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Density Functional Study of the Structure and Properties of Cu_9 and Cu_9^- †

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Abstract: This work presents a study of the structure of neutral and anionic copper cluster nonamers with density functional theory calculations. The structure optimization and frequency analysis were performed at the local density approximation (LDA) level of theory with the exchange correlation functional by Vosko, Wilk, and Nusair (VWN). Improved calculations for the structure stability were based on the generalized gradient approximation (GGA) where the exchange correlation functional of Perdew and Wang (PW) was used. For both neutral and anionic clusters, new isomers are found that are more stable than those already presented in the literature. Adiabatic and vertical electron affinities are calculated and compared with the experimental value reported for Cu_9. The calculated values are in good agreement with the available experimental data. An analysis of the most relevant molecular orbitals (MOs) of the low-lying neutral and anionic copper cluster nonamers is reported, too.

1. Introduction

The study of clusters and metal compounds has become an increasingly interesting topic in the last years.[1−10] This is due to their role as precursors of bulk material. In this sense the knowledge of their properties furnishes information how the transition from an atom or molecule to the solid state may occur. Due to the experimental and theoretical techniques developed in the last years these systems are now better characterized. There is a considerable number of different theoretical and experimental works on copper clusters. Although it is not the purpose of the present work to review all of them, we would like to address the reader to the following literature on copper clusters and references therein.[11−56] Copper clusters with up to 5 atoms were studied about 10 years ago[15] with the density functional program deMon.[57] In the meantime using a new density functional program[58] a systematic study of larger copper clusters was performed in order to gain insight into the structure growth. At the same time experiments became available[59] which allow a reasonable comparison between experimental and theoretical data. In a recent work we developed a structural concept of copper clusters presenting the structures of small copper clusters with up to 10 atoms.[33] The stability of the structures was tested by a frequency analysis. Based on these results, structures of the corresponding cations and anions were also determined. Further analysis of the clusters furnished information on their binding energies, ionization potentials, and electron affinities. Finally, the energies for the fragmentation of cationic clusters into smaller cationic clusters and neutral atoms or dimers were presented.[33] The search for stable structures of larger clusters is very difficult because of the increasing number of possible arrangements for isomers. In our previous work we used the strategy of capping of smaller clusters or solid-state fragments in order to determine the energetic lowest structures for Cu_9 and Cu_{10}. The global minimum for Cu_9 was found in a C_s symmetry, and it was derived from the Cu_7 bipyramid by double capping of two adjacent upper triangles. For Cu_9^- we found a C_{2v} structure as global minimum which had no topological equivalent for the neutral cluster.[33] We found that the scaled electron affinities for copper clusters up to the octamer are in fair to good agreement with the experimental vertical detachment energies. However, for Cu_9 and Cu_{10} we found that the theoretical and experimental values differ by more

† Dedicated to Dennis R. Salahub on the occasion of his 60th birthday.

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Table 1. Point Group (PG), Relative LDA and GGA Energies [kcal/mol], Structure Parameters [Å], and Frequencies [cm^{-1}] of Neutral Copper Cluster Nonamers[a]

