

## LETTERS TO THE EDITOR

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## NOTES

Stability and structure of  $\text{Ni}^+\text{Ar}_n$  and  $\text{Pt}^+\text{Ar}_n$  clusters

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In a series of previous papers,<sup>1-4</sup> we have systematically investigated the structure and the stability of noble gas clusters doped with metal cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^+$ ,  $\text{Sr}^+$ ,  $\text{Al}^+$ ,  $\text{In}^+$ ) using time of flight mass spectrometry. The metal ions in these complexes exhibit spherical electronic configurations (*s* orbitals). Therefore, applying either geometrical models of hard sphere packing<sup>3</sup> or molecular dynamics simulations<sup>4</sup> based on pairwise additive potentials we could explain the magic numbers (the fingerprint of the most stable clusters) appearing in the mass spectra. Furthermore, calculations with more elaborate potentials have also been performed for  $\text{Mg}^+\text{Ar}_n$ <sup>5</sup> and  $\text{Sr}^+\text{Ar}_n$ <sup>6</sup> clusters.

On the other hand, very little is known for the structure and stability of noble gas clusters doped with transition metal ions, where the interaction is expected to be strongly anisotropic. Only a few such examples have appeared in the literature containing metals with *d<sup>k</sup>* orbitals such as  $\text{Co}^+\text{Ar}_n$ ,<sup>7,8</sup>  $\text{V}^+\text{Ar}_n$ ,<sup>8</sup>  $\text{Nb}^+\text{Ar}_n$ ,<sup>9</sup>  $\text{Rh}^+\text{Ar}_n$ ,<sup>9</sup> and  $\text{Fe}^+\text{Ar}_n$ .<sup>10</sup>

The structural properties of this type of clusters could not successfully be explained by the application of pairwise additive potentials as was the case of the extra stability found for  $\text{V}^+\text{Ar}_4$  and  $\text{Co}^+\text{Ar}_6$  clusters.<sup>7,8</sup> Recently, Beyer *et al.*<sup>9</sup> observed strong signals for  $\text{Nb}^+\text{Ar}_4$  and  $\text{Rh}^+\text{Ar}_6$  in similar studies. The authors used simple arguments based on the geometry of the empty or half-filled *d* orbitals as well as *ab initio* calculations to explain the appearance of the magic numbers.

In this Note, we present the time of flight spectra of  $\text{Ni}^+\text{Ar}_n$  and  $\text{Pt}^+\text{Ar}_n$  clusters. The structures and the nature of bonding between the cation and the inert gas atoms are inferred by performing *ab initio* calculations.

The experiments have been performed in a molecular beam apparatus equipped with a reflectron time of flight (TOF) mass spectrometer. It is described in detail elsewhere.<sup>2</sup> The metal ion-doped argon clusters are produced using a combination of nozzle expansion and laser ablation. We study the positive ions which are produced directly from the plasma/noble gas mixing without the use of postionization, therefore, it is expected that these clusters are suffi-

ciently relaxed and the measured size distribution reflects the stability of these species.

The theoretical treatment of the transition metal ion-doped argon aggregates involves density functional theory (DFT) calculations with the GAUSSIAN94 program package.<sup>11</sup> The three-parameter hybrid functional of Becke<sup>12</sup> using the Lee-Yang-Parr correlation functional<sup>13</sup> (B3LYP), was employed for the geometry optimizations. The atomic basis set for the complexes of  $\text{Ni}^+\text{Ar}_n$ ,  $n=1-6$ , includes Gaussian functions of triple zeta quality augmented with *d*-polarization functions (6-311G\*).<sup>11</sup> For larger clusters ( $\text{Ni}^+\text{Ar}_7$ ) we use the effective core potential, double zeta basis set, LanL2DZ.<sup>14</sup>

