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Mixed $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ van der Waals clusters created by pick-up technique

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Abstract. A comparison of the adsorption efficiencies for Ar atoms on large $(\mathrm{N}_2)_m$ ($m = 1320-10600$) clusters and N_2 molecules on large $(\mathrm{Ar})_n$ ($n = 7900-17000$) clusters has been investigated by the pick-up technique. Using mass spectroscopy, it has been shown that mixed $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ clusters can be created either by depositing Ar atoms from buffer gas on the surface of $(\mathrm{N}_2)_m$ clusters or by depositing N_2 molecules from buffer gas on the surface of $(\mathrm{Ar})_n$ clusters. The composition of mixed $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ clusters has been determined as a function of cluster size and buffer gas pressure. The adsorption efficiency for Ar on $(\mathrm{N}_2)_m$ clusters is found to be significantly higher than that for N_2 on $(\mathrm{Ar})_n$ clusters. This effect is attributed to the difference in Ar–Ar, N_2–N_2 and Ar–N_2 binding energies.

PACS. 36.40.-c Atomic and molecular clusters – 68.03.Fg Evaporation and condensation

1 Introduction

The production and stability of mixed clusters is a particularly interesting subject in the growing fields of cluster physics. The study of mixed clusters, in which one species is in an excess of another, can provide also a useful method of studying solute-solvent interactions. Generally, mixed clusters can be obtained through two main techniques [1], and the dopant species can be incorporated into a host cluster in two ways. It can either occupy a site within the bulk of the cluster or it can be located on the surface of the cluster. The former case generally results when a premixture is co-expanded through a supersonic molecular beam source. The second case can be achieved using pick-up technique [2] in which atoms or molecules are deposited on the surface of cluster formed by supersonic expansion, then, the deposited atoms or molecules can migrate into host cluster due to the collision induced heating-cooling processes. Mixed $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ clusters produced by co-expansion of Ar+N_2 gas mixture have been largely studied [3–6]. An interesting phenomenon observed in such mixture co-expansion is that the mixed clusters are enriched in argon compared to the initial gas mixture compositions [4]. This prompted us to make pick-up experiments that could bring information about efficiency of adsorption of atoms or molecules on large clusters. The first experiment of mixed $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ clusters produced by pick-up technique was reported by Ozaki et al. [6]. In their work, however, only small-sized clusters with $n < 12$ have been studied. In this paper, we focus on N_2 molecules deposited onto large Ar clusters (more than 5000 atoms/cluster) and Ar atoms deposited onto large N_2 clusters (more than 1000 molecules/cluster) by using pick-up technique. Under these experimental conditions, we are able to get more information on the binary nucleation mechanism and to compare the adsorption efficiency for N_2 molecules onto large Ar clusters with that for Ar atoms onto large N_2 clusters.

In Section 2 we briefly present the experimental set-up and experimental conditions, and in Section 3 we discussed the evidence of mixed $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ clusters produced by the pick-up technique, and the adsorption efficiencies for Ar atoms on large $(\mathrm{N}_2)_m$ clusters and for N_2 molecules on large $(\mathrm{Ar})_n$ clusters. Discussion and conclusions are given in Sections 4 and 5.

2 Experimental details

The experimental set-up is shown schematically in Figure 1. It is a modification of that described earlier [7]. 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. After passing through three differentially pumped vacuum chambers, the cluster beam enters the detection