cluster	PG	LDA	GGA	structure parameters		frequencies					
1) Cu_9	C_s	1.95	0.0	$r_{12} = 2.35$	$r_{13} = 2.37$	59	75	83	107	113	121
				$r_{14} = 2.39$	$r_{15} = 2.37$	125	128	133	138	155	161
				$r_{16} = 2.39$	$r_{17} = 2.39$	184	192	201	203	221	232
				$r_{24} = 2.40$	$r_{26} = 2.40$	240	246	270			
				$r_{29} = 2.41$	$r_{34} = 2.38$						
				$r_{35} = 2.48$	$r_{37} = 2.38$						
				$r_{38} = 2.39$	$r_{46} = 3.12$						
				$r_{48} = 2.38$	$r_{49} = 2.40$						
				$r_{56} = 2.38$	$r_{58} = 2.39$						
				$r_{68} = 2.38$	$r_{69} = 2.40$						
2) Cu_9	C_s	0.0	0.69	$r_{12} = 2.36$	$r_{13} = 2.36$	72	73	80	110	118	122
				$r_{14} = 2.36$	$r_{15} = 2.36$	128	129	132	138	140	147
				$r_{16} = 2.41$	$r_{17} = 2.47$	165	167	190	200	215	222
				$r_{18} = 2.41$	$r_{23} = 2.49$	250	254	283			
				$r_{27} = 2.42$	$r_{37} = 2.42$						
				$r_{38} = 2.42$	$r_{45} = 2.49$						
				$r_{48} = 2.41$	$r_{49} = 2.42$						
				$r_{56} = 2.42$	$r_{59} = 2.42$						
				$r_{67} = 2.40$	$r_{69} = 2.40$						
				$r_{56} = 2.42$	$r_{59} = 2.42$						
				$r_{78} = 2.40$	$r_{79} = 2.40$						
3) Cu_9	C_{2v}	3.23	1.61	$r_{12} = 2.37$	$r_{15} = 2.38$	57	62	68	93	98	121
				$r_{16} = 2.41$	$r_{19} = 2.44$	122	136	149	152	154	164
				$r_{29} = 2.44$	$r_{36} = 2.40$	165	179	185	202	217	250
				$r_{56} = 2.37$	$r_{68} = 2.44$	256	256	263			
4) Cu_9	C_{3v}	7.70	13.12	$r_{12} = 2.35$	$r_{14} = 2.39$	78	84	87	92	92	99
				$r_{17} = 2.43$	$r_{18} = 2.43$	106	108	134	136	161	179
				$r_{26} = 2.39$	$r_{29} = 2.43$	180	191	195	195	216	242
				$r_{35} = 2.39$	$r_{39} = 2.43$	260	269	270			
				$r_{85} = 2.37$	$r_{89} = 2.38$						
5) Cu_9	C_{2v}	24.39	23.30	$r_{12} = 2.49$	$r_{15} = 2.49$	69	79	82	107	112	114
				$r_{16} = 2.34$	$r_{18} = 2.34$	122	126	145	150	150	153
				$r_{38} = 2.41$	$r_{48} = 2.41$	175	180	186	192	222	236
				$r_{56} = 2.41$	$r_{78} = 2.46$	253	255	255			
6) Cu_9	C_{2v}	30.03	26.31	$r_{12} = 2.48$	$r_{13} = 2.48$	52	53	70	98	101	105
				$r_{14} = 2.48$	$r_{24} = 2.36$	109	120	131	135	138	170
				$r_{26} = 2.36$	$r_{29} = 2.36$	173	188	195	212	226	235
				$r_{34} = 2.36$	$r_{35} = 3.89$	238	259	260			
				$r_{37} = 2.32$	$r_{38} = 2.48$						
				$r_{48} = 2.48$	$r_{49} = 2.36$						

[a] The cluster structures and atom numbers are given in Figure 1.

than 0.5 eV. From these results we could not exclude that lower minima may exist on the anionic potential energy surface (PES) of these systems. Very recently a new and very robust algorithm[60] for structure optimization was developed and implemented in the new density functional code deMon2k.[62] It was shown that this algorithm provides reliable geometrical parameters even for very large systems.[60] In this work we present the results of a more extended investigation of the ground-state structure of Cu_9^- and Cu_9. The electron affinity is recalculated considering the new ground-state structures presented here. The calculated value of the vertical electron affinity shows now an excellent agreement with the experimental vertical detachment energy measured for the copper nonamer. An analysis of the most relevant molecular orbitals (MOs) of the neutral and anionic copper nonamer low-lying structures is presented, too.