In Fig. 1 we show the TOF spectra for  $\text{Ni}^+\text{Ar}_n$  and  $\text{Pt}^+\text{Ar}_n$  clusters. The small peaks between the main series of  $\text{M}^+\text{Ar}_n$  complexes correspond to the  $\text{M}^+(\text{H}_2\text{O})\text{Ar}_n$  clusters originating from water impurities in the Ar-gas inlet line. In both  $\text{M}^+\text{Ar}_n$  cluster series for  $n>2$  the peak at  $n=4$  dominates, accompanied by a less intense local maximum at  $n=6$ , and then follows a relatively structureless spectrum. We could clearly observe clusters up to  $n\approx 60$  for both transition metal ions. These spectra are similar to the  $\text{Nb}^+\text{Ar}_n$  and  $\text{V}^+\text{Ar}_n$  clusters with the exception that besides the very pronounced peak at  $n=4$ , the  $\text{M}^+\text{Ar}_6$  complex appears to be stable as well.

The electronic configuration of  $\text{Ni}^+$  is  $[\text{Ar}]3d^9$  and that of  $\text{Pt}^+$  is  $[\text{Xe}]5d^9$ , that is, there are four doubly occupied *d* orbitals and one singly occupied. Following the picture of the coordinative saturation of  $\text{Nb}^+$  and  $\text{Rh}^+$  with Ar ligands presented in Ref. 9, we expect for the case of  $\text{Ni}^+$  and  $\text{Pt}^+$  that the singly occupied orbital  $d_{x^2-y^2}$  will expose to the Ar ligands four sites of lower electron density, thus, allowing the Ar atoms to experience lower repulsion and therefore approach closer to the central ion. This results in a strong interaction for only four Ar atoms, and thus a special stable square planar  $\text{M}^+\text{Ar}_4$  complex. In the framework of this simple picture, the enhanced intensity observed for  $\text{M}^+\text{Ar}_6$  is not expected.

The DFT calculations for  $\text{Ni}^+\text{Ar}$  gave a bond length of

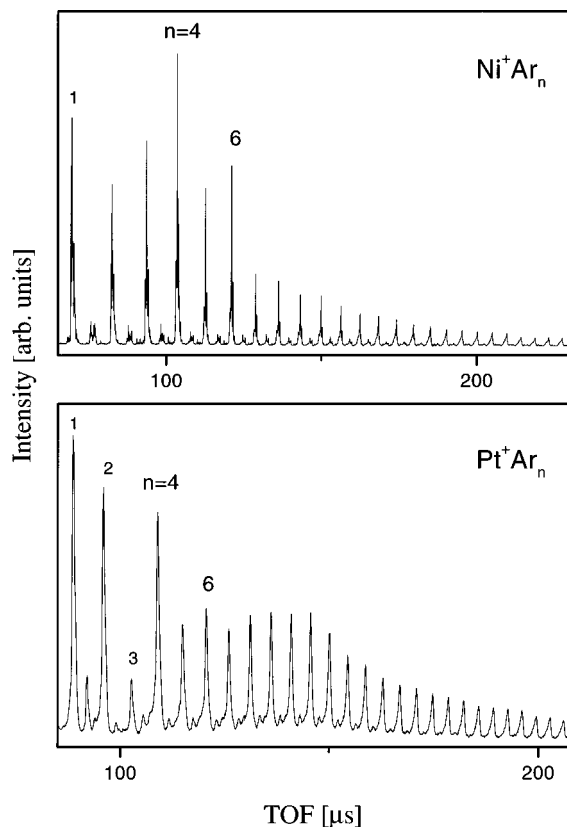


FIG. 1. Time of flight spectra of the  $\text{Ni}^+\text{Ar}_n$  and  $\text{Pt}^+\text{Ar}_n$  clusters. The most stable clusters are indicated by the number  $n$  of Ar atoms.

