There has long been a discrepancy between the size distributions of \( \mathrm{Ar}_n^+ \) clusters measured by different groups regarding whether or not magic numbers appear at sizes corresponding to the closure of icosahedral (sub-)shells. We show that the previously observed magic cluster size distributions are likely the result of an unresolved \( \mathrm{Ar}_n \mathrm{H}^+ \) component, that is, from protonated argon clusters. We find that the proton impurity gives cluster geometries that are much closer to those for neutral rare gas clusters, which are known to form icosahedral structures, than the pure cationic clusters, explaining why the mass spectra from protonated argon clusters better matches these structural models. Our results thus show that even small impurities, e.g. a single proton, can significantly influence the properties of clusters.

Rare gas clusters are some of the simplest chemical systems studied, with many of their structural properties deduced from basic sphere packing models \[1\] or classical two-body interactions such as the Lennard-Jones 6-12 potential \[2, 3\]. Theoretical studies have shown that the global energy minima of such clusters containing less than a few hundred particles (with few exceptions \[4\]) prefer icosahedral geometries where shell closures (and the filling of faces on the polyhedra) are associated with enhanced stabilities \[5–7\].

It is, alas, difficult to experimentally study the structures and stabilities of neutral rare-gas clusters \[8\]. Charged clusters are, however, easily studied using mass spectrometric techniques. In 1981, Echt et al. reported that clusters of xenon formed by supersonic expansion and ionized by electron impact showed enhanced abundances of clusters that are free of helium. The inset of Figure 1 shows a zoom-in of the mass range covering \( \mathrm{Ar}_n^+ \) clusters that can be separated up to cluster sizes of \( n \approx 100 \). We find that the pure \( \mathrm{Ar}_n^+ \) cluster series show few abundance anomalies in agreement with results from Refs. \[15–20\], while the protonated \( \mathrm{Ar}_n \mathrm{H}^+ \) clusters show pronounced magic numbers in agreement with the results on \( \mathrm{Ar}_n^+ \) clusters by Harris et al. \[11, 12\] and neutral Lennard-Jones clusters \[5\]. We thus come to believe that the significant differences observed in past studies of argon clusters is due to contributions from protonated clusters. This conclusion is further motivated by \textit{ab initio} calculations of pure and protonated argon clusters.

In Figure 1 we show an overview spectrum from He nanodroplets doped with Ar and H\(_2\) prior to ionization. At low masses (below about 400 u/e) we mainly see the contribution from pure \( \mathrm{He}_n^+ \) clusters from larger neutral droplets that fragment upon ionization. At higher masses the spectrum is dominated by \( \mathrm{Ar}_n^+ \), \( \mathrm{Ar}_n \mathrm{H}^+ \), and \( \mathrm{Ar}_n \mathrm{H}_2^+ \) clusters that are free of helium. The inset of Figure 1 shows a zoom-in of the mass range covering \( \mathrm{Ar}_{19}^+ \) and \( \mathrm{Ar}_{20}^+ \) systems. With the resolution of the mass spectrometer (\( R \approx 4000 \)) we can clearly separate the individual cluster series, the relative intensities of which can be

---

**Magic Sizes of Cationic and Protonated Argon Clusters**

Michael Gatchell\(^1,2\) Paul Martini\(^1\), Lorenz Kranabetter\(^1\), Bilal Rasul\(^1,3\) and Paul Scheier\(^1\)

\(^1\)Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria

\(^2\)Department of Physics, Stockholm University, 106 91 Stockholm, Sweden

\(^3\)Department of Physics, University of Sargodha, 40100 Sargodha, Pakistan

(Dated: December 4, 2019)

The droplets are formed by the supersonic expansion of compressed (2.5 MPa) He through a nozzle that is cooled to 9.5 K. The droplets capture Ar and H\(_2\) gas, that is injected in a pickup chamber, which condense into clusters in the superfluid 0.37 K droplets. The droplets are ionized by impact of 76 eV electrons and the positively charged products are analyzed with a reflectron time-of-flight mass spectrometer (ToFwerk AG model HTOF). The mass spectra are calibrated and analyzed using the Isotope-Fit software \[25\]. This method of producing rare gas clusters has been used in the past to study \( \mathrm{Ar}_n^+ \) \[20\] and \( \mathrm{Kr}_n^+ \) \[20\] clusters, giving results is good agreement with other techniques \[15, 19\].