2. Computational Details

The linear combination of Gaussian-type orbitals Kohn–Sham density functional theory (LCGTO-KS-DFT) method[61] as implemented in the program deMon2k[62] was used to carry out all geometry optimizations and harmonic vibrational frequency calculations. The exchange–correlation potential was numerically integrated on an adaptive grid.[63] The grid accuracy was set to 10^{-5} in all calculations. The Coulomb energy was calculated by the variational fitting procedure proposed by Dunlap, Connolly, and Sabin.[64,65] For the fitting of the density the auxiliary function set A2[66] was used in all calculations. In order to localize different minima on the potential energy surface (PES) of the neutral and anionic copper nonamer, the structures of both clusters have been optimized considering as starting points different initial

Table 2. Point Group (PG), Relative LDA and GGA Energies [kcal/mol], Structure Parameters [Å], and Frequencies [cm^{-1}] of Anionic Copper Cluster Nonamers[a]

cluster	PG	LDA	GGA	structure parameters		frequencies					
1) Cu_9^-	C_s	0.0	0.0	$r_{12} = 2.41$	$r_{13} = 2.37$	62	76	80	102	103	113
				$r_{14} = 2.43$	$r_{15} = 2.37$	116	117	121	139	155	168
				$r_{16} = 2.43$	$r_{17} = 2.50$	179	193	193	201	227	239
				$r_{24} = 2.33$	$r_{26} = 2.33$	243	247	257			
				$r_{29} = 2.46$	$r_{34} = 2.36$						
				$r_{35} = 2.41$	$r_{37} = 2.39$						
				$r_{38} = 2.45$	$r_{46} = 2.90$						
				$r_{48} = 2.33$	$r_{49} = 2.42$						
				$r_{56} = 2.36$	$r_{58} = 2.45$						
				$r_{68} = 2.33$	$r_{69} = 2.42$						
2) Cu_9^-	C_{2v}	3.00	0.11	$r_{12} = 2.40$	$r_{13} = 2.41$	15	67	91	93	110	110
				$r_{14} = 2.36$	$r_{24} = 2.40$	123	127	127	131	154	160
				$r_{26} = 2.40$	$r_{29} = 2.37$	189	192	201	208	226	230
				$r_{34} = 2.39$	$r_{35} = 2.39$	240	245	256			
				$r_{37} = 2.36$	$r_{38} = 2.42$						
				$r_{48} = 2.36$	$r_{49} = 2.41$						
3) Cu_9^-	C_2	4.00	2.07	$r_{12} = 2.50$	$r_{14} = 2.38$	52	61	77	96	110	117
				$r_{18} = 2.33$	$r_{23} = 2.38$	121	126	127	135	145	172
				$r_{27} = 2.39$	$r_{29} = 2.36$	173	176	193	202	224	232
				$r_{34} = 2.50$	$r_{35} = 2.43$	249	257	257			
				$r_{54} = 2.36$	$r_{89} = 2.45$						
4) Cu_9^-	C_s	2.53	2.55	$r_{12} = 2.35$	$r_{14} = 2.55$	53	70	80	86	110	121
				$r_{15} = 2.35$	$r_{18} = 2.48$	123	132	134	140	150	152
				$r_{56} = 2.39$	$r_{67} = 2.43$	169	184	192	201	213	246
				$r_{67} = 2.43$	$r_{68} = 2.36$	250	253	263			
5) Cu_9^-	C_s	10.84	11.30	$r_{12} = 2.41$	$r_{13} = 2.41$	65	76	82	82	112	121
				$r_{14} = 2.41$	$r_{15} = 2.41$	129	130	132	139	140	144
				$r_{48} = 2.39$	$r_{71} = 2.48$	159	168	191	194	220	224
				$r_{72} = 2.40$	$r_{68} = 2.40$	246	247	254			
6) Cu_9^-	C_s	11.54	13.37	$r_{12} = 2.46$	$r_{13} = 2.46$	74	78	83	115	117	118
				$r_{14} = 2.46$	$r_{15} = 2.46$	120	131	137	143	150	153
				$r_{48} = 2.42$	$r_{71} = 2.57$	176	186	192	196	218	234
				$r_{72} = 2.39$	$r_{68} = 2.42$	242	245	247			
7) Cu_9^-	C_{3v}	19.14	15.68	$r_{12} = 2.33$	$r_{13} = 2.33$	54	55	83	94	94	98
				$r_{14} = 2.46$	$r_{24} = 2.46$	102	102	133	133	148	161
				$r_{35} = 2.46$	$r_{36} = 2.46$	182	182	197	198	217	252
				$r_{38} = 2.43$	$r_{39} = 2.43$	252	253	271			
				$r_{81} = 2.43$	$r_{92} = 2.43$						
8) Cu_9^-	C_{2v}	18.44	17.52	$r_{12} = 2.43$	$r_{13} = 2.47$	42	51	76	100	101	102
				$r_{14} = 2.47$	$r_{24} = 2.34$	107	110	121	143	143	163
				$r_{29} = 2.50$	$r_{37} = 2.31$	172	182	208	210	228	235
				$r_{38} = 2.47$	$r_{46} = 3.34$	237	242	254			
				$r_{56} = 2.35$	$r_{57} = 2.31$						
9) Cu_9^-	C_s	19.83	17.99	$r_{12} = 2.37$	$r_{13} = 2.39$	22	67	92	99	101	115
				$r_{14} = 2.43$	$r_{24} = 2.40$	125	126	132	139	141	154
				$r_{29} = 2.40$	$r_{37} = 2.36$	177	185	203	207	209	228
				$r_{38} = 2.41$	$r_{94} = 2.38$	229	238	259			
				$r_{96} = 2.38$	$r_{98} = 2.40$						