2.42 Å which can be compared with that of Bauschlicher *et al.*<sup>15</sup> (2.38 Å). The binding energy is 0.456 eV compared to 0.464 eV of Ref. 15. For  $\text{Ni}^+\text{Ar}_2$  we found that the most stable configuration is linear with a bond length of 2.33 Å a value which is in good agreement with that of Ref. 15 (2.36 Å). The binding energies are 0.964 and 0.942 eV, respectively. The  $\text{Ni}^+\text{Ar}_3$  complex has a T-shaped geometry with the two symmetric Ar atoms bonded strongly to  $\text{Ni}^+$  (2.29 Å) and the third sitting at the top of  $\text{Ni}^+$  at a distance of 3.27 Å. The two equal Ar–Ar distances are 4.03 Å. For  $\text{Ni}^+\text{Ar}_4$  we found the expected square planar geometry with a  $\text{Ni}^+\text{–Ar}$  distance of 2.51 Å. The structure of  $\text{Ni}^+\text{Ar}_5$  is formed by adding a fifth Ar atom on the top of  $\text{Ni}^+$  and at the distance of 3.48 Å. The geometry of the square base does not change. Hence, the fifth Ar atom is weakly bonded to the  $\text{Ni}^+\text{Ar}_4$  square planar base. The  $\text{Ni}^+\text{Ar}_6$  cluster was found to be a square bipyramid ( $D_{4h}$  symmetry). The geometry of the square base is slightly changed ( $\text{Ni}^+\text{–Ar}=2.52$  Å,  $\text{Ar–Ar}=3.56$  Å), whereas the top and the bottom Ar atoms come closer to the  $\text{Ni}^+$  (3.38 Å) than in  $\text{Ni}^+\text{Ar}_5$ . The theoretical results for the total and binding energies, as well as atomic charges produced by Mulliken population analysis of the  $\text{Ni}^+\text{Ar}_n$  clusters are presented in Table I.

Analysis of the molecular orbitals reveals that the singly occupied  $d$  orbital is the  $d_{x^2-y^2}$ . According to a simple elec-

TABLE I. Binding energies and Mulliken population analysis of  $\text{Ni}^+\text{Ar}_n$  clusters.

$n$	Total energy (hartree)	Binding energy (eV)	Ni	Mulliken population Ar	
				In the plane	Out of plane
1	−2035.46257	0.456	0.92	0.08	
2	−2563.03442	0.964	0.78	$2 \times 0.11$	
3	−3090.59941	1.284	0.78	$2 \times 0.105 + 1 \times 0.01$	
4	−3618.15475	1.342	0.77	$4 \times 0.06$	
5	−4145.70860	1.359	0.77	$4 \times 0.06$	$1 \times 0.005$
6	−4673.26266	1.383	0.78	$4 \times 0.054$	$2 \times 0.006$

trostatic picture we expect the first four ligands to approach  $\text{Ni}^+$  in the  $x$ – $y$  plane saturating four strong bonds. In this way we understand the stable planar geometry of  $\text{Ni}^+\text{Ar}_4$ . The next bonding saturation occurs by adding two more argon atoms to form the  $D_{4h}$  symmetry structure of  $\text{Ni}^+\text{Ar}_6$ . The two new bonds are weaker and at longer distances from  $\text{Ni}^+$  since the Ar atoms face a doubly occupied  $d$  orbital ( $d_{z^2}$ ). However, plots of the electron density show an interaction among the  $\text{Ni}^+\text{–Ar}$  orbitals something which is reflected in the Mulliken population analysis (Table I). Larger clusters will be formed by filling a second shell of argon atoms with even weaker bonds. Indeed, calculations with the effective core potential double zeta basis set, LanL2DZ,<sup>14</sup> show that in the  $\text{Ni}^+\text{Ar}_7$  the extra Ar atom is capping one triangular face of the  $\text{Ni}^+\text{Ar}_6$  square bipyramid with two Ar–Ar distances equal to 4.24 Å and one of 4.81 Å from the top (bottom) argon atom.

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