

# Binding energies and structures of $C^+Ar_n$ ( $n = 1-5$ ), clusters from first principles

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Received 9 June 1998; in final form 20 July 1998

## Abstract

We report the minimum energy geometries, binding energies and vibrational spectra of the  $C^+Ar_n$  ( $n = 1-5$ ), clusters which were recently recorded in a time-of-flight mass spectrometer. The  $C^+Ar_3$  cluster has a planar structure with two long and one short C–Ar bonds while the  $C^+Ar_4$  cluster forms a square of  $D_{4h}$  symmetry with the carbon atom in the center. The observed drop in the incremental binding energy for the successive Ar atom addition from  $n = 2$  to  $n = 3$  and from  $n = 4$  to  $n = 5$  justifies the classification of the  $n = 2$  and 4 as magic number clusters in the experimental mass spectrum. © 1998 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The mass spectra of inert gas atom clusters doped with various metal and non-metal cations have recently been the subject of a systematic study by Velegrakis and coworkers [1–5]. Structural information for the clusters which show pronounced intensities in the mass spectra was extracted from simple theoretical models [4,5]. At the same time the experimental work has initiated a number of complementary theoretical studies aimed at the determination of the structural and dynamical properties of some metal doped complexes such as,  $Mg^+Ar_n$  [6–8] and  $Sr^+Ar_n$  [9,10]. The latter utilized a variety of computational methods starting from ab initio calculations on the

small aggregates coupled with semiempirical models that were used for the construction of the multidimensional potential energy surfaces (PESs) needed to probe the dynamics of the clusters. The first principles calculations offer additional information regarding the nature of bonding in each type of cluster.

Among the non-metal cation doped inert gas clusters studied experimentally are the  $C_x^+Ar_n$  species. Lüder et al. [2] have recently demonstrated the production of these clusters in a time of flight mass spectrometry apparatus. Particularly for  $C^+Ar_n$ , they observed the formation of clusters with more than 500 argon atoms and recorded their mass spectrum which showed several interesting characteristics. Among them, pronounced intensity peaks corresponding to usually called magic number clusters appear for the number of argon atoms  $n = 2, 4, 14, 19, 29, 55, 57, 77, 116, 147, 309$  and 561. The sizes

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of these clusters are in good correspondence with the magic numbers of pure  $\text{Ar}_n^+$  clusters [11] for  $n > 18$ . It is well known that the pure argon complexes exhibit icosahedral symmetry with  $n = 13, 55, 147, 309$  and  $561$  to be the Mackay icosahedra [12], and those with  $n = 19, 29$  and  $32$  are due to partial shell closing (pentagonal caps) [11]. Thus, it was concluded by Lüder et al. [2], that for  $n \geq 19$  the carbon atom does not participate in the formation of the icosahedral structure. For the smaller clusters ( $n$  between 3 and 14) conclusive structural assignment could not be obtained from the examination of the mass spectra.

$\text{C}^+(1s^2 2s^2 2p^1)$  has an open-shell ground state,  $^2\text{P}$ . Hence, we expect neither the sphere packing model nor the additive electrostatic potential method to be applicable for modeling small  $\text{C}^+\text{Ar}_n$  complexes. It is therefore necessary to carry out accurate calculations from first principles in order to describe the atomic interactions in these clusters.

Potential energy curves for the ground and a few excited states of the diatomic,  $\text{C}^+\text{Ar}$ , were constructed some time ago by Hillier et al. [13] using Configuration Interaction (CI) type calculations. Spectroscopic constants were determined for the ground state and the results were compared with experimental values extracted from elastic scattering cross section measurements with an inversion method. Frenking et al. [14] have also optimized the bond length of  $\text{C}^+\text{Ar}$  at the second order perturbation theory (MP2) level using a double zeta quality basis set (6-31G(d,p)) and performed single point energy calculations at the equilibrium geometry at the fourth order perturbation theory (MP4) level using a triple zeta quality basis set, 6-311G(2df,2pd). These investigators analyzed the electronic structure of  $\text{C}^+\text{Ar}$  and concluded that the bond is of covalent type.