In Figure 1 we show an overview spectrum from He nanodroplets doped with Ar and H\(_2\) prior to ionization. At low masses (below about 400 u/e) we mainly see the contribution from pure \( \mathrm{He}_n^+ \) clusters from larger neutral droplets that fragment upon ionization. At higher masses the spectrum is dominated by \( \mathrm{Ar}_n^+ \), \( \mathrm{Ar}_n \mathrm{H}^+ \), and \( \mathrm{Ar}_n \mathrm{H}_2^+ \) clusters that are free of helium. The inset of Figure 1 shows a zoom-in of the mass range covering \( \mathrm{Ar}_{19}^+ \) and \( \mathrm{Ar}_{20}^+ \) systems. With the resolution of the mass spectrometer (\( R \approx 4000 \)) we can clearly separate the individual cluster series, the relative intensities of which can be
tuned by varying the Ar and H$_2$ pressures in the pickup region.

Size distributions of Ar$_n^+$, Ar$_n$H$^+$, and Ar$_n$H$_3^+$ clusters are shown in Figure 2 from separate measurements where we have optimized the intensities of each series. This does not affect the specific structures in each series, but can shift the underlying log-normal distributions that result from the pickup statistics. Vertical dashed lines in each panel show the magic cluster sizes reported by Harris et al. [11, 12] for pure Ar$_n^+$ clusters and the most prominent of these features are labeled above the top panel. The pure Ar$_n^+$ series (top panel of Figure 2) displays a log-normal size distribution with few anomalies. The depleted Ar$_{20}^+$ channel reported numerous times in the past [15, 20] is clearly visible, as are a few other anomalies. There is a clear drop-off in intensity between Ar$_{23}^+$ and Ar$_{24}^+$, one that has been reported before [20], as well as what could be interpreted as magic peaks from Ar$_{16}^+$ and Ar$_{27}^+$. Although small on an absolute scale due to the underlying cluster size distribution, there are also clear abundance anomalies visible for Ar$_{81}^+$ and Ar$_{87}^+$, which match magic numbers previously reported for Ar$_n^+$ [11, 12], Kr$_n^+$ [13], and Xe$_n^+$ [1] clusters.

The distribution of protonated Ar clusters (middle panel of Figure 2) is clearly different from that of the pure argon clusters (top panel). It is immediately clear that every single magic size identified by Harris et al. [11] for pure Ar$_n^+$ clusters is associated with an abundance anomaly in our Ar$_n$H$^+$ series. In addition to this, there are several more subtle features that agree between the two works, such as the particularly low abundance of Ar$_{50}^+$ clusters that is followed by a plateau of relatively abundant Ar$_{51}^+$ through Ar$_{54}^+$ peaks. The main standout feature is that we also identify a magic Ar$_7$H$^+$ peak, which lies below the lower limit of most Ar$_n^+$ mass spectra found in the literature and is rarely discussed.

In the bottom panel Figure 2 we show a size distribution of Ar$_n$H$_3^+$ clusters. Some anomalies match the magic sizes seen with Ar$_n$H$^+$ clusters (e.g. $n = 19, 29, 43, 55$) though most do not. It is thus clear that the specific positions of abundance anomalies, i.e. magic numbers, is indeed dependent on the types of impurities present in the argon clusters. For the remainder of this letter we will mainly focus on the Ar$_6^+$ and Ar$_n$H$^+$ clusters.