[a] The cluster structures and atom numbers are given in Figure 2.

geometries and multiplicities. In order to avoid spin contamination the restricted open shell Kohn−Sham (ROKS) method was employed. The calculations were performed with the local density approximation (LDA) using the exchange-correlation contributions proposed by Vosko, Wilk, and Nusair[67] and employing all-electron basis sets.[66] The same functional was used for the frequency analysis. We already showed that LDA studies on copper clusters with the double-ζ plus valence polarization (DZVP) basis set and the A2 auxiliary function set[66] give reliable geometries in structure optimizations.[15,32,33] Single point energies were then calculated at the optimized structures using the same basis and auxiliary function set with the exchange-correlation functional of Perdew and Wang (PW).[68,69] A quasi-Newton method in internal redundant coordinates with analytic energy gradients was used for the structure optimization.[60] The convergence was based on the Cartesian gradient and displacement vectors with a threshold of 10^{-4} and 10^{-3} au,

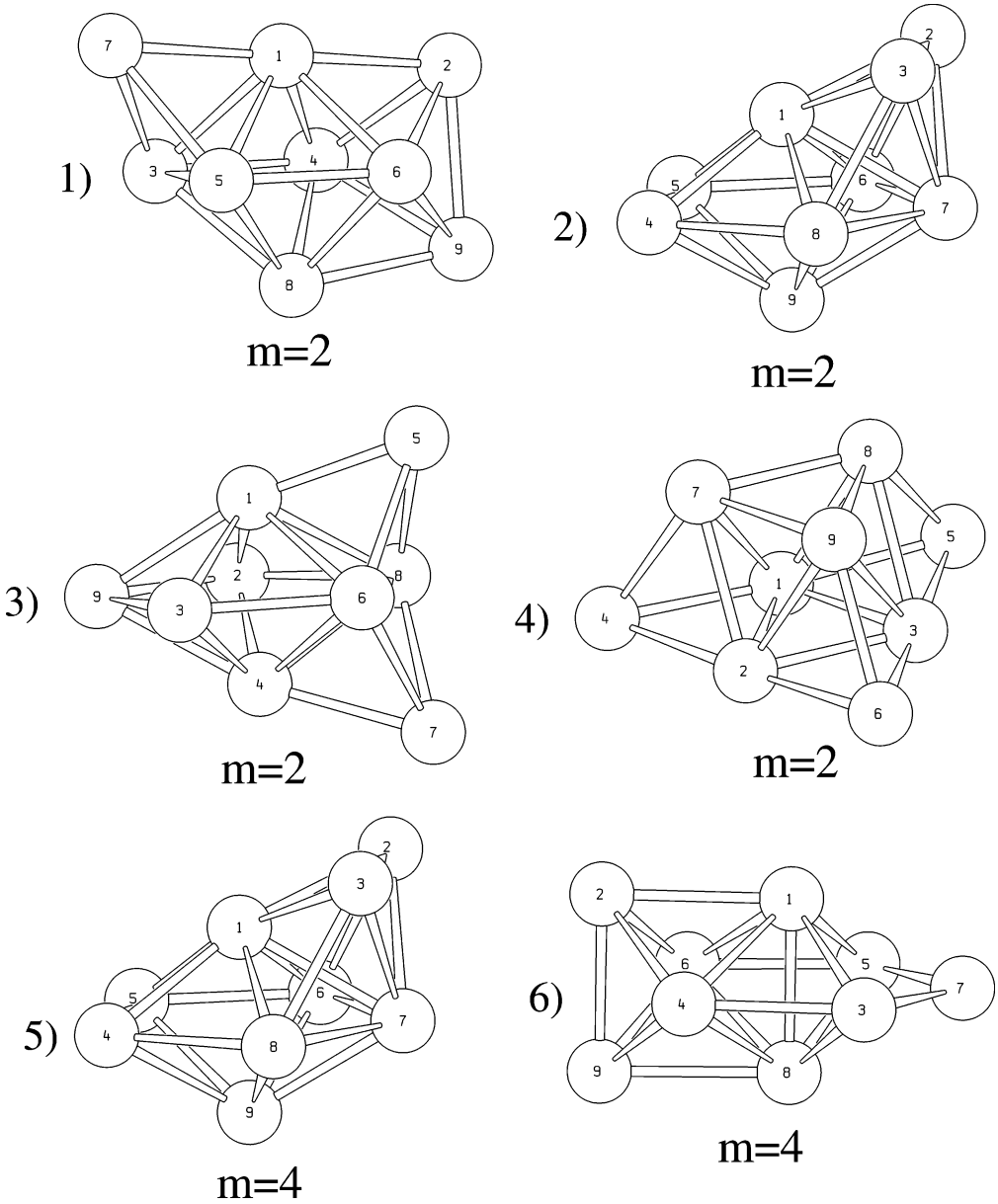

Figure 1. Structures and multiplicities of the neutral copper cluster nonamers.

respectively. A vibrational analysis was performed in order to discriminate between minima and transition states. The second derivatives were calculated by numerical differentiation (two-point finite difference) of the analytic energy gradients using a displacement of 0.001 au from the optimized geometry for all 3N coordinates. The harmonic frequencies were obtained by diagonalizing the mass-weighted Cartesian force constant matrix.

