beam-broadening technique can be found in the literature [12], only a brief description is given here. When passing through a buffer gas, the clusters are slowed down and the beam profile is broadened in regard with the buffer gas pressure. The broadening is decreasing when the cluster size is increasing. From the measurement of the width of the broadened beam profile, FWHM, as a function of the buffer gas pressure P_B , it is possible to deduce the size of the cluster. The square “ q ” of the FWHM is proportional of the product of the pressure P_B with the broadening coefficient β which is related to the average cluster size by the following relationships:

$$q = q_0 + \frac{2\beta P_B}{kT_B} \quad (1)$$

$$\beta = AL \left[1 + B \frac{1}{N^{2/3}} \right]^2 \quad (2)$$

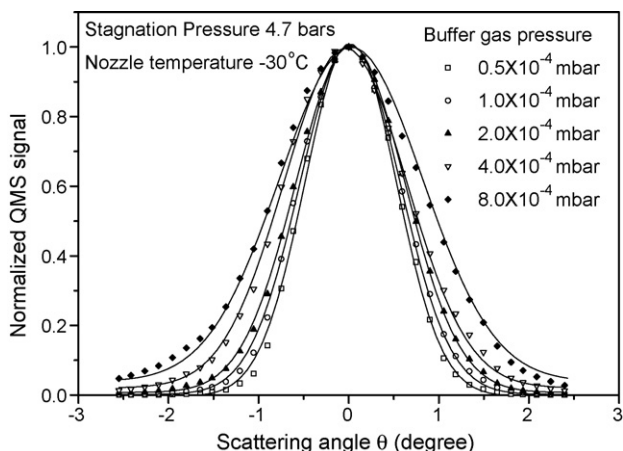


Fig. 3. Same experimental data as in Fig. 2, normalized, and best-fit Gaussian distributions.

T_B is the buffer gas temperature, q_0 is related to the FWHM of the beam profile without buffer gas and L is the total length of the beam through the buffer gas. The constants A and B are depending on the effective hard-sphere radius of CH₄ molecule, on the distance between CH₄ molecule in the solid phase [16], on the CH₄ and Ar masses and on the average speed of the cluster beam. This average speed is measured without buffer gas by TOF method and we obtain values of 2000 and 700 m/s for mixture gas and pure gas, respectively. According to Eq. (1), the β values are therefore determined by extrapolating the slope of the linear relation of q versus P_B , and the average cluster size is calculated using the relation (2) which depends on the shape and width of the beam profile after scattering by the buffer gas and the atom-cluster collision cross-section.

Therefore, each supersonic expansion is treated as follows: for each buffer gas pressure, the beam profile is first recorded. Then, these beam profiles are fitted to Gaussian distributions, which then give the values of FWHM for each beam profile. The presence of clusters in the beam is detected through a linear relationship between q and P_B , and if it is the case, from this linear dependence, we obtain the value of β and the average cluster size as described just above.

The values of q are deduced from the values of FWHM of the beam profiles for each buffer gas pressure. The resulting values of q are plotted as a function of the buffer gas pressure in Fig. 4. The results for the supersonic expansion of a gaseous mixture

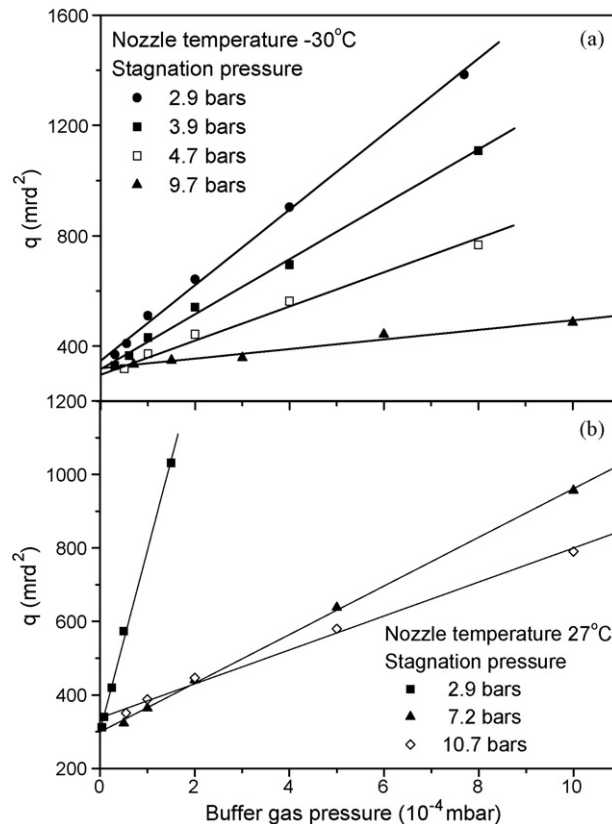


Fig. 4. Plot of the q fitting parameter as a function of buffer gas pressure for mixture 90% H₂ + 10% CH₄ at different stagnation pressures at nozzle temperature of (a) -30 °C and (b) 27 °C.