The present theoretical investigation extends the ab initio calculations to larger clusters using quantum chemistry methods that take into account electron correlation. The primary aim of our study is to identify the most stable isomers of small positively charged carbon-argon complexes, and therefore contribute in the interpretation of the recorded mass spectrum for these species [2]. Different basis sets were employed in order to investigate the sensitivity of the optimal geometries on the basis set.

## 2. Computational methods

Our calculations were performed in two different stages. First, we optimized the geometries of the clusters at the Møller-Plesset second-order perturbation level of theory (MP2). Several different configurations of the  $\text{C}^+\text{Ar}_n$ ,  $n = 1-5$ , clusters were probed in order to identify the existence of various isomers. For each converged geometry vibrational frequency analysis was carried out in order to determine whether the stationary point is a minimum or a transition state. In the second stage of our calculations, single point energies at the MP2 optimized geometries were carried out with the use of Coupled Cluster level of theory including single and double excitations with a perturbative estimation of the triple excitations (CCSD(T)).

The basis sets employed are of two different categories. We used the triple zeta plus polarization (6-311G\*) and diffuse (6-311 + G\*) functions basis sets [15] as well as the augmented correlation consistent basis sets of Dunning and coworkers [16–19]. For the latter and in the case of argon, we used the doubly augmented polarized valence double zeta (d-aug-cc-pVDZ) basis set. This consists of the regular aug-cc-pVDZ set augmented with one additional diffuse function of each symmetry (s, p, d) whose exponents are determined in an even-tempered fashion. The d-aug-cc-pVDZ set produces 11.05 au for the polarizability of Ar at the CCSD(T) level of theory, a value very close to the basis set limit of 11.19 au [20]. For carbon, we used the augmented correlation consistent polarized valence triple zeta (aug-cc-pVTZ) basis set (10s5p2d1f) contracted to [4s3p2d1f] plus one set of diffuse functions of each symmetry, (1s1p1d1f). For brevity, we will denote the correlation consistent basis sets as CC.

The MP2 geometry optimizations were performed with the GAUSSIAN 94 package of programs [15]. Single point CCSD(T) calculations were carried out with the MOLPRO program suite [21]. The coupled cluster calculations were based on a restricted Hartree–Fock (RHF) reference wavefunction.

## 3. Results

The geometries of the global minima of the  $\text{C}^+\text{Ar}_n$ , ( $n = 2-5$ ), clusters are shown in Fig. 1. For

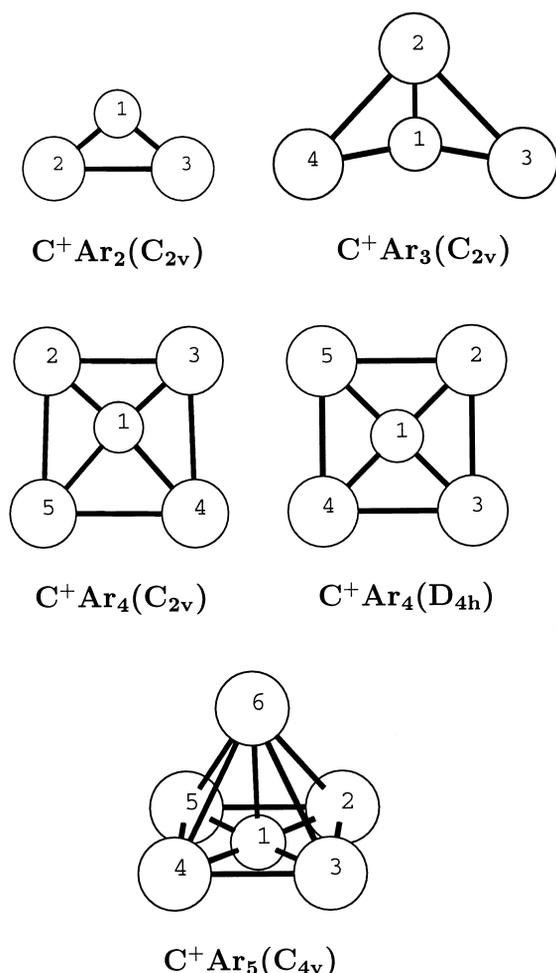


Fig. 1. The MP2/CC optimal geometries of the global minima of  $C^+Ar_n$ , ( $n = 2-5$ ), clusters. For  $C^+Ar_4$  the  $C_{2v}$  optimal geometry with the 6-311G\* basis set is also shown.