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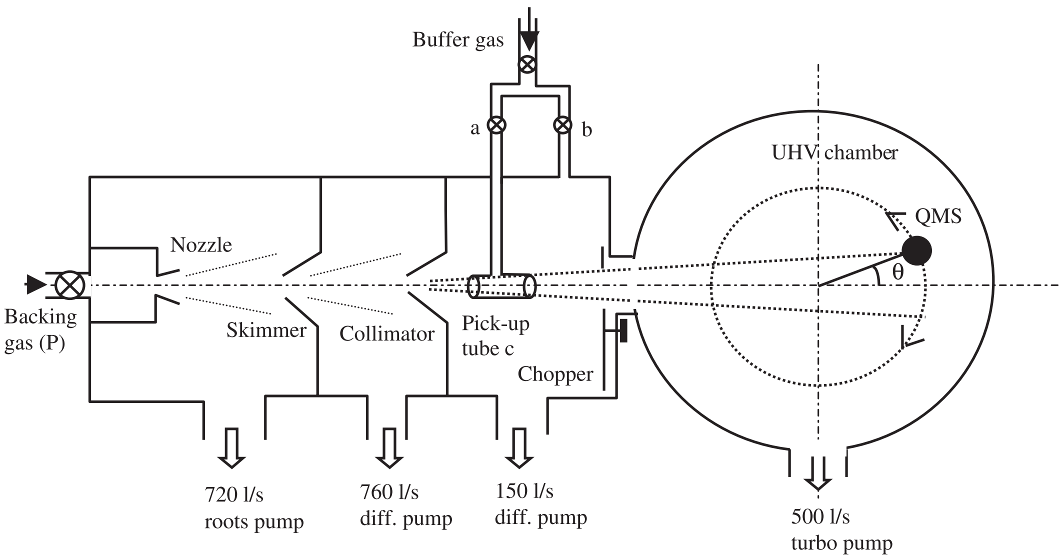

Fig. 1. Experimental set-up.

Table 1. Experimental parameters.

Backing gas	Ar				N$_2$		
Buffer gas	N$_2$				Ar		
Buffer gas pressure (Torr)	0.01 ∼ 0.5				0.01 ∼ 0.5		
Cluster velocity (m/s)	560				750		
Backing pressure (bar)	4	6	8	11	13	20	30
Average cluster size n (particles/cluster)	2900	7900	10600	17000	1320	6600	10500

ultrahigh vacuum (UHV) chamber with the base pressure of $\sim 10^{-10}$ Torr. Beam diagnostics are performed with a rotatable quadruple mass spectrometer (QMS). The cluster size can be varied by changing the backing pressure. The cluster beam is modulated at 173 Hz by a chopper placed in the third vacuum chamber to allow flux lock-in detection and time-of-flight (TOF) measurements. The velocity of clusters is determined from TOF measurements. The average cluster size is determined by the buffer gas induced beam-broadening technique [8]. The uncertainty of the average cluster size deduced from this method is ∼50%. The actual beam parameters used in the present experiments are given in Table 1.

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 angular resolution of rotatable QMS is better than 0.05° (spatial resolution <0.1 mm). The QMS mass range extends to 200 amu and can consequently only detect monomers and quite small van der Waals complexes (dimers and trimers). When large cluster enter the ionization head of the QMS, they are fragmented into small particles by electron impact ionization. The finally detected particles 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.

The deposition of dopant atoms or molecules on host clusters ("pick-up technique") was performed using a small tube (tube 'c' in Fig. 1) with a diameter of $d = 4$ mm and a length of 50 mm mounted in the beam path in the third chamber. This tube is filled with the buffer gas through the tube 'a'. Pure Ar or N$_2$ clusters will collide with the buffer gas (N$_2$ or Ar) in the tube 'c'. The results of such collisions are mixed $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ clusters. The relative composition of the mixed $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ clusters is determined from QMS flux measurements directly within the cluster beam at each species mass settings using the appropriate sensitivity corrections.

3 Experimental results

In order to supplement the information of mixed $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ clusters obtained from the gas mixture expansion experiments, two systems, $(\mathrm{Ar})_n + m\mathrm{N}_2$ and $(\mathrm{N}_2)_m + n\mathrm{Ar}$, were investigated by means of the pick-up technique. The existence and the characterization of mixed $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ clusters rely on the analysis of beam profiles for different mass settings of the QMS. The beam composition is deduced from the signal intensities of the profiles