3. Results and Discussion

The optimized structure parameters (in Å), relative energies (in kcal/mol), and vibrational frequencies (in cm^{-1}) of the ground-state structure and low-lying minima of neutral and anionic copper nonamers are listed in Tables 1 and 2, respectively. The corresponding cluster structures are depicted in Figures 1 and 2, respectively. In these figures the spin multiplicities for each structure are indicated, too. For Cu_9 and Cu_9^- we investigated several initial structures including the one obtained by capping of the Cu_8 ground-state structure reported in our previous work,[33] the ones derived from the Cu_7 bipyramid by double capping of two adjacent upper triangles and by double capping of adjacent upper and lower triangles, and a C_{3v} isomer obtained by relaxation of a crystal fragment. For the neutral Cu_9 cluster the multiplicities 2, 4, and 6 are studied for all investigated isomers, whereas for the charged Cu_9^- cluster the multiplicities 1, 3, and 5 are considered. In the case of the neutral copper nonamer six minima structures are found (Figure 1). For Cu_9, a C_s structure in multiplicity 2 (structure 1 of Figure 1) is found as ground state. This structure results from the capping of the ground-state Cu_8 structure reported in ref 33. To the best of our knowledge this structure has never been reported so far in the literature. At the PW86/DZVP/A2 level of theory the next isomer is only 0.69 kcal/mol above this ground state. It is a doublet with C_s symmetry that can be obtained from the Cu_7 bipyramid by the double capping of