Clusters of the form Ar$_n$X$^+$, where X is some impurity atom or molecule, have been studied in the past [20, 27, 30], displaying magic features similar to those reported for pure Ar$_n^+$ clusters. For example, a magic Ar$_{54}$N$_2^+$ cluster has been identified where one of the Ar atoms in an icosahedral geometry is replaced with a N$_2$ molecule [20]. Protonated argon has also been well studied for small systems such as the ArH$^+$ dimer [31, 32] and the linear ArHAr$^+$ system [33, 34]. However, previous experimental studies on protonated argon clusters have only investigated small clusters containing less than 10 Ar atoms [27, 30], while theory has covered Ar$_n$H$^+$ sizes up to $n = 35$ [29, 30, 34].
To better understand our experimental results, we have performed \textit{ab initio} structure calculations of neutral \( \text{Ar}_n \) clusters, cationic \( \text{Ar}_n^+ \) clusters, and protonated \( \text{Ar}_n \text{H}^+ \) clusters for sizes up to \( n = 21 \). The calculations were performed at MP2(Full)/def2-SVPP level using Gaussian 16 \cite{Gaussian16}. This method was selected based on previous theoretical studies \cite{29, 30}, test-calculations on the geometries of small cluster sizes, and due to the favorable scaling that allows us to study clusters with up to relatively large sizes. The vaporization energy for losing a single, neutral Ar atom as a function of cluster size of these systems is shown in Figure 3, and the optimized structures of \( \text{Ar}_{13}^+ \), \( \text{Ar}_{13} \text{H}^+ \), \( \text{Ar}_{14}^+ \), \( \text{Ar}_{14} \text{H}^+ \), and \( \text{Ar}_{14}^+ \) in Figure 4. The geometry optimizations were carried out starting from the structures of neutral Lennard-Jones clusters \cite{16} and in the case of the pure \( \text{Ar}_n^+ \) clusters, geometries from Ref. \cite{36} were also tested. The atomic coordinates for the lowest energy structure of each cluster is given in the supplementary information.

In Figure 3 we can see that the curves for \( \text{Ar}_n \) clusters (blue circles) and \( \text{Ar}_n \text{H}^+ \) clusters (green triangles) show the same main features, i.e. relatively tightly bound systems with \( n = 7, 13, 19 \) followed by weaker systems for \( n = 8, 14, 20 \). The main difference is that the protonated clusters are more tightly bound due the presence of the charge that attracts the surrounding argon atoms to the \( \text{ArHAr}^+ \) unit that forms the core of the cluster (see Figure 4). Our calculations agree well with the structure determined in previous theoretical studies of protonated \cite{29, 30, 33} and cationic \cite{36} argon clusters where sizes overlap and they readily explain the first few magic numbers observed in out experiments.

The purely cationic clusters (orange squares in Figure 3) on the other hand show a very different behavior. We find no step in binding energy after \( n = 7 \) and the first local maxima is instead located at \( n = 14 \). The reason for the difference in this curve compared to the other two is due to the existence of an \( \text{Ar}_3^+ \) or \( \text{Ar}_4^+ \) core that these clusters form around. The linear \( \text{Ar}_3^+ \) core in \( \text{Ar}_{13}^+ \) is significantly contracted compared to other Ar–Ar distances as seen in Figure 4. This strains the icosahedral geometry so that when a fourteenth Ar atom is added it interacts relatively strongly with this core, forming the basis for the \( \text{Ar}_4^+ \) system that is present in larger cluster sizes \cite{36}. This elongated charged core means that there are more possible positions that other the Ar atoms in the cluster may interact with the charge-center, leading to competition between different cluster geometries so that there is less preference for a single dominant structure at small sizes (this could play a role for sizes smaller than 14 as well). This could explain the poorer agreement between the theory and experiments for the \( \text{Ar}_n \) cluster distribution compared to the other systems. The optimal geometries of the protonated clusters on the other hand are very similar to the neutral systems, with the proton slotting in between two Ar atoms without significantly altering the distance between them (see Figure 4). These compact structures are well explained by icosahedral geometries, giving the magic number series that is observed in the experiments.

The fact that the protonated argon clusters essentially retain the geometries of the neutral clusters is why the magic numbers predicted by sphere packing models are
so well reproduced in the $\text{Ar}_n\text{H}^+$ series. The pure $\text{Ar}_n^+$ clusters instead behave as packed spheres with a structural defect (e.g. $\text{Ar}_3^+$) at their core $^{19}$. However, as the cluster sizes increase the overall effect of this distortion on the entire cluster will decrease. This likely the reason why abundance anomalies matching sphere packing models $^1$ begin to appear in the $\text{Ar}_n^+$ mass spectrum (Figure 2) for $n \geq 81$.