these geometries we performed CCSD(T) single point calculations with the basis sets described in the previous section. The energetics are tabulated in Table 1. For  $C^+Ar$  we optimized the bond length in the CCSD(T) calculations as well. The binding energy of a cluster with  $n$  Ar atoms is computed according to:

$$E_{\text{BIND}}^n = E_{\text{ELECT}}^n - E(C^+) - n * E(\text{Ar}), \quad (1)$$

where  $E(C^+)$  and  $E(\text{Ar})$  are the ground state electronic energies of the isolated atoms. Estimates of the basis set superposition error (BSSE) correction

are computed using the function counterpoise method [22].

The optimal geometries of the  $n = 1-5$  clusters are presented in Table 2 for 6-311G\* and CC basis sets. The labels on the atoms are the same as those in Fig. 1.

The ground state of  $C^+Ar$  is  $X^2\Pi$  with the single electron occupying the  $2p$  orbital perpendicular to the  $C^+-Ar$  bond. The calculated binding energies are 0.756 (MP2) and 0.774 (CCSD(T)) eV with the 6-311G\* basis set and 0.968 (MP2) and 1.008 (CCSD(T)) eV with the CC basis sets. The basis set superposition error (BSSE) correction with the CC sets amounts to 0.103 eV at the MP2 and 0.112 eV at the CCSD(T) levels, respectively.

The bond lengths are 2.016 (MP2) and 2.027 (CCSD(T)) Å for the 6-311G\* and 2.001 (MP2) and 2.004 (CCSD(T)) Å for the CC basis sets. The corresponding experimental estimates are 0.999 eV for the binding energy and 1.995 Å for the bond length given in Ref. [13]. It is readily seen that the CC sets produce quite accurate results at the CCSD(T) level of theory.

The inclusion of diffuse functions in the 6-311G\* basis slightly improves the agreement of the computed binding energy and bond length with respect to experiment. The previous CI results of Hillier et al. [13] are 2.000 Å for the bond length and 1.18 eV for the binding energy. The corresponding values of Frenking et al. [14] are 2.059 Å for the bond length at the MP2 level and double zeta basis set and 0.89 eV for the binding energy at the MP4 level of theory with a triple zeta basis set.

The calculations on the diatomic species demonstrate the systematic improvement in the binding energy and geometrical parameters achieved by increasing the size and quality of the basis functions. The CC basis sets produce quite accurate results for the binding energy both at the MP2 and CCSD(T) levels of theory. This observation encourages the study of the larger clusters.

The minimum of  $C^+Ar_2$  has a triangular geometry (Fig. 1). A linear configuration is found to be a transition state, both with the 6-311G\* and CC basis sets. As we can see in Table 2, the C–Ar bond length is 2.193 Å at the MP2/6-311G\* level, while the Ar–C–Ar angle is 100 degrees. The Ar–Ar distance is 3.40 Å. The optimization with the CC

Table 1

Electronic and absolute values of total binding energies for the global minima of  $C^+Ar_n$  ( $n = 19-5$ ) clusters

