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# The structure of mixed nitrogen-argon clusters

## A comparison of simulation results with experimental electron diffraction patterns

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**Abstract.** Using realistic pair potentials, we investigate the structures of mixed clusters of argon and nitrogen in order to interpret the experimental electron diffraction patterns reported by the Torchet group. Simulations of small clusters indicate that argon tends to segregate at the center of the clusters. For larger clusters, in the range of 50 to 200 molecules, MC methods have been used to simulate structures that are likely to be generated in the molecular beam. By comparing predicted electron diffraction patterns with those recorded in the experiments, our models allow us to estimate the average size and composition of the mixed clusters for a given set of experimental conditions (nozzle stagnation pressure and Ar partial pressure).

**PACS.** 36.40.-c Atomic and molecular clusters – 82.20.Wt Computational modeling; simulation – 61.14.-x Electron diffraction and scattering

## 1 Introduction

Recent work by the Torchet group at Orsay [1] and the Châtelet group at Palaiseau [2] has shown that neutral mixed argon-nitrogen clusters can be produced in a supersonic expansion [3]. The Châtelet group used beam deflection (by background scattering) to estimate the size of the clusters as a function of stagnation pressure and to estimate the proportion of Ar in the clusters as compared to the Ar:$N_2$ ratio in the gas mixture [2]. Their results indicate that clusters are enriched in argon compared to the starting gas mixture. In addition, the size of the clusters increases superlinearly with the pressure at the nozzle. As a point of reference, Fort *et al.* [3] show that for a total pressure of 10 bar with 10% Ar, the expansion produces clusters of less than 100 molecules with about 1/3 of them argon atoms.

The electron diffraction work of the Torchet group [1] provides somewhat more detailed information about the clusters in the beam since the diffraction rings can, in principle, be Fourier inverted to give radial distribution functions. However, it must be noted that the distribution of cluster sizes is rather broad for these neutral expansions. As noted by Bartell, the half-width at half maximum of the distribution of cluster radii ranges "from 10 to 40% of the most probable radius [4]". Thus the wide range of cluster sizes (and stoichiometries for mixed clusters) in the beam makes direct interpretation of the patterns impossible. A careful analysis [1] of the relative heights of two peaks (at 2 $\text{Å}^{-1}$ and 3.5 $\text{Å}^{-1}$) in the experimental patterns with partial pressure of $N_2$ showed that these patterns were not consistent with a possible superposition of pure Ar and pure $N_2$ patterns (both of which had been analyzed previously [5–8]). Thus the gas mixture is thought to give rise to mixed clusters in agreement with the Palaiseau experiments.

In order to analyze the electron diffraction patterns, it is necessary to construct model clusters to generate radial distribution functions and electron diffraction patterns. The usefulness of this approach is perhaps even greater in the mixed cluster case than it was for pure clusters of Ar, $N_2$, $CO_2$, etc. [4–9].

## 2 Potentials

We have used realistic pair potentials for the Ar-Ar, Ar-$N_2$, $N_2$-$N_2$ interactions to construct mixed clusters of size up to about 200 particles with a complete range of stoichiometries. Our starting point for the Ar-Ar potential is the Aziz-Chen potential [10], which, however, we have fit to a slightly simpler and computationally less expensive form following Weerasinghe and Amar [11] and used by Hermine *et al.* [12]. For the $N_2$-$N_2$ interaction we have adopted the potential of Böhm and Ahlrichs [13] which represents the dispersion and repulsion terms by Lennard-Jones spheres on the nuclei and the quadrupole of $N_2$ by 3 point charges distributed along the

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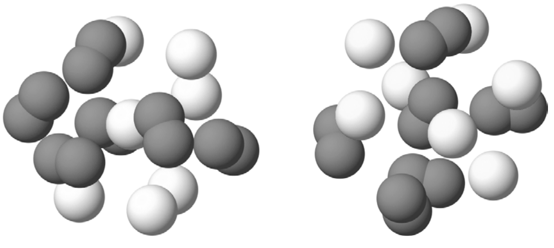
**Table 1.** Intermolecular distance and dissociation energy for equilibrium dimers of Ar-Ar, Ar-$N_2$ and $N_2$-$N_2$.

| Dimer | $R_e$ (Å) | $D_e$ ($cm^{-1}$) |
|---|---|---|
| Ar-Ar | 3.75 | 99.4 |
| Ar-$N_2$ | 3.64 | 111.9 |
| $N_2$-$N_2$ | | |
| canted parallel | 3.98 | 102.5 |
| ⊤-shaped | 4.15 | 102.8 |



(a) (b)

**Fig. 1.** Two isomers of $Ar_7(N_2)_6$ cluster, with Ar at center (a) and with $N_2$ at center (b).

internuclear axis. Finally, we have adopted the Ar-$N_2$ potential of Bowers, Tang and Toennies [14]. The equilibrium dimer energies are given in Table 1. Note that while the two $N_2$ dimers and the Ar-$N_2$ dimer have lower equilibrium energies than the Ar-Ar dimer, the anisotropy of both the $N_2$-$N_2$ and Ar-$N_2$ interactions is significant. Additional details about and discussion of our treatment of the potentials will be found elsewhere [15,16]. We shall use the Ar-Ar well depth of the potential described above as our unit of energy, $\epsilon^*$.