In light of the present results we have re-evaluated data from previous studies of $\text{Kr}_n^+$ clusters $^{26}$ performed with the same setup as the current work. While that study did identify magic cluster sizes $^{26}$, we do not find any evidence that protonated clusters played a role in those results. We suspect this is because for heavier rare gas clusters, the effect the charge has on the core of the clusters decreases, thus putting less strain on icosahedral packing of atoms. We thus do not believe that protonation plays an important role in the the magic series of $\text{Kr}_n^+$ $^{11,12,15–20}$ and $\text{Ne}_n^+$ $^{11}$ clusters. It does, however, seem likely that for the lighter rare gases (Ne and He) protonation can have a strong effect on the geometries of charged clusters. Test calculations that we have performed on $\text{Ne}_n\text{H}^+$ clusters show a similar behavior as we see for argon clusters, i.e. that protonated clusters better match the structures of neutral clusters. Isotopic mixtures of Ne atoms would make the experimental distinction between protonated and pure Ne clusters more difficult (this is not a problem for the nearly isotopically pure Ar), but we are nonetheless currently performing measurements on these systems with our setup.

We have shown that protonated argon clusters show very different characteristics than pure, cationic argon clusters. The protonated clusters display magic sizes that perfectly match the magic cluster series reported by Harris et al. $^{11,12}$ for pure $\text{Ar}_n^+$ clusters, indicating that their measurements may have contained an unresolved contribution from protonated clusters, likely originating from some impurity (e.g. water) in their setup. This could thus solve the long standing disagreement between different studies on argon clusters regarding the nature and origin of abundance anomalies in the mass spectra $^{11,12,15,20}$. It also highlights the dramatic differences small impurities can play in the formation and characteristics of clusters and small nanoparticles, similar to what has been observed regarding the electronic properties of small carbon cluster anions and their hydrides $^{37}$, and the role that hydrogen plays in stabilizing metal clusters $^{38}$.

This work was supported by the Austrian Science Fund FWF (projects P26635 and W1259) and the Swedish Research Council (Contract No. 2016-06625). The computational results presented have been achieved (in part) using the HPC infrastructure LEO of the University of Innsbruck.

---

**FIG. 4.** Two-dimensional projections of icosahedral structures of $\text{Ar}_{13}$, $\text{Ar}_{13}\text{H}^+$, and $\text{Ar}_{14}$, and structures of $\text{Ar}_{14}$, $\text{Ar}_{14}\text{H}^+$, and $\text{Ar}_{14}^+$ optimized at MP2(Full)/def2-SVPP level. Atoms are colored based on their Mulliken charge and the proton in the center column is identified by a circle with a smaller radius than the rest. Coordinates of all calculated cluster geometries are given in the supplementary information.