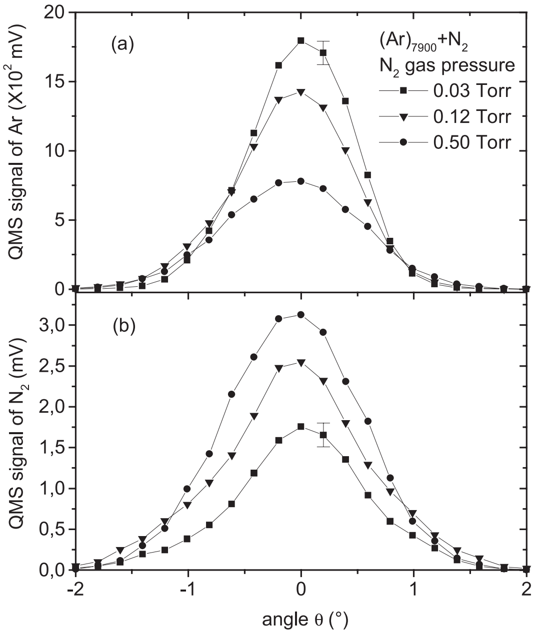

Fig. 2. Angular distributions of flux for $(Ar)_{7900}$ clusters pick-up N_2 with different N_2 gas pressure, for Ar (a) and N_2 (b). The solid curves are provided as a guide for the eye.

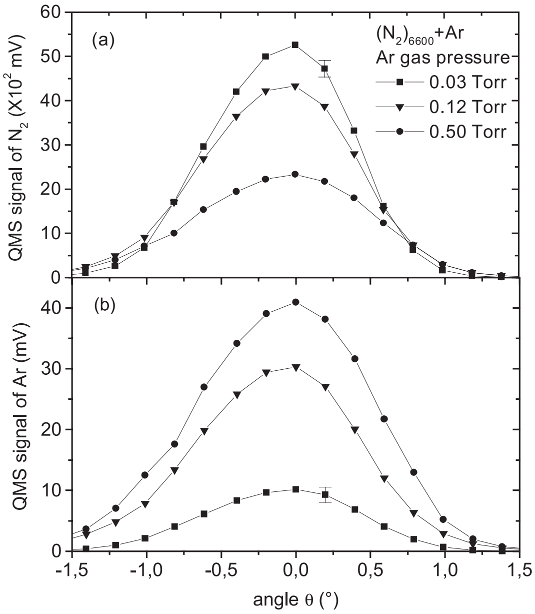

Fig. 3. Angular distributions of flux for $(N_2)_{6600}$ clusters pick-up Ar with different Ar gas pressure, for N_2 (a) and Ar (b). The solid curves are provided as a guide for the eye.

given by the QMS. Figure 2 shows a typical set of QMS signals for large $(Ar)_n$ clusters colliding with N_2 molecules with different N_2 gas pressure. The average cluster size n of the incoming Ar clusters is 7900 atoms/cluster. The QMS signals of host Ar species are decreasing as the N_2 gas pressure is increasing, while the N_2 QMS signals are increasing as the N_2 gas pressure is increasing. These results show that N_2 molecules have been deposited onto the large Ar clusters in the pick-up tube. An additional measurement of the QMS signals for (ArN_2) complex mass settings was performed in order to verify that mixed $(Ar)_n(N_2)_m$ clusters have been formed. For a given N_2 gas pressure, we find that the normalized beam profiles measured for Ar, N_2, and (ArN_2) complexes are quite identical. The (ArN_2) complexes have survived from the QMS fragmentation. This means that they are issued from fragmentation of large mixed $(Ar)_n(N_2)_m$ clusters. The velocities of Ar, N_2, and (ArN_2) complexes in the cluster beam were determined from TOF measurements. The quite same values were obtained for these three velocities. These two factors confirm that mixed $(Ar)_n(N_2)_m$ clusters have been formed during the collision of large Ar clusters with N_2 molecules. It is obvious that the percentage of N_2 molecules deposited onto large Ar clusters is increasing when increasing the N_2 gas pressure.

Figure 3 shows a typical set of QMS signals of large $(N_2)_m$ clusters colliding with Ar atoms for different Ar gas pressure. The average size m of the incoming N_2 clusters is 6600 molecules/cluster. The variation trends for N_2 and Ar QMS signals with different Ar gas pressure are similar to those shown in Figure 2. The same measurement as large $(Ar)_n$ clusters colliding with N_2 molecules was performed for large $(N_2)_m$ clusters colliding with Ar atoms. For a given Ar gas pressure, we also find that the normalized beam profiles measured for Ar, N_2, and (ArN_2) complexes are quite identical and the velocities of Ar, N_2, and (ArN_2) complexes in the cluster beam are the same. From these cluster-atom or molecule collision results described above, we can conclude that mixed $(Ar)_n(N_2)_m$ clusters can be created either by large $(Ar)_n$ clusters colliding with N_2 molecules or by large $(N_2)_m$ clusters colliding with Ar atoms. We define from that point the mixed ratio between the dopant and the host cluster as the ratio between dopant QMS signal at maximum and the host's one. As a result, we find that different mixed ratios for mixed $(Ar)_n(N_2)_m$ clusters can be produced by changing the buffer gas pressure (P_b).