## 3 Structures of mixed clusters

We have systematically constructed, equilibrated and quenched all the mixed clusters, $Ar_{13-m}(N_2)_m$, $0 \leq m \leq 13$, starting from the "magic" $Ar_{13}$ regular icosahedron. Figure 1 shows two quenched structures of the $Ar_7(N_2)_6$ cluster: (a) an argon centered icosahedron; and (b) an $N_2$-centered icosahedral structure. While we observe small deviations from regular icosahedral structure, it is more important to note that the Ar-centered structure is $2.1\epsilon^*$ more stable than the corresponding nitrogen-centered isomer.

This preferential stability is apparent across the whole series of 13-mers as is shown in Figure 2. We attribute this extra stability of the Ar-centered clusters to a frustration effect: $N_2$ at the center cannot be optimally oriented with all 12 of its surface neighbors; this orientation dependence is less problematic with Ar at the center.

Molecular dynamics simulations of larger clusters such as $Ar_{13}(N_2)_{42}$ (argon icosahedral core) and $Ar_{42}(N_2)_{13}$ (nitrogen cuboctahedral core) show that larger clusters with Ar cores tend to be stable while those with nitrogen cores display mixing behavior (at temperatures at or above the melting temperature of the clusters). Further details of the structure, energetics and thermodynamic properties of small mixed Ar-$N_2$ clusters are given elsewhere [15,16].

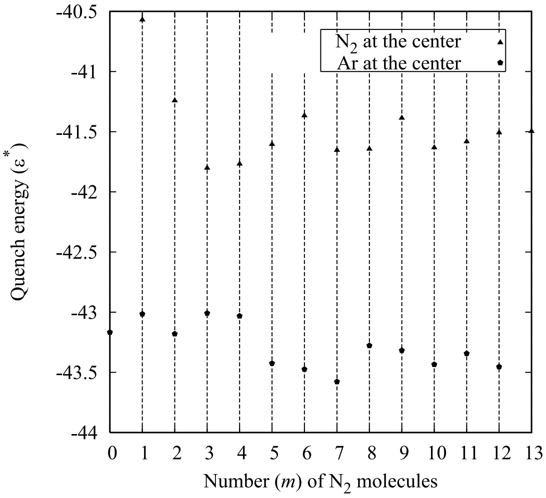


**Fig. 2.** Quench energies of lowest energy isomers of $Ar_{13-m}(N_2)_m$ clusters, with Ar at center and with $N_2$ at center.

The conclusion of this section is that, at equilibrium, mixed Ar-$N_2$ clusters will tend to have a stable, compact core of Ar atoms surrounded by $N_2$ molecules at the surface. We have assumed this general structure in designing a growth sequence for generating and equilibrating cluster models from which we can calculate electron diffraction patterns.

## 4 Growth models and electron diffraction patterns

We have constructed models of mixed clusters by starting from pure Ar clusters and then replacing a number of atoms with $N_2$ molecules. It is known from the studies of pure Ar [5] and pure $N_2$ [8] that small clusters, from $N = 13$ to about 40 particles, are polyicosahedral, that is made up of interpenetrating primitive icosahedra [17]. Above this size, multi-shell icosahedral structures (Mackay icosahedra–complete or incomplete) begin to dominate the patterns seen [6]. Finally, above about 1000 atoms, Ar clusters display a transition to cubic structures. For pure $N_2$, the same basic patterns are seen though the transition to the bulk structures occurs at smaller sizes, around 200 molecules. We have used these same basic templates in constructing mixed particle models. To create the polyicosahedral models used in the intermediate size range we have used a Monte Carlo (MC) procedure to add Ar atoms to a previously quenched cluster by selecting an orientation at random and having the new atom just touch the closest cluster atom along the line of centers between the atom and the cluster center of mass. We then equilibrate the cluster using Metropolis MC at a temperature a little below the melting temperature of the cluster. Finally we quench this structure to a local minimum. This procedure can be repeated for every size to generate a series of pure Ar clusters. Choosing a total number of particles, $N$, we then replace $m$ Ar atoms with $N_2$ molecules (starting from the surface sites) to create clusters of chemical formula, $Ar_{N-m}(N_2)_m$ with relatively compact argon cores.

