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Control and characterization of the nucleation process during co-expansion of ternary mixtures

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Abstract. In this paper, we show how the use of a third non-condensable species gives both new insight and control on the binary nucleation process during supersonic expansion of gas mixtures. We present the case of an oxygen-nitrogen mixture diluted in various proportions of helium. Using beam diagnostics, we determine the mean cluster composition and size as well as the percentage of uncondensed matter present in the beam. The presence of helium permits us to understand the cooling and clustering role played by each species during the expansion process. We discuss, in particular, its influence on the dramatic composition change observed at the nucleation onset.

PACS. 36.40.-c Atomic and molecular clusters – 68.03.Fg Evaporation and condensation – 68.49.Fg Cluster scattering from surfaces

1 Introduction

About twenty years ago, evidence of cluster formation was given in supersonic beams. Till then, beam generators have become an indispensable device for both free cluster and cluster/surface interaction studies [1,2]. In many applications, a second gas is added to the clustering one to favor nucleation and to tune the cluster kinetic energy during the expansion process. Recent experimental studies have shown that mixture expansions could also be used to produce binary clusters directly by co-expansion [3,4].

An interesting phenomenon observed in mixture expansions is mass separation downstream the skimmed beam. It can lead to large differences between the composition inside the molecular beam source and after expansion. This phenomenon has been well studied both experimentally and theoretically for gas expansions without or at the very beginning of the nucleation onset [5,6]. It has been attributed to the effect of Mach number focusing: the depletion of the lighter species in the beam centerline being caused by their higher transversal velocities [7].

We have shown in a previous study on binary nucleation by co-expansion that the nucleation onset has a dramatic effect on the beam composition: as the stagnation pressure increases the beam composition changes from one constant composition to another with a threshold at the nucleation onset [3]. A recent experimental study by Li *et al.* confirms the role of cluster formation in inducing downstream gas depletion “which exceeds the levels commonly seen” [8]. This change is attributed to an enhancement of the Mach number focusing due to an increased mass separation between forming nuclei and uncondensed molecules.

In the case of mixture co-expansion and binary nucleation, the clustering process is highly complex due to the interplay between kinetic and thermodynamic factors. The nuclei composition is the result of a dynamic equilibrium with the surrounding gas (competition between continually evaporating and condensing molecules). Conversely, the gas composition and density varies with the heat released by the condensation process and by the mass focusing effect. As a consequence the final cluster composition depends on the ability of the surrounding gas to evacuate the heat of condensation and to favor or limit the growth of the forming nuclei.

In this paper, we use a third non-condensable component (helium) in the co-expansion of a binary oxygen-nitrogen mixture to separately study the cooling effect and the condensation process. With the help of other beam diagnostic techniques like surface scattering which gives the percentage of uncondensed matter present in the beam, we discuss how the presence of this third component influences the nucleation process. We show how it provides new information on the role of the seeded component during the expansion to better understand the nucleation process. Besides, it provides an easy way to tune the cluster composition and size.

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2 Experimental setup

Our experimental setup has been described in detail previously [9]. In this section, we only summarize the essential features that are of interest for the new results presented in the following.

The gas mixtures are prepared by compressing the different pure components in a gas bottle. Their proportions are controlled by a weighting technique. For the measurements presented in this paper, we use a reference mixture with 0.9 molar fraction (mf) of oxygen and 0.1 mf of nitrogen. We dilute this binary mixture in helium with 0.3, 0.45, 0.6, 0.75 and 0.9 mf.

The resulting mixtures are expanded into a supersonic Campargue-type beam generator with a conical nozzle (0.12 mm diameter, 5° half-angle). The beam passes through three differentially pumped chambers before entering an Ultra-High Vacuum (UHV) chamber. Beam diagnostics are performed using a rotatable Quadrupole Mass Spectrometer (QMS) in the UHV chamber. The QMS rotates about the center of the UHV chamber where a surface sample can be placed to intercept the beam. The beam is modulated by a chopper placed in the third vacuum chamber to allow flux lock-in detection and time-of-flight (TOF) measurements.

When entering the ionization head of the QMS, clusters are fragmented into small particles before being detected. Hence, the relative composition of the mixed clusters is obtained from QMS flux measurements directly within the cluster beam at each species mass setting after appropriate sensitivity corrections. In this manner, the species molar fractions are determined within 10% uncertainty.