In Figure 4, the mixed ratios for $(Ar)_n(N_2)_m$ clusters are plotted as a function of P_b values. For both systems, $(Ar)_n + mN_2$ and $(N_2)_m + nAr$, the mixed ratios increase with increasing P_b up to 0.5 Torr. For incoming $(Ar)_n$ and $(N_2)_m$ clusters with comparable average cluster size, the mixed ratios of $((Ar)_{10600} + mN_2)$ case are quite smaller than these of $((N_2)_{10500}+nAr)$ case for the same buffer gas pressure. These results indicate that the efficiency of large $(N_2)_m$ clusters picking up Ar atoms is higher than that of large $(Ar)_n$ clusters picking up N_2 molecules. Taking this behavior into account, we could already infer that it is more difficult to exchange Ar atoms by N_2 molecules during the $(Ar)_n$ clusters collision with N_2 molecules, than the opposite. That means that the $(Ar)_n$ cluster is more stable than the $(N_2)_n$ cluster.

From Figure 4, we also find that the mixed ratios of $(Ar_n + mN_2)$ case are quite smaller than these of $((N_2)_n + mAr)$ case for all cluster-atom or molecule

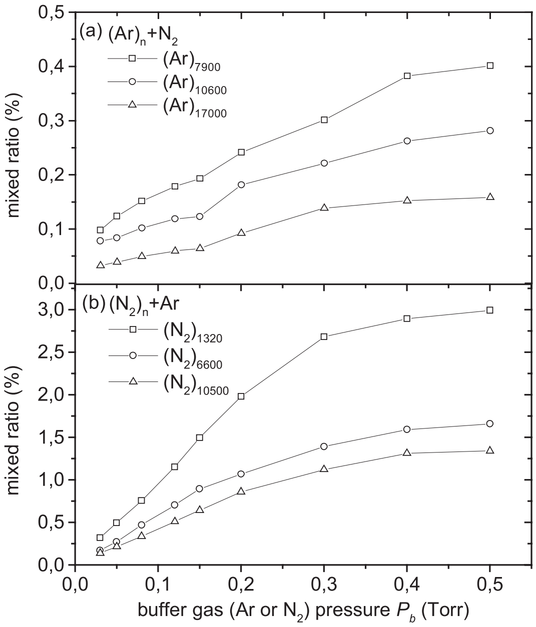

Fig. 4. Variation of the mixed ratios in mixed $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ clusters versus buffer gas pressure for large Ar and N_2 clusters with different cluster sizes. The solid curves are provided as a guide for the eye.

collisions studied here. These results further confirm that the efficiency of large $(\mathrm{N}_2)_n$ clusters picking up Ar atoms is much higher than that of large $(\mathrm{Ar})_n$ clusters picking up N_2 molecules. There is obvious variation corresponding to the mixed ratios with the cluster sizes n. The larger the incoming cluster size, the smaller the mixed ratios is obtained.

In order to evaluate the efficiency of the pick-up process for Ar atoms on large $(\mathrm{N}_2)_m$ clusters and N_2 molecules on large $(\mathrm{Ar})_n$ clusters, we define the adsorption efficiency as the ratio of the number of adsorbed atoms or molecules per cluster and the number of collisions per cluster. The number of adsorbed atoms or molecules per cluster can be deduced from the QMS signal and the initial cluster size. For a tube of length L the number of collisions per cluster is given as $k = N_B \sigma L$ [9], where N_B denotes the density of buffer gas and σ is the cross-section. In the supersonic expansion, the Ar and N_2 clusters are solid [10,11]. As a rough estimate one can use the "hard-sphere-model" and the Wigner-Seitz radii to determine the cross-section. These values are evaluated and the results of the adsorption efficiency of Ar atoms on large $(\mathrm{N}_2)_m$ clusters and N_2 molecules on large $(\mathrm{Ar})_n$ clusters as a function of buffer gas pressure are shown in Figure 5. It can be seen that the adsorption efficiencies of Ar atoms on large $(\mathrm{N}_2)_m$ clusters are larger than these of N_2 molecules on large $(\mathrm{Ar})_n$ clusters. The curve of the adsorption efficiencies versus buffer gas pressures is dependent of the cluster size. The larger the incoming cluster size, the smaller is the adsorption efficiency. The adsorption efficiencies also depend on the buffer gas pressure. They decrease as the buffer gas pressure increases.