In order to generate electron diffraction patterns from these configurations, we perform a short dynamics run (slightly below the melting temperature) to generate the three radial distribution functions of interest: $g_{\text{Ar-Ar}}(r)$, $g_{\text{Ar-N}}(r)$, and $g_{\text{N-N}}(r)$. Then we use the following equation to calculate the diffraction pattern for a given cluster of $n$ atoms (Ar) and $m$ rigid diatomics ($N_2$) [9,18]

$$
\begin{aligned}
I(s) &= n\left(f_{\text{Ar}}^2(s) + \frac{S_{\text{Ar}}(s)}{s^4}\right) + 2m\left(f_{\text{N}}^2(s) + \frac{S_{\text{N}}(s)}{s^4}\right)\\
&\quad + n f_{\text{Ar}}^2(s)\frac{4\pi}{s}\int_0^{r_{\max}} r g_{\text{Ar-Ar}}(r)\sin sr\,\mathrm{d}r\\
&\quad + 2m f_{\text{N}}^2(s)\frac{4\pi}{s}\int_0^{r_{\max}} r g_{\text{N-N}}(r)\sin sr\,\mathrm{d}r\\
&\quad + 2nm f_{\text{Ar}}(s) f_{\text{N}}(s)\frac{4\pi}{s}\int_0^{r_{\max}} r g_{\text{Ar-N}}(r)\sin sr\,\mathrm{d}r\\
&\quad + 2m f_{\text{N}}^2(s)\frac{\sin sr_{\text{mol}}}{sr_{\text{mol}}}\exp\left[-\frac{l_{\text{mol}}^2 s^2}{2}\right],
\end{aligned}
$$

where

$$
\begin{aligned}
\int_0^{r_{\max}} 4\pi r^2 g_{\text{Ar-Ar}}(r)\sin sr\,\mathrm{d}r &= n-1,\\
\int_0^{r_{\max}} 4\pi r^2 g_{\text{Ar-N}}(r)\sin sr\,\mathrm{d}r &= 2nm,\\
\int_0^{r_{\max}} 4\pi r^2 g_{\text{N-N}}(r)\sin sr\,\mathrm{d}r &= 2(m-1).
\end{aligned}
$$

The first two terms are atomic structure factors; the next three terms are Fourier integrals of the radial distribution functions. Note that the fourth term does not include the intermolecular N-N distances in $g_{\text{N-N}}(r)$. These are given in the sixth term so that the effect of nonrigidity can be calculated (using Gaussian broadening) in the simulation of the diffraction pattern.

## 5 Results

Torchet *et al.* [1] present a series of electron diffraction patterns at a stagnation pressure of 10 bar. In this series, shown in Figure 3, the mole percent of Ar is varied from as little as 5% to 60%.

Previous studies on pure argon [5,6] and pure nitrogen [7,8] have interpreted the features seen in these diffraction patterns. The splitting of the second peak into a doublet is characteristic of an amorphous structure, mainly polyicosahedral, in both argon and nitrogen diffraction patterns. In pure nitrogen patterns, the wide oscillation of the third peak (around 6.5 Å$^{-1}$) is due to interference from N-N intramolecular distances of both free nitrogen molecules and nitrogen molecules in the cluster. The strong angular damping of the first peak in pure nitrogen patterns, in contrast to the pure argon patterns, is due to large librational motions of nitrogen molecules.

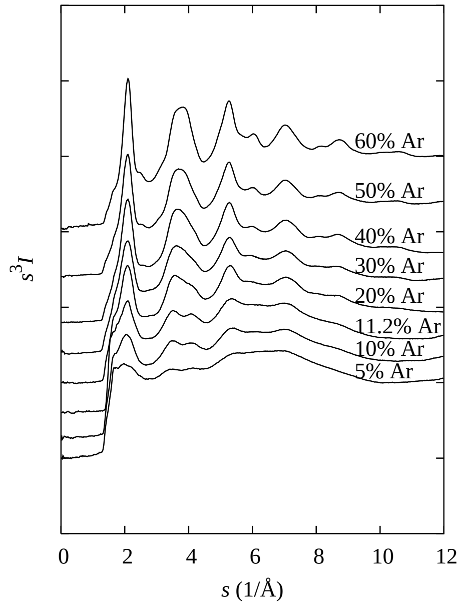


**Fig. 3.** Experimental diffraction patterns at 10 bar for different argon mole percentages in the beam [1].

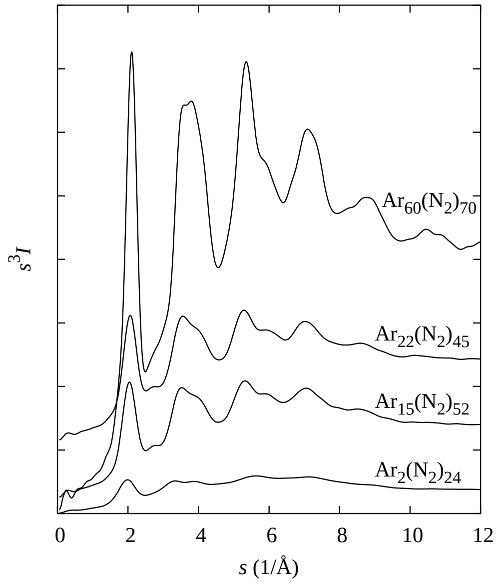


**Fig. 4.** Calculated diffraction patterns of some $Ar_n(N_2)_m$ clusters for $(n+m) < 130$. The composition of each cluster is given above each curve.