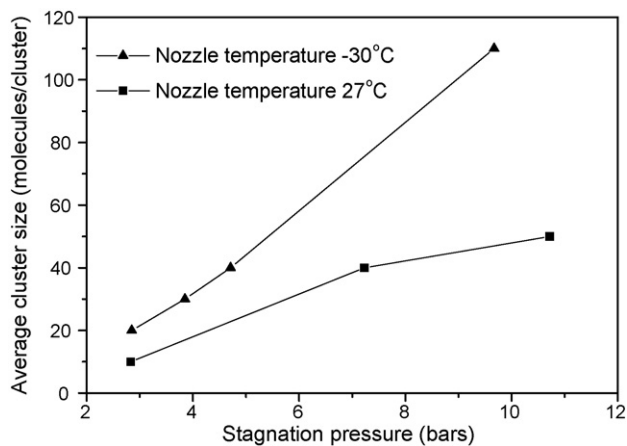


Fig. 5. Average cluster size derived from the data shown in Fig. 4 for both nozzle temperatures of -30 and 27 °C. The lines joining the experimental data are simply guides for the eye.

at a nozzle temperature of -30 °C for four stagnation pressures are shown in Fig. 4(a). The results obtained with a nozzle temperature of 27 °C for three stagnation pressures are shown in Fig. 4(b). For all supersonic expansions which have been investigated, the parameter q is found to increase linearly with P_B , and the slope of $q(P_B)$ decreases monotonically with the stagnation pressure. When the beam consists only of large clusters the integral of the angular distribution is expected to be almost independent of the buffer gas pressure; the buffer gas merely broadens the beam slightly but the total number of detected clusters remains constant. On the other hand, the monomers present in the beam are largely scattered. This effect is responsible for the larger angular distribution broadening observed in monomer beams and some of the scattered monomers disappear from the measured beam profile. This mass filtering effect of a scattering chamber has been used already in a previous work [17] to remove monomers from a partially condensed beam. As shown in Fig. 4, the q value increases linearly with the buffer gas pressure P_B and the integrated beam profile is also a slowly decreasing function of P_B . The linear behavior of $q(P_B)$ shown in Fig. 4 can certainly be traced back to the presence of large clusters in the beam.

Finally, from the measured broadening coefficients β and Eq. (2), we have determined the average cluster size of the supersonic CH_4 beam. The average size of the $(\text{CH}_4)_N$ clusters – obtained from the broadening coefficients β – versus stagnation pressure is shown in Fig. 5 for both nozzle temperatures. The overall uncertainty related to the average cluster size is estimated to be of the order of $\pm 50\%$ [12]. The cluster size grows with increasing stagnation pressure to reach an average size of 120 molecules for a nozzle temperature of -30 °C, and 60 molecules for a nozzle temperature of 27 °C at 10 bar. For the same stagnation pressure, the $(\text{CH}_4)_N$ cluster size produced by expansion at nozzle temperature of -30 °C is larger than the one produced by expansion at a nozzle temperature of 27 °C. Hence, cooling down the nozzle helps CH_4 molecules to nucleate.

For a beam of very small clusters, the parameter q is expected to depend exponentially on P_B when scattered by a buffer gas, and for monomers, the collision model is no longer applicable.

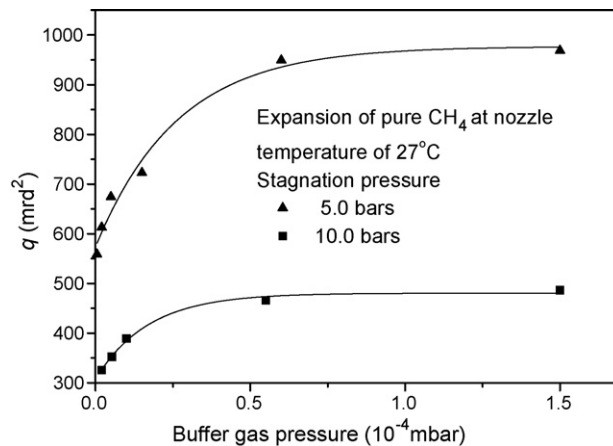


Fig. 6. Plot of the q fitting parameter as function of buffer gas pressure for pure CH_4 at two stagnation pressures of 5 and 10 bar at nozzle temperature of 27 °C.

This is what we have observed in the experimental data recorded for supersonic expansion of pure CH_4 gas at a nozzle temperature of 27 °C with two stagnation pressures of 5 and 10 bar (as shown in Fig. 6). Therefore, we can conclude that $(\text{CH}_4)_N$ cluster formation does not occur by seeded supersonic expansion of pure CH_4 gas at a nozzle temperature of 27 °C. These results show that the presence of H_2 has a dramatic influence on the nucleation process. During the supersonic expansion of mixtures $\text{H}_2 + \text{CH}_4$ at a nozzle temperature of 27 °C, the presence of H_2 allows the evacuation of the heat of condensation due to the very low mass. Thus, its presence promotes the nucleation of CH_4 molecules and large $(\text{CH}_4)_N$ clusters are formed. Evidence of this mechanism can be found in the literature [18,19].

4. Summary

Large $(\text{CH}_4)_N$ van der Waals clusters have been clearly detected and their sizes measured for the first time. These clusters are produced by the supersonic expansion of a gas mixture consisting of 90% H_2 and 10% CH_4 at nozzle temperatures of -30 and 27 °C. The $(\text{CH}_4)_N$ cluster size produced with the cooled nozzle is larger than that produced with the uncooled down nozzle. The formation of large $(\text{CH}_4)_N$ clusters and the measurement of their size will create some new possibilities for fabrication of some nanomaterials by impacting these clusters on surfaces.

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