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The effect of carrier gas on formation of ammonia clusters

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ABSTRACT

Expanding nozzle beams have been used for many years both as a source to obtain clusters and as a method to study nucleation and growth of clusters. In many cases the addition of the inert carrier gas to the condensing species is essential for the clustering processes. In this paper, the formation of ammonia clusters is investigated experimentally with a supersonic free molecular jet of NH_3-X binary mixtures (X = Ar, He), especially noticing the effect of second species X on the cluster formation. The ion currents of protonated ammonia clusters $(NH_3)_nH^+$ (n = 2–4) were measured with a combined cluster source system and a double focusing sector field mass spectrometer. Experiments were made both by changing the species concentration at constant total pressure and by changing total pressure at constant composition of each mixture. It is observed that, the formation process of ammonia clusters strongly depends on the nature of the carrier gas. The most likely explanation seems to lie in a local thermodynamic equilibrium between the excited clusters and its surroundings.

1. INTRODUCTION

Nucleation and condensation in supersaturated gases and vapours have a long history. The cluster physics has just its origins in early studies of colloids, aerosols and condensation phenomena. Clusters are not only interesting as a “new state” of matter, but they are important due their essential role in many fields of application and technology. This includes such diverse areas as: nucleation phenomena, combustion processes, solvation, crystallography, nuclear physics and photography.

The combination of a gasdynamic technique and mass spectrometers was to play an important role in cluster science. An adiabatic expansion of gas is the most commonly used technique to produce the molecular cluster beams and to study nucleation and growth of clusters [1–3]. In many cases the addition of the inert carrier gas (He, Ne or Ar) to the gas investigated is essential for clustering processes [4–11]. The carrier gas plays a particularly role in the production of metallic clusters or clusters from liquid probes. Based on the nucleation theory for binary nucleation Kashchiev shoved that the carrier gas pressure may increase or decrease the nucleation rate, depending on the nature of the carrier gas [12, 13]. The results presented here concern the molecular clusters that are aggregates of molecules (NH_3, CO_2, for example) which are weekly bonded by hydrogen or van der Waals bonding.

2. EXPERIMENTAL

In our laboratory we constructed a conventional cluster source for the mass spectrometric investigations of gaseous clusters [14–20]. A detailed view of the cluster beam production and the ion extraction optics of double-focussing sector field mass spectrometer was discussed in detail previously [14, 16]. Briefly, the cluster source consists of a liquid-nitrogen-cooled stagnation chamber equipped with a supersonic nozzle of axisymmetric geometry. The nozzle is a simple orifice (diameter of 40 μm) in 0.15 mm thin metal foil. The core of the expanding beam transmitted into the ion source of mass spectrometer is geometrically defined by the skimmer of 0.4 mm diameter. The skimmer-nozzle distance is fixed at 11 mm. The resulting molecular beam containing neutral clusters is introduced to the mass spectrometer ion source. The ion source can operate with an electron current of 40 μA at an electron impact energy of 90 eV. The mass spectrometer is able to perform mass analyses in the mass range 1–1000 u. The spectrum of clusters ions can be observed immediately on the oscilloscope and recorded by the computer counting system.

3. RESULTS AND DISCUSSION

The typical mass spectrum of protonated ammonia clusters $(NH_3)_nH^+$ obtained from the pure gas, at stagnation conditions p_0 = 1750 hPa and T_0 = 293 K, is shown in Figure 1. For the purpose of study the carrier-gas effect our experiments were made both by varying the species concentration at constant total pressure and by varying total pressure at constant composition for each mixture. Figures 2, 3 present the intensity of ion current of $(NH_3)_2H^+$, $(NH_3)_3H^+$ and $(NH_3)_4H^+$ as a function of abundance of ammonia in NH_3/Ar gas mixtures. All experiments have been made at stagnation gas temperature T_0 = 293 K. The diagram points represent the average from seven separate measurements. As results from these figures the highest yield of ammonia clusters production was achieved for the abundance of 40–80% NH_3 in the used mixtures. A higher fraction of the molecular constituent resulted in the decrease of cluster intensity. Only the intensities of $(NH_3)_nH^+$ ion current for cluster size $n = 2$ at stagnation pressure 1500 hPa of the NH_3/Ar mixture not exhibit the maximum. We also observed that for the same concentrations of used mixtures the NH_3/He mixture gives about two times higher production of $(NH_3)_n$ clusters. The optimal concentration of expanded mixtures from the yield clusters point of view should be study for each case, separately.