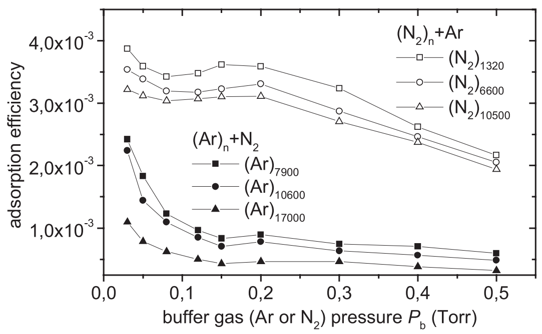

Fig. 5. The adsorption efficiency of Ar atoms on large $(\mathrm{N}_2)_m$ clusters and N_2 molecules on large $(\mathrm{Ar})_n$ clusters as a function of buffer gas pressure and cluster size. The solid curves are provided as a guide for the eye.

4 Discussion

During the collisions of large clusters with atoms or molecules, we generally consider a two-stage mechanism where an atom or a molecule, A, is attached to a cluster, B_n:

$$\mathrm{A} + \mathrm{B}_n \underset{\text{desorption}}{\overset{\text{absorption}}{\rightleftarrows}} (\mathrm{AB}_n)_{surf} \xrightarrow{\text{accommodation}} (\mathrm{AB}_{n-1}).$$

The first step corresponds to the adsorption of the atom or molecule onto the cluster to give an energized surface intermediate state, $(\mathrm{AB}_n)_{surf}$. If the binding energy of the atom or molecule is large enough, the heat of adsorption will be dissipated in the cluster by the evaporation of a small number of cluster atoms or molecules which stabilizes the cluster. For large enough clusters, this additional energy can be accommodated without any melting of the cluster. For the more weakly bound species, desorption from the cluster will become an important process. For the strongly bound species, pick-up atoms or molecules might interact with each other to form complexes or subclusters in the case of a multiple capture whereby the bound host always compensates for heating due to the momentum transfer by the same evaporation mechanism.

Chartrand et al. have shown [12] that a critical consideration as to whether an atom or a molecule will be solvated or remain on the surface of a cluster is the relative strength of the solute-solvent interaction compared with the solvent-solvent interaction. If the solvent-solvent interaction is greater than that between the solvent and solute, solvation will not be energetically favorable. Our results indicate that it is relatively easier for Ar atoms to be adsorbed onto large N_2 clusters than for N_2 molecules to be adsorbed onto large Ar clusters. This is expected, because the argon-nitrogen (solute-solvent) binding energy is higher than the nitrogen-nitrogen (solvent-solvent) one (121 K [13] versus 95 K [14]). It is likely that the neat argon clusters are more stable than neat nitrogen clusters and that the replacement of an argon atom in the argon clusters by a nitrogen molecule is always more difficult than that of a nitrogen molecule in the nitrogen clusters by an argon atom. The weakly nitrogen-nitrogen bound in nitrogen clusters is also especially beneficial to the pick-up process as the nitrogen is preferentially evaporated from the resulting $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ clusters giving rise to its stabilization. In addition, nitrogen molecules have additional degree of freedom like rotation and vibration which might result in less stability of nitrogen clusters [15,16]. One can imagine that to replace particles from less stability nitrogen clusters is easier than the reverse. According to these mechanisms, Ar subclusters in $((\mathrm{N}_2)_n + m\mathrm{Ar})$ case is easily formed due to the stronger Ar–Ar interaction (120 K [14]) during pick-up processes [17], and the relative weaker N_2–N_2 interaction can evaporate N_2 molecules to stabilize the mixed $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ clusters. Furthermore, because of the stronger Ar–Ar interaction, the Ar atoms or subclusters can be solvated by large N_2 clusters. For $(\mathrm{Ar}_n + m\mathrm{N}_2)$ case, the situation will be reverse. We can speculate that if the interaction between the adsorbed N_2 molecules and the condensed Ar clusters is not strong enough to overcome the Ar–Ar interaction, most of the N_2 molecules will be rapidly evaporated from surface of the Ar clusters. This might present an explanation for our experimental results.