		MP2		(BSSE)	CCSD(T)	
		electronic	total bind		electronic	total bind
6-311G*	$C^+Ar$	-564.319486	0.756		-564.358277	0.774
	$C^+Ar_2$	-1091.284688	1.068		-1091.336414	1.067
	$C^+Ar_3$	-1618.242074	1.156		-1618.307618	1.171
	$C^+Ar_4$	-2145.198318	1.218		-2145.277366	1.235
	$C^+Ar_5$	-2672.153234	1.244		-2672.245665	1.261
CC	$C^+Ar$	-564.338636	0.968	(0.865)	-564.377926	1.008
	$C^+Ar_2$	-1091.311780	1.443	(1.239)	-1091.365137	1.475
	$C^+Ar_3$	-1618.274442	1.634	(1.416)	-1618.342657	1.677
	$C^+Ar_4$	-2145.236759	1.815	(1.535)	-2145.319813	1.870
	$C^+Ar_5$	-2672.197027	1.941	(1.606)	-2672.294146	1.986

Electronic energies are in hartree, total binding energies in eV. BSSE corrected binding energies are shown in parentheses.

basis sets does not change the geometry drastically, only resulting in a shorter bond length.

For  $C^+Ar_3$  we find that the optimal geometry corresponds to a planar structure of  $C_{2v}$  symmetry. We were not able to locate any stable non-planar isomer. The  $C^+Ar_3$  ground state has one short C–Ar bond of 2.166 Å and two longer bonds of 2.505 Å at the MP2/6-311G\* level of theory. This arrangement is stabilized by the interaction of the two Ar

atoms which are at a separation of 3.589 Å. The CC basis sets produce shorter bond lengths (2.148 Å and 2.434 Å) and larger binding energies (Tables 1 and 2).

The geometry of the global minimum for  $C^+Ar_4$  is shown in Fig. 1. The 6-311G\* basis set produces a global minimum that has a trapezoid structure of  $C_{2v}$  symmetry with two short C–Ar bond lengths of 2.321 Å and two long ones of 2.734 Å. The Ar–Ar

Table 2

Optimal MP2 geometrical parameters of  $C^+Ar_n$  ( $n = 1-5$ )

	6-311G*			CC		
	sym	geometrical parameters		sym	geometrical parameters	
$C^+Ar$	$C_{\infty v}$	MP2 CCSD(T)	C(1)–Ar(2) = 2.016 C(1)–Ar(2) = 2.027	$C_{\infty v}$	MP2 CCSD(T)	C(1)–Ar(2) = 2.001 C(1)–Ar(2) = 2.004
$C^+Ar_2$	$C_{2v}$	C(1)–Ar(2) = 2.193	Ar(2)–C(1)–Ar(3) = 100	$C_{2v}$	C(1)–Ar(2) = 2.156	Ar(2)–C(1)–Ar(3) = 98
$C^+Ar_3$	$C_{2v}$	C(1)–Ar(2) = 2.166 Ar(2)–Ar(3) = 3.589	C(1)–Ar(3) = 2.505 Ar(2)–C(1)–Ar(3) = 100	$C_{2v}$	C(1)–Ar(2) = 2.148 Ar(2)–Ar(3) = 3.428	C(1)–Ar(3) = 2.434 Ar(2)–C(1)–Ar(3) = 97
$C^+Ar_4$	$C_{2v}$	C(1)–Ar(2) = 2.321 Ar(2)–Ar(3) = 3.445 Ar(4)–Ar(5) = 3.663	C(1)–Ar(4) = 2.734 Ar(2)–Ar(5) = 3.589 Ar(2)–C(1)–Ar(3) = 96	$D_{4h}$	C(1)–Ar(2) = 2.430 Ar(2)–Ar(3) = 3.436	Ar(2)–C(1)–Ar(3) = 90
$C^+Ar_5$	$C_s$	C(1)–Ar(3) = 2.321 C(1)–Ar(6) = 3.491 Ar(2)–Ar(3) = 3.589 Ar(3)–Ar(6) = 4.184 Ar(2)–Ar(6) = 4.437	C(1)–Ar(2) = 2.736 Ar(3)–Ar(4) = 3.479 Ar(2)–Ar(5) = 3.663 Ar(3)–C(1)–Ar(4) = 96	$C_{4v}$	C(1)–Ar(3) = 2.426 C(1)–Ar(6) = 3.226 Ar(3)–Ar(6) = 4.851	Ar(3)–Ar(4) = 3.430 Ar(3)–C(1)–Ar(4) = 90