We can introduce a buffer gas in the third chamber to permit average cluster size determination and mixed cluster detection. The evidence for the presence of mixed clusters in our beam is given by the detection of mixed O_2–N_2 dimers after fragmentation of the parent clusters in the QMS head [3]. The analysis of the broadening of the beam profiles for various buffer gas pressures yields the mean size of our mixed oxygen-nitrogen clusters [10].

Using surface scattering, it is possible to retrieve for each species the percentage of monomers, *i.e.* of uncondensed matter, present within the beam. This method described in details in reference [3] takes advantage of the different surface scattering channels when monomers or clusters impinge on a non-reactive surface with a certain incident angle. Scattered flux measurements for various detection angles yield the proportion of incident uncondensed matter.

3 Results and discussion

3.1 General trends

We present in Figure 1 the evolution of the oxygen molar fraction in the beam *versus* the stagnation pressure for a [0.1 mf O_2]–[0.9 mf N_2] mixture non-diluted and diluted in various proportions of helium. For the non-diluted mixture, two behavior are clearly visible: for stagnation pressures smaller than 2.5 bar, the oxygen molar fraction is constant at 0.15, a value close to the one before expansion; between 2.5 bar and 5.5 bar the oxygen molar fraction undergoes a sharp increase and reaches a constant value of 0.72 for larger stagnation pressures.

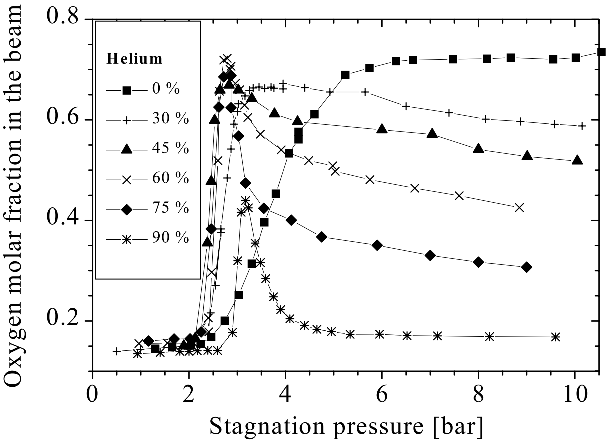

Fig. 1. Oxygen molar fraction *versus* stagnation pressure in the beam for the [0.1 mf O_2]–[0.9 mf N_2] mixture diluted in various proportion of helium.

The dilution in helium has two main effects. First, it sharpens the increase of the oxygen molar fraction between small and large stagnation pressures. For a 30% dilution in helium the transition is, for instance, completed within a 0.5 bar variation of the stagnation pressure. This transition takes place around 2.5 bar for dilutions between 30% to 75% and is slightly delayed at 3 bar for very large helium dilution (90%). The second effect of dilution is a decrease of the oxygen molar fraction for large stagnation pressures. This effect becomes so important that the transition is reduced to a peak with a maximum in the oxygen molar fraction of 0.45 centered around 3 bar in the case of a 90% dilution.

In addition to these composition results, it is possible to measure the percentage of monomers, *i.e.* uncondensed matter, of each species present in the beam using the surface scattering technique [3]. In Figure 2, we present the evolution of uncondensed oxygen and nitrogen fractions *versus* stagnation pressure for the binary oxygen-nitrogen mixture non-diluted (a) and diluted in 0.9 mf of helium (b).

For the non-diluted mixture (Fig. 2a), the proportion of uncondensed oxygen then decreases sharply from 2 bar until oxygen is completely condensed at about 4 bar. Nitrogen condensation follows a similar trend but takes place at larger stagnation pressures: it begins at 2.5 bar and is completed at 7 bar. In the case of a highly diluted mixture (Fig. 2b), the condensation onset is sharper: oxygen nucleates between 2.6 bar and 3.2 bar while nitrogen condensation takes place at slightly larger stagnation pressures: between 2.8 bar and 3.5 bar. The presence of helium reduces considerably the difference between oxygen and nitrogen condensation processes. For intermediate helium dilutions (not shown), the same trends are observed: oxygen