In addition to these characteristic differences in the two pure patterns, the position of the first peak for nitrogen is at a lower $s$ value than that for argon. This variation can be seen in the diffraction patterns generated from argon-nitrogen mixed clusters.

We attempted to reproduce the features of the experimental diffraction patterns, in particular the doublet at around 3.8 Å$^{-1}$, by generating polyicosahedron structures as described in Section 3 in the size range from 15 to 67 particles. As shown in Figure 4, polyicosahedral structures replicate the evolution of the doublet at 3.8 Å$^{-1}$ with stagnation pressure (size). We come back to these

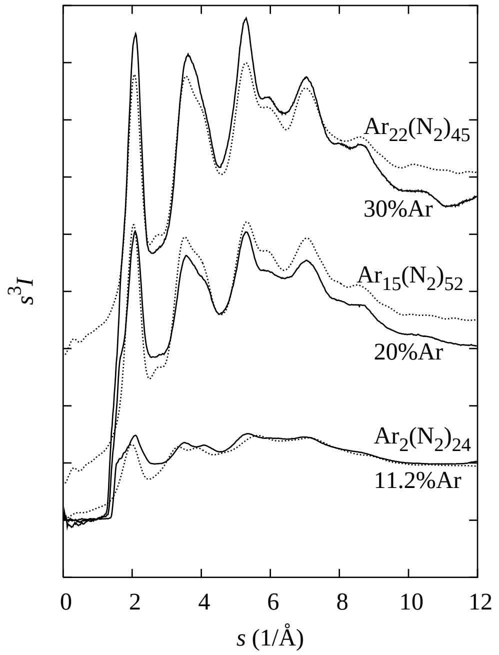


**Fig. 5.** Comparison of the calculated diffraction patterns of $Ar_2(N_2)_{24}$, $Ar_{15}(N_2)_{52}$ and $Ar_{22}(N_2)_{45}$ with experimental curves at 10 bar. The experimental patterns (solid line) for each Ar mole percent have been multiplied by a constant factor to raise them closer to the calculated patterns (dotted line).

curves below. The top curve of Figure 4 corresponds to a multi-shell icosahedral cluster, $Ar_{60}(N_2)_{70}$. This pattern is in much better agreement with the experiment at 40% Ar than any polyicosahedral models that have been tried.

Figure 5 displays the calculated patterns for $Ar_2(N_2)_{24}$, $Ar_{15}(N_2)_{52}$ and $Ar_{22}(N_2)_{45}$ along with the experimental patterns (at 10 bar) for 11.2%, 20% and 30% argon respectively. In comparing the calculated pattern for $Ar_2(N_2)_{24}$ with the experimental pattern at 10 bar with 11.2% Ar, we see good overall agreement (much better than pure $N_2$ patterns, for example). We do, however, still see small discrepancies in the peak positions and in the intensity of the trough at around 2.5 $Å^{-1}$. The discrepancies *may* be explained by presence of a distribution of cluster sizes and composition in the beam and by the presence of gas molecules which add a scattering background to the experimental measurements. We can conclude, however, that under these conditions, the cluster beam contains polyicosahedral clusters of size $20 < N < 30$ with nitrogen making up at least 90% of the particles.

The calculated patterns for $Ar_{15}(N_2)_{52}$ and $Ar_{22}(N_2)_{45}$ are remarkably similar to the experimental patterns for 20% and 30% Ar, respectively. The good match of the evolution of the second peak (at $\sim 3.8$ $Å^{-1}$) and the doublet structure around 6.5 $Å^{-1}$ indicates that the model structures capture the overall change in composition and size reasonably well. We conclude that polyicosahedral structures of size between 60 and 70 molecules are responsible for diffraction patterns at 20% and 30% Ar at 10 bar.

## 6 Conclusions and further work

So far our exploration of larger cluster structures and diffraction patterns has been limited to a survey of characteristic structures. This has allowed us to identify general size ranges and stoichiometries that match patterns generated under a given set of experimental conditions (total stagnation pressure and mole %Ar. The clusters generated in the beam are composed of relatively compact Ar cores with $N_2$ molecules at the surface. A more detailed discussion of these structures will be found in references [15,19].

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