The labels on the atoms are the same with those in Fig. 1. Bond length are in Ångström, bond angles in degrees. For  $C^+Ar$  the geometry has been optimized both at the MP2 and CCSD(T) levels.

interatomic distances vary from 3.445 Å to 3.663 Å. The  $C_{2v}$  trapezoid geometry predicted with the 6-311G\* basis set changes to a square of  $D_{4h}$  symmetry with the CC basis sets. The four equivalent C–Ar bonds are 2.430 Å and the Ar–Ar distances are 3.436 Å. The binding energy changes from 1.235 eV to 1.870 eV at the CCSD(T) level of theory with the two basis sets. The “symmetry breaking” in  $C^+Ar_4$  with the 6-311G\* basis set (i.e., the deviation from the perfect square found with the CC sets) can be probably attributed to the limited description of the Ar polarizability with this basis set, an issue that is less of a problem with the CC basis sets.

The geometry of the  $n = 4$  cluster is a precursor for building up the next size cluster. The optimal geometry of  $C^+Ar_5$  is a pyramid in which the carbon atom lies in the center of its base. The 6-311G\* basis set produces a pyramid which has a base with the same geometry as that of  $C^+Ar_4$  and the fifth Ar atom out of plane at the distance of 3.491 Å. Thus, the “out of plane” C–Ar bond is weaker than the “in-plane” ones. The second lowest lying  $C^+Ar_5$

isomer also has a non-planar geometry (a triangular bi-pyramid with the  $C^+$  at the center of the triangle), while all the planar pentagonal isomers are energetically above these two. The CC basis sets predict a square pyramid of ( $C_{4v}$ ) symmetry with the carbon atom slightly below the plane of four argon atoms which form a regular square like in the  $n = 4$  minimum with these basis sets. The C–Ar bonds are 2.426 Å in the base of pyramid and the fifth argon atom is above the plane at distance 3.226 Å. The conformation with the carbon cation exactly in the center and in the plane of four argon atoms is only 0.2 kcal/mol above the minimum of the cluster.

The harmonic frequencies and intensities computed at the MP2 level of theory with both basis sets, 6-311G\* and CC, are tabulated in Table 3. For the correlation consistent basis sets we find that the IR intensities of  $C^+Ar_3$  are mainly distributed in two modes, 159 and 314  $cm^{-1}$ . These two modes correspond to the motion of the carbon atom in the plane of the molecule, the first parallel to the base of the Ar(3)–Ar(4) atoms (Fig. 1), the second perpendicu-

Table 3

Vibrational frequencies (in  $cm^{-1}$ ) and IR Intensities (in  $kM/mole$ ) for the  $C^+Ar_n$  ( $n = 1-5$ ) clusters at the MP2 level of theory

	$C^+Ar$		$C^+Ar_2$		$C^+Ar_3$		$C^+Ar_4$		$C^+Ar_5$	
	Freq.	IR. Int	Freq.	IR. Int	Freq.	IR. Int	Freq.	IR. Int	Freq.	IR. Int
6-311G*	391.8	295	105.0	0	39.5	78	24.3	0	8.5	0
			209.5	323	44.2	0	37.5	164	9.4	1
			328.7	127	106.9	9	54.5	10	25.2	1
					107.6	10	64.1	47	32.1	1
					137.9	271	64.8	13	38.2	160
					288.4	229	101.8	27	54.4	10
							111.2	215	64.3	48
							123.8	9	65.0	11
							180.6	236	101.5	27
									110.9	210
									134.6	13
						179.6	231			
CC	409.6	272	114.7	0	57.0	0	36.7	0	16.4	83.5
			254.5	275	68.0	63	64.6	90	16.4	112.3
			356.3	111	117.3	5	64.6	90	38.7	113.0
					128.0	6	83.0	0	55.0	113.0
					159.4	316	111.2	0	64.5	144.2
					314.1	176	114.7	280	64.5	187.9
							114.8	280		
							142.8	0		
				156.7	5					

lar to it. A smaller contribution is made by the mode with harmonic frequency of  $68\text{ cm}^{-1}$  which corresponds to the in-plane asymmetric motion of the three Ar atoms.