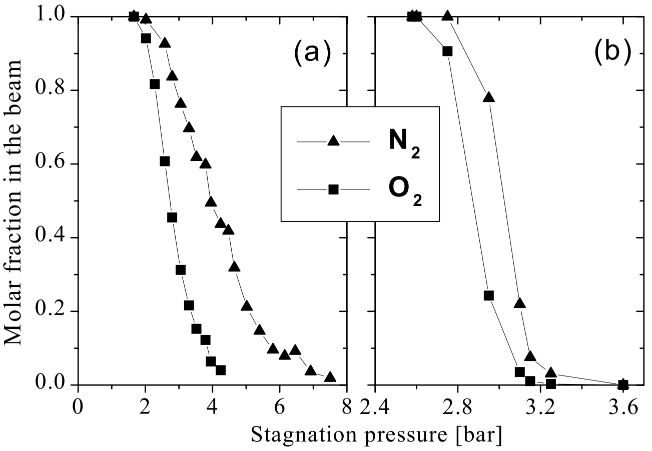

Fig. 2. Molar fraction of uncondensed oxygen (squares) and nitrogen (triangles) *versus* stagnation pressure for the [0.1 mf O_2]–[0.9 mf N_2] mixture non-diluted (a) and diluted in 90% of helium (b).

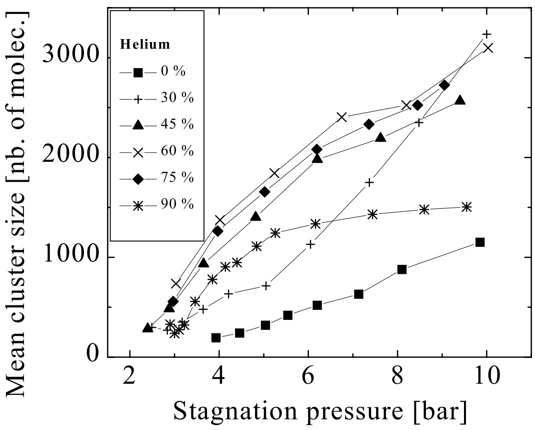

Fig. 3. Mean cluster size *versus* stagnation pressure for the [0.1 mf O_2]–[0.9 mf N_2] mixture diluted in various proportions of helium.

nucleates at smaller stagnation pressures than nitrogen; the presence of helium favors the nucleation process.

In Figure 3 we present the evolution of the mean cluster size with stagnation pressure for our binary mixtures (both non-diluted and diluted in various proportions of helium). For the non-diluted mixture, the cluster size grows linearly with increasing stagnation pressure to reach an average size of 1 200 molecules at 10 bar. For a 30% dilution, the nucleation is favored and the size increase is slightly super-linear with stagnation pressure: on the average, clusters now consist of 3 200 molecules at 10 bar. For dilutions between 45% and 75%, the curves are quite identical: the variation is slightly under-linear even though the nucleation is globally favored by the presence of helium. For the 90% dilution, however, the nucleation is considerably less favored: the cluster size rapidly grows up to 1 300 molecules at 5.5 bar and saturates thereafter at about 1 500 molecules at 10 bar.

3.2 Cluster composition

The results presented in Figures 1 and 2 prove that the dramatic changes in the beam composition occur at the nucleation onset. Those changes have also been observed in other recent experimental studies for various binary mixtures [8,11]. Mach number focusing effects are expected to play a major role in the condensation dynamics. For the small stagnation pressures for which there is no nucleation, the beam composition is about the same as the one prior to expansion since the Mach number focusing effect is negligible because of the small molecular mass difference between nitrogen and oxygen molecules (28 and 32 amu, respectively). On the contrary, at the nucleation onset, the mass difference between the forming clusters and the uncondensed particles becomes very large inducing the cluster focalisation toward the beam centerline. Besides, since oxygen nucleates before nitrogen (*cf.* Fig. 2a), the oxygen molar fraction increases dramatically within the condensed beam. Moreover, this effect is further increased by the heat released during the nucleation process which tends to increase the downstream temperature and thus to scatter the uncondensed nitrogen molecules out of the beam centerline.

As the nucleation proceeds for larger stagnation pressures, nitrogen begins to nucleate partially inhibiting the increase of the oxygen molar fraction. The ability for nitrogen to nucleate depends on the temperature reached during the expansion process. This temperature depends on the expansion itself, but also on the heat released during the nucleation process and on the efficiency for the gas to evacuate this heat. As a consequence, apart from its intrinsic properties, nitrogen nucleation is determined by the initial mixture composition. The molar fraction of oxygen prior to expansion determines the number density of seeds formed in the beam and thus the global heat to be evacuated. It also imposes the proportion of nitrogen which controls the cooling process.