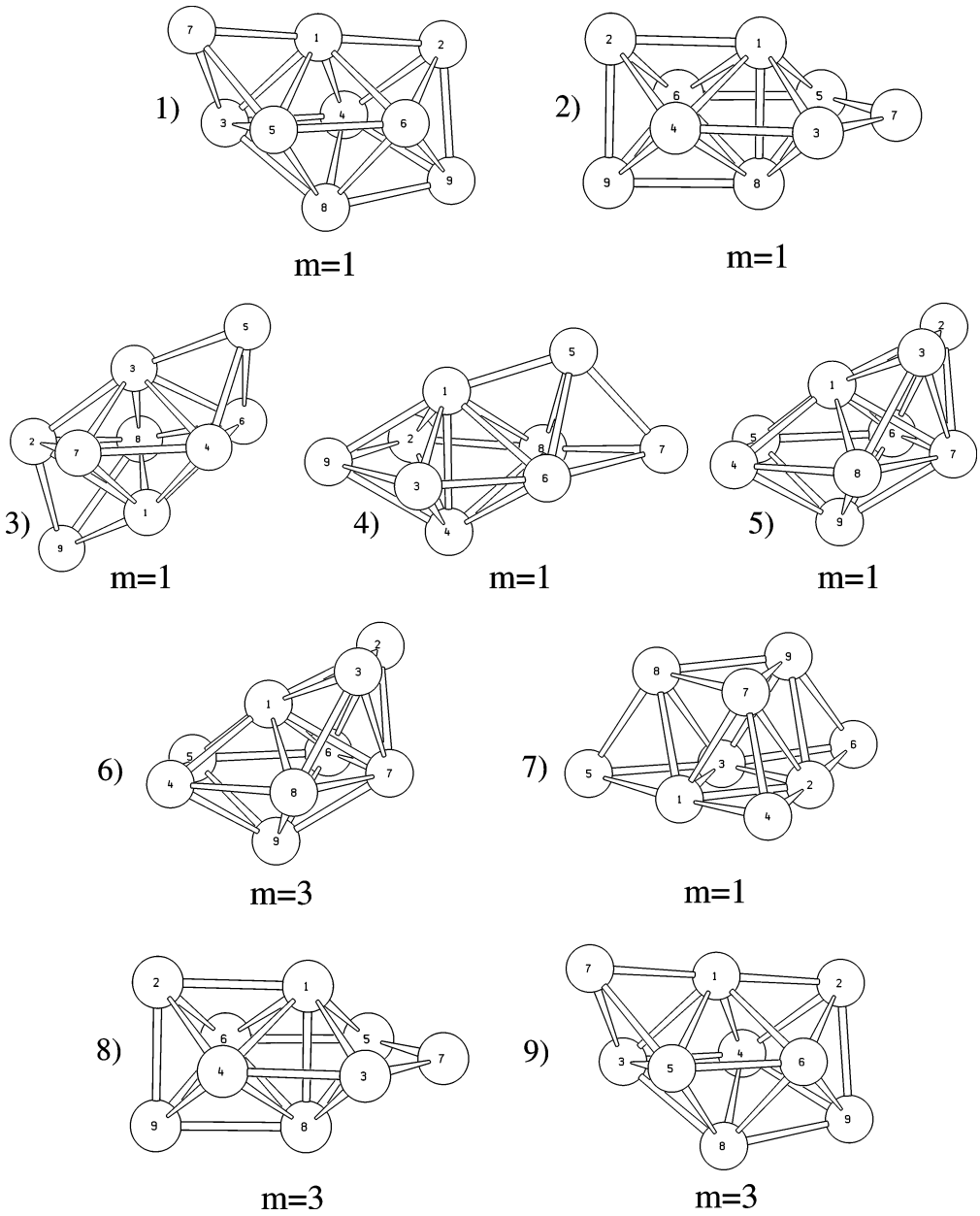

Figure 2. Structures and multiplicities of the anionic copper cluster nonamers.

two adjacent upper triangles (structure 2 of Figure 1). This structure was proposed as the global minimum in our previous work.[33] A C_{2v} isomer on the doublet potential energy surface (PES) obtained from the Cu_7 bipyramid by the double capping of adjacent upper and lower triangles follows 1.61 kcal/mol (structure 3 of Figure 1) above the ground-state C_s structure. The relaxation of a crystal fragment results in a C_{3v} low-lying isomer on the doublet PES (structure 4 of Figure 1), 13.12 kcal/mol above the ground-state structure. The average bond distance of this isomer is still considerably shorter than the copper bulk distance of 2.56 Å. The minima found on the quartet PES are lying much higher in energy as can be seen from Table 1.