In  $\text{C}^+\text{Ar}_4$  the IR active modes are mainly two degenerate ones at  $115\text{ cm}^{-1}$  and  $65\text{ cm}^{-1}$ . The first one corresponds to the stretching of the carbon atom along the C–Ar bonds, the other to the movement of the linear Ar(2)–C(1)–Ar(4) fragment vertically to Ar(3)–Ar(5) axis (see Fig. 1).

For  $\text{C}^+\text{Ar}_5$  the 6-311G\* basis set showed that the high intensity modes correspond to vibrations of the atoms in the base of the pyramid. They are almost identical to the three most intense modes of  $\text{C}^+\text{Ar}_4$  since, the base of  $\text{C}^+\text{Ar}_5$  pyramid is practically the same with that of  $\text{C}^+\text{Ar}_4$ . The bending frequency associated with the vibration of the out-of-plane Ar atom (atom 6 in Fig. 1) is only  $9\text{ cm}^{-1}$  and has almost zero IR intensity, a trend consistent with the longer C–Ar bond length.

#### 4. Discussion

Good agreement with the experimental values was obtained at the CCSD(T)/CC level of theory for  $\text{C}^+\text{Ar}$ . Mulliken population analysis estimates that the carbon atom is positively charged by  $+0.55e$  and the argon atom by  $+0.45e$ . This is an indication that charge transfer between carbon and argon takes place as a result of orbital mixing. Analysis by Frenking et al. [14] has characterized the  $\text{C}^+\text{–Ar}$  bond as covalent. Another indication of the inadequacy of the charge-induced dipole interaction model for describing the  $\text{C}^+\text{–Ar}$  bond is the size of induction energy,

$$E_{\text{ind}} = -\frac{q^2\alpha}{2R^4}, \quad (2)$$

where  $q$  is the atomic charge of C,  $R$  is the interatomic distance and  $\alpha$  is the atomic polarizability of Ar. This model yields  $E_{\text{ind}} = -0.73\text{ eV}$ , i.e., about 73% of the binding energy.

In the  $\text{C}^+\text{Ar}_2$  ground state geometry the two Ar atoms are oriented along the  $p_y$  and  $p_z$  orbitals of C atom, while the singly occupied carbon  $p_x$  orbital is

perpendicular to the molecular plane. The Ar–Ar repulsion forces the argon-carbon-argon angle to increase from 90 to 98 degrees (Table 2, MP2/CC). At the same time, the charge transfer from Ar atoms to  $\text{C}^+$  (almost half an electron) causes a back polarization on the C atom. Since both the  $p_y$  and  $p_z$  orbitals are saturated, an energetically optimal configuration is obtained, a fact that could explain the larger abundance of this species in the mass spectrum [2].

Calculating the values of the binding energies of ArAr and  $\text{C}^+\text{Ar}$  at bond lengths equal to the equilibrium point of  $\text{C}^+\text{Ar}_2$  (Table 2) we infer a repulsive 3-body contribution in the potential of the triatomic species. Indeed, the formation of a second  $\text{C}^+\text{Ar}$  bond increases the energy only by 0.47 eV at the CCSD(T)/CC level of theory. For  $\text{C}^+\text{Ar}_3$  the  $C_{2v}$  configuration of one strong (short) and two weaker (longer) bonds is stabilized with respect to a  $D_{3h}$  structure with three equivalent bonds because of the Ar–Ar interaction between the two Ar atoms that are bonded to carbon via the longer bonds. With four argon atoms, saturation of carbon bonding is achieved. However, the optimum geometry of the complex turns out to be basis set dependent for the basis sets that we examined in this study. The 6-311G\* basis set favors two strong (short) and two weaker (longer) bonds, whereas the CC basis sets favor the formation of four equivalent bonds. Obviously, these differences should be attributed to the quality of the argon atom basis set and the ability to describe its polarizability. Moreover, the CC sets produce larger binding energies than the 6-311G\* set.