Choosing the initial composition of the binary mixture designates, therefore, the final mixed cluster composition. Increasing the oxygen proportion eventually results in the formation of pure oxygen clusters (for oxygen molar fractions larger than about 0.3). Recent experimental studies on argon-nitrogen mixtures show the same behavior [11]. Note that it is, however, quite difficult to predict the cluster composition for a given mixture since many factors are only poorly known: for instance, the coupling between the number of seeds and the cluster-gas energy [12].

Because of the released condensation heat, the expansion process is not adiabatic downstream the nucleation onset. As the nucleation begins, the local beam temperature is expected to follow the border of the condensation domain for which the temperature is almost constant [13]. The temperature can, thus, be considered constant downstream the position where nucleation starts. This is confirmed by experimental measurements of the cluster internal temperature which prove that cluster growth is limited by evaporation (as soon as they are not too small) [1,14]. It also agrees with the constant oxygen molar fraction for the non-diluted mixture at large stagnation pressures observed in Figure 1. Such a behavior has also been observed for nitrogen–argon co-expansion for which binary nucleation occurs [3].

3.3 The role of helium

We now focus our discussion on the role of helium in the nucleation and expansion processes. Figures 1 and 2 clearly show that the presence of helium has a dramatic influence on the nucleation process.

The very presence of helium influences the expansion before the nucleation onset since, as a mono-atomic gas, it increases the average specific heat ratio of the expanding mixture [12]. This effect does not significantly shift the nucleation onset towards smaller stagnation pressures. For dilutions between 30% and 75%, oxygen begins to nucleate at about 2.5 bar. However, for large dilutions (90%), the nucleation onset is slightly shifted toward larger stagnation pressures (3 bar) which is probably a consequence of the lower oxygen–oxygen collision rate and less efficient dimer formation. Due to the very low mass of helium, changing the third partner X from nitrogen or oxygen to helium in the reaction $2O_2 + X \leftrightarrow (O_2)_2 + X^*$ does not favor the oxygen dimer formation [15].

Experimental results show that helium plays a crucial role after the nucleation onset. Reducing the fraction of condensing matter, it allows the mixture to further cool down downstream the position where nucleation starts. Evidence of this mechanism can be found experimentally in cluster temperature measurements by electron diffraction [16]. This "more" adiabatic expansion shifts the transition point between an uncondensed and a completely condensed beam (*cf.* Fig. 2). The presence of helium permits to evacuate the heat of condensation and, thus, promotes the oxygen and nitrogen nucleation.

The decrease of the oxygen molar fraction at large stagnation pressures with increasing helium dilution is another evidence of the cooling role of helium. The use of a ternary mixture permits us to observe the shift, and eventually the take over, of helium over nitrogen as the "cooling species." As the proportion of helium increases, the cluster temperature decreases during the nucleation process which enhances the nitrogen sticking probability. Eventually, for large values of the helium dilution (see Fig. 1), this sticking probability becomes nearly unity resulting in a cluster composition close to the initial composition before expansion.

Another direct consequence of the cooling efficiency of helium is visible in the average cluster size measurements presented in Figure 3. They show that helium greatly enhances the oxygen–nitrogen nucleation process. For dilutions between 30% and 75%, for instance, the clusters are at least twice as large as without helium. Besides, the growth is rapid in the presence of helium in agreement with the sharper decrease of the quantity of uncondensed oxygen and nitrogen with increasing stagnation pressure (*cf.* Fig. 1). The rarefaction of the condensing species is only visible for a 90% dilution for which the average cluster size is actually smaller than for the intermediate dilutions in helium (see Fig. 3).

4 Conclusion

In this paper, we show that the addition of a non-condensable third gas to a binary mixture permits us to control and to better understand both the expansion and the binary nucleation process. In the case of a [0.1 mf O_2]–[0.9 mf N_2] mixture diluted in various proportions of helium, we show that helium favors nucleation of the other species. From beam composition measurements, it is possible to observe the cooling role of helium and to trace the subsequent increase of the nitrogen sticking probability.

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