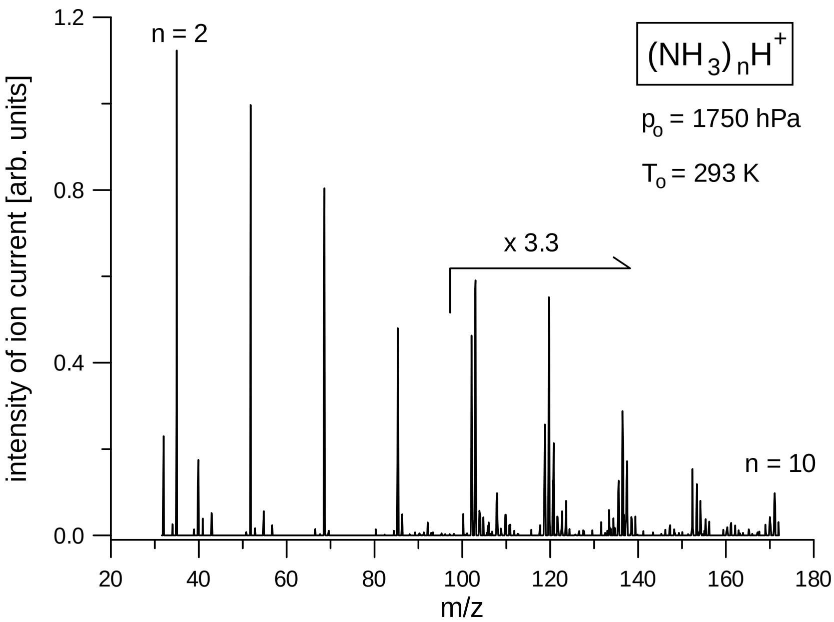

Fig. 1. Mass spectrum of $(NH_3)_nH^+$ cluster ions obtained from pure ammonia at stagnation conditions p_0 = 1750 hPa and T_0 = 293 K

Similar effects were observed by Haberland et al. [7] in the supersonic expansion of water and ammonia seeded in rare gases, and by Ding et al. [8] in experiments with heterogeneous clusters formed from mixtures of Ar with CO and N_2. In the second mentioned work was found that the highest formation of $Ar_{n-m}X_m^+$ (X = CO, N_2) clusters was achieved using 25% N_2 or CO in Ar.

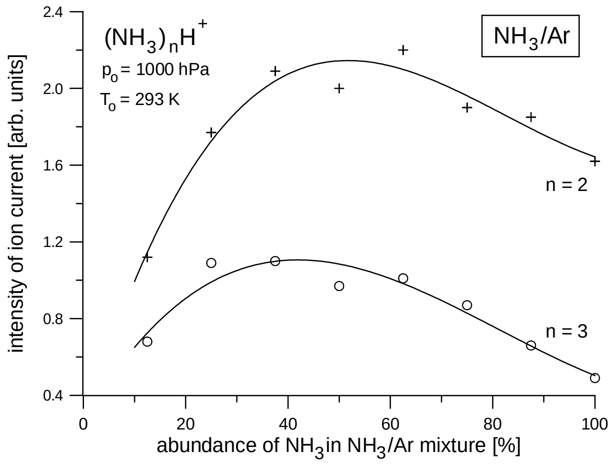

Fig. 2. Intensity of ammonia clusters as a function of abundance of ammonia in NH_3/Ar mixture at stagnation pressure 1000 hPa

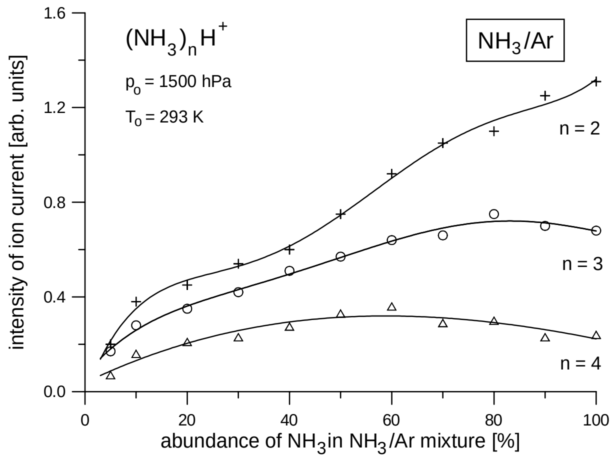

Fig. 3. Intensity of ammonia clusters as a function of abundance of ammonia in NH_3/Ar mixture at stagnation pressure 1500 hPa

Cluster formation in the supersonic beams is a complex process and no complete theory exists [2]. A detailed discussion of the kinetic of cluster growth for pure gases and short discussion for gas mixtures was presented by Hagena [5]. The production of clusters can be described in term of a balance between a process of aggregation and heating, and a process of evaporation and cooling. We suppose that for the results of ammonia clusters presented here the next added molecule during the cluster growth process causes increase its internal energy. In another words, the clusters leave the condensation zone vibrationally hot, because of the heat released during condensation. In the absence of a cooling collision, the number of clusters decreases by unimolecular dissociation. The growth and stabilisation of clusters can be greatly enhanced by cooling collisions with a third body in the expanding beam. The addition of an inert gas to a condensing molecular gas leads to increase of the cluster nucleation in expanding nozzle flows. The knowledge of optimal composition of tested mixtures is very useful in cluster investigations.

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