The incremental binding energies are 0.467 eV, 0.202 eV, 0.193 eV and 0.116 eV at the CCSD(T)/CC level of theory for the successive addition of Ar atoms to  $\text{C}^+\text{Ar}$ . MP2 calculations produce the same qualitative trends (cf. Table 1) for both, uncorrected and BSSE corrected results. We note a significant drop in the incremental binding energy for  $\text{C}^+\text{Ar}_3$  and  $\text{C}^+\text{Ar}_5$ . The approach of a third argon atom in plane weakens the two carbon-argon bonds in the case of  $\text{C}^+\text{Ar}_3$ , whereas for  $\text{C}^+\text{Ar}_5$  the fifth Ar atom approaches along the singly occupied  $p_x$  orbital of carbon which results in a weak bond. For the diatomic,  $\text{C}^+\text{Ar}$ , the approach of Ar along this direction will produce a repulsive state.

It is therefore not surprising that the incremental binding energy between  $C^+Ar_4$  and  $C^+Ar_5$  drops. The above remarks can be used to illustrate the classification of the  $n = 2$  and 4 aggregates as magic number clusters.

We could speculate that the sixth argon atom will approach carbon from the bottom of the  $n = 5$  pyramid to produce a square bi-pyramid for the cluster  $C^+Ar_6$ , whereas a complete second shell will be formed with the addition of eight more argon atoms capped at the eight faces of the square bi-pyramid to give the geometry of  $C^+Ar_{14}$ . Because of computer limitations, it is currently difficult to explore these ideas by ab initio techniques. Furthermore, the question of the transition to icosahedral structures for larger clusters speculated in Ref. [2], remains. To elucidate the structures of larger  $C^+Ar_n$  complexes, we are planning to construct a model potential function based on the current ab initio results. The modeling of the structural and dynamic properties of the  $C^+Ar_n$  clusters using this potential function will be presented elsewhere.

## 5. Conclusions

Minimum energy structures of  $C^+Ar_n$  small clusters ( $n = 1-5$ ) have been obtained using ab initio calculations at the MP2 and CCSD(T) level of theory. The augmented correlation consistent polarized valence sets (d-aug-cc-pVDZ on Ar and aug-cc-pVTZ on C) produced the largest absolute binding energies. In the case of  $C^+Ar$  both the binding energy and bond length are in excellent agreement with the experimental values. For  $C^+Ar_4$  we found that the geometry is sensitive to the type of basis set used. The 6-311G\* produces a trapezoid with two short and two long bonds, whereas the CC basis sets predict a square with four equal bonds. Based on the agreement of the CC results with experiment for the  $n = 1$  cluster we suggest that the geometry of  $C^+Ar_4$  cluster is of  $D_{4h}$  symmetry and that of the  $C^+Ar_5$  cluster is of  $C_{4v}$  symmetry. With the saturation of the coordination number 4, more argon atoms are bonded by weak forces. Thus, the scenario of having pure argon atom magic numbers for large clusters observed in the mass spectrum is supported by the present calculations.

## Acknowledgements

We are grateful to Dr. Velegrakis for the many useful discussions that we had during the course of this project. Financial support from the Hellenic General Secretariat for Research and Technology under the program for support of scientific staff  $\Pi$  ENE  $\Delta$  - 1994 (15774/296) is gratefully acknowledged. Part of this work was performed under the auspices of the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy under Contract DE-AC06-76RLO 1830 with Battelle Memorial Institute, which operates the Pacific Northwest National Laboratory. Computer resources were provided by the Division of Chemical Sciences and by the Scientific Computing Staff, Office of Energy Research, at the National Energy Research Supercomputer Center (Berkeley, CA).

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