According to the results of Vach's work [17–19], further discussion can be made on our experimental results. Vach has performed a molecular dynamics study of the pick-up process for Ne, SiF_4, Kr, and Xe dopants deposited onto Ar_n clusters with n ranging from 53 to 5000 atoms. He found both Ne and SiF_4 dopants always stay upon the surface of the Ar clusters but are never fully encapsulated within the cluster, while Kr and Xe dopants penetrate into the Ar host clusters and remain there permanently. Subclusters of Kr and Xe dopants can be formed inside of the host Ar clusters due to strong Kr–Kr and Xe–Xe interaction. In our case, for the N_2 molecules interacting with the large Ar clusters, the situation is just like Ne dopant deposited onto large Ar clusters. We believe that the N_2 molecules stay upon the surface of the Ar clusters and will be lost easily in the scattering process leading to lower adsorption efficiency. For the Ar atoms interacting with the large N_2 clusters, the situation is just like Xe dopant deposited onto large Ar clusters. The Ar atoms penetrate into the large N_2 host clusters and remain there permanently. Subclusters of Ar dopants can be formed inside of the large N_2 host clusters due to strong Ar–Ar interaction. These trends result in higher adsorption efficiency for Ar atoms deposited onto large N_2 clusters.

Fort et al. [4] have shown that the large mixed argon-nitrogen clusters produced by co-expansion are enriched in argon compared to the starting gas mixture compositions. The loss of nitrogen may also explain our observation that Ar atoms prefer to be solvated by large nitrogen clusters, but N_2 molecules do not prefer to be solvated by large Ar clusters and will be lost in the colliding processes. Torchet et al. [3] also found evidence for mixed argon-nitrogen clusters in their electron diffraction experiments on co-expansions of premixture of Ar in N_2. They found in the mixed clusters a proportion of argon is larger than that in the premixture gas, and the clusters generated by coexpansion were composed of relatively compact argon cores with nitrogen molecules at surface [15]. These results are quite similar to those reported by Fort et al.

The decrease of the adsorption efficiency with the buffer gas pressure is explained by the fact that the weakly bonded dopant atoms or molecules are evaporated due to the collisions. With increasing of buffer gas pressure, the incoming flux of buffer gas increases. This results in more collisions and evaporating more weakly bonded atoms or molecules. In fact, the number of atoms or molecules absorbed by the cluster depends sensitively on the buffer gas pressure. Under the assumption that the capture cross-section does not vary upon the pick-up process, it is given by a Poisson distribution [20]. Thus, one can conclude that the adsorption efficiency will decrease when the buffer gas pressure is increased. This is quite in agreement with our finds.

Finally, the work of Vigué et al. [21] may explain our observation that the mixed ratios depend on the incoming cluster sizes n. In their work, they have shown the sticking cross-section of atoms or molecules onto large vdW clusters, σ_{cap}, is proportional to n^{α} with the n is the incoming cluster size and α is a constant ($\alpha = 1/3$ or $2/3$). Such dependence would result in the mixed ratios decreasing when increasing the incoming cluster size n. These results are in agreement with our findings.

5 Conclusions

We have shown that the pick-up technique can be used as an alternative to co-expansions of Ar/N_2 mixtures to produce mixed $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ clusters. Comparison of the composition of mixed $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ clusters produced by depositing of Ar atoms on large N_2 clusters with that of mixed $(\mathrm{Ar})_n(\mathrm{N}_2)_m$ clusters obtained by depositing N_2 molecules on large Ar clusters shows that the adsorption efficiency of Ar is significantly higher. The result is attributed to the different interaction of Ar–Ar, N_2–N_2, and Ar–N_2. This study gives complementary interpretation of the results obtained by co-expansions.

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