---

* michael.gatchell@uibk.ac.at

[1] O. Echt, K. Sattler, and E. Recknagel, *Physical Review Letters* **47**, 1121 (1981).
[2] T. Ikeshoji, B. Hafskjold, Y. Hashi, and Y. Kawazoe, *Physical Review Letters* **76**, 1792 (1996).
[3] C. Rey, L. J. Gallego, M. P. Iniguez, and J. A. Alonso, *Physica B: Condensed Matter* **179**, 273 (1992).
[4] R. H. Leary and J. P. K. Doye, *Physical Review E* **60**, R6320 (1999).
[5] D. J. Wales and J. P. K. Doye, *The Journal of Physical Chemistry A* **101**, 5111 (1997).
[6] Y. Xiang, H. Jiang, W. Cai, and X. Shao, *The Journal of Physical Chemistry A* **108**, 3586 (2004).
[7] Y. Xiang, L. Cheng, W. Cai, and X. Shao, *The Journal of Physical Chemistry A* **108**, 9516 (2004).
[8] R. Brühl, R. Guardiola, A. Kalinin, O. Kornilov, J. Navarro, T. Savas, and J. P. Toennies, *Physical Review Letters* **92**, 185301 (2004).
[9] P. W. Stephens and J. G. King, *Physical Review Letters* **51**, 1538 (1983).
[10] H. Buchenau, E. L. Knuth, J. Northby, J. P. Toennies, and C. Winkler, *The Journal of Chemical Physics* **92**, 6875 (1990).
[11] I. A. Harris, R. S. Kidwell, and J. A. Northby, *Physical Review Letters* **53**, 2390 (1984).
[12] I. A. Harris, K. A. Norman, R. V. Mulkern, and J. A. Northby, *Chemical Physics Letters* **130**, 316 (1986).
[13] T. D. Märd and P. Scheier, *Chemical Physics Letters* **137**, 245 (1987).
[14] M. Lezius, P. Scheier, A. Stamatovic, and T. D. Märd, *The Journal of Chemical Physics* **91**, 3240 (1989).
[15] W. Miehle, O. Kandler, T. Leisner, and O. Echt, The Journal of Chemical Physics 91, 5940 (1989).
[16] T. A. Milne and F. T. Greene, The Journal of Chemical Physics 47, 4095 (1967).
[17] A. Ding and J. Hesslich, Chemical Physics Letters 94, 54 (1983).
[18] P. Scheier and T. D. Märk, International Journal of Mass Spectrometry and Ion Processes 76, R11 (1987).
[19] N. E. Levinger, D. Ray, M. L. Alexander, and W. C. Lineberger, The Journal of Chemical Physics 89, 5654 (1988).
[20] F. Ferreira da Silva, P. Bartl, S. Denifl, O. Echt, T. D. Märk, and P. Scheier, Physical Chemistry Chemical Physics 11, 9791 (2009).
[21] K. Vafayi and K. Esfarjani, Journal of Cluster Science 26, 473 (2015).
[22] H. Schöbel, P. Bartl, C. Leidlmair, S. Denifl, O. Echt, T. D. Märk, and P. Scheier, The European Physical Journal D 63, 209 (2011).
[23] T. Kurzthaler, B. Rasul, M. Kuhn, A. Lindinger, P. Scheier, and A. M. Ellis, The Journal of Chemical Physics 145, 064305 (2016).
[24] M. Kuhn, M. Renzler, J. Postler, S. Raiser, S. Spieler, M. Simpson, H. Linnartz, A. G. G. M. Tielens, J. Cami, A. Mauracher, Y. Wang, M. Alcamí, F. Martín, M. K. Beyer, R. Wester, A. Lindinger, and P. Scheier, Nature Communications 7, 13550 (2016).
[25] S. Raiser, J. Postler, M. Harnisch, A. M. Ellis, and P. Scheier, International Journal of Mass Spectrometry 379, 194 (2015).
[26] H. Schöbel, P. Bartl, C. Leidlmair, S. Denifl, O. Echt, T. D. Märk, and P. Scheier, The European Physical Journal D 63, 209 (2011).
[27] G. Hvistendahl, O. W. Saastad, and E. Uggerud, International Journal of Mass Spectrometry and Ion Processes 98, 167 (1990).
[28] M. Lezius, P. Scheier, and T. D. Märk, Chemical Physics Letters 196, 118 (1992).
[29] K. T. Giju, S. Roszak, and J. Leszczynski, The Journal of Chemical Physics 117, 4803 (2002).
[30] D. C. McDonald, D. T. Mauney, D. Leicht, J. H. Marks, J. A. Tan, J. L. Kuo, and M. A. Duncan, The Journal of Chemical Physics 145, 231101 (2016).
[31] V. E. Bondybey and G. C. Pimentel, The Journal of Chemical Physics 56, 3832 (1972).
[32] J. W. C. Johns, Journal of Molecular Spectroscopy 106, 124 (1984).
[33] H. M. Kunttu and J. A. Seetula, Chemical Physics 189, 273 (1994).
[34] T. Ritschel, P. J. Kuntz, and L. Züllicke, The European Physical Journal D - Atomic, Molecular, Optical and Plasma Physics 33, 421 (2005).
[35] M. J. Frisch et al., "Gaussian 16 rev. a.03," (2016).
[36] T. Ikegami, T. Kondow, and S. Iwata, The Journal of Chemical Physics 98, 3038 (1993).
[37] G. Ito, T. Furukawa, H. Tanuma, J. Matsumoto, H. Shiroumaru, T. Majima, M. Goto, T. Azuma, and K. Hansen, Physical Review Letters 112, 183001 (2014).
[38] B. Kiran, P. Jena, X. Li, A. Grubisic, S. T. Stokes, G. F. Gautefor, K. H. Bowen, R. Burgert, and H. Schöckel, Physical Review Letters 98, 256802 (2007).