Similar to the neutral copper nonamer, we found as a ground-state structure for the anionic copper nonamer the isomer obtained by single capping of the ground-state Cu_8 structure in lower multiplicity (structure 1 of Figure 2). Again, we notice that, as in the case of the neutral Cu_9 cluster, this structure has never been reported in the literature as a possible ground-state structure for this system. A singlet minimum in C_s symmetry obtained from the Cu_7 bipyramid by double capping of two adjacent upper triangles (structure 2 of Figure 2) lies only 0.11 kcal/mol above the ground state (see Table 2). This minimum was reported as the ground-state structure for Cu_9^- in our previous work.[33] Seven other different local minima are found above the ground state within an energy range of less than 20.00 kcal/mol (see Table 2 and Figure 2). This result shows the variety of energetically low-lying isomers on the PES for this kind of clusters.

Higher spin neutral and anionic copper nonamer structures are not reported, because these structures are much higher in energy as the ones reported in Figure 1 and 2. Tables 1 and 2 show that the order of several Cu_9 and Cu_9^- isomers exchanges if the local density approximation is used. Therefore, the GGA corrections are very important for the

Table 3. Adiabatic and Vertical Electron Affinities (EA) of the Anionic Copper Cluster Nonamer at the LDA Level[a]

	adiabatic		vertical		
cluster	EA	scaled EA	EA	scaled EA	exp.[b]
Cu_9^-	2.58	2.14	2.67	2.22	2.40 ± 0.05[b]

[a] All values are in eV. [b] Vertical detachment energy.

correct prediction of the global minimum and for the relative stability order of these systems.

In order to characterize the optimized structures of the neutral and anionic copper clusters and to give clues for further desirable experimental investigations, the harmonic vibrational frequencies have been calculated. The calculated harmonic frequencies for all minima are listed in Tables 1 and 2, respectively. From the assigned ground-state structures of Cu_9 and Cu_9^- the adiabatic and vertical electron affinities are calculated. The obtained results are compared with the available experimental data[70] and are presented in Table 3. Scaled values are also obtained using a scaling factor of 0.831 that results from the adjustment of the atomic electron affinity as described in ref 33. As Table 3 shows, the obtained new results for the electron affinity are in good to fair agreement with the reported experimental value. This result indicates that here the newly reported ground-state structures for the neutral and anionic copper nonamer are the ones most likely observed in the vertical detachment experiments. Because of the very small energy separation to the previously assigned ground states in ref 33 the reported binding energies are almost not effected. Experimental investigations which provide vibrational resolved photoelectron spectra for small copper clusters would be highly desirable in order to give a final answer concerning the ground-state structure of these systems.

The shell model of metal clusters is based on fully delocalized molecular orbitals for the cluster electrons.[71−75] Investigations have shown that clusters with 2, 8, or 18 electrons have special properties, like a high stability independent of the kind of metal. These so-called magic numbers are directly related to the cluster growth and the electronic structure. In the shell model the valence electrons of the cluster are placed in shells of *s*, *p*, and *d* character of the overall system like in the particle-in-a-box model. In this context clusters of metal atoms with only one valence electron in an *s* orbital are of particular interest, because their structure can be ascribed to the influence of these valence electrons.

With the intention of clarifying whether the molecular orbitals furnish information on the nonamer copper cluster structures the most relevant molecular orbitals (MOs) for the two low-lying structures of Cu_9 and Cu_9^- are calculated. The resulting MOs are depicted in Figures 3 and 4, respectively. As Figures 3 and 4 show the lower MOs for the neutral and anionic ground-state structures show a local bonding or antibonding situation of the 3*d* orbitals of the individual copper atoms. In contrast, the MOs closed to the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital gap possess shapes according to the shell model (see Figures 3 and 4) and mainly formed by the 4*s* valence electrons.[71−75] The HOMO is of d_{z^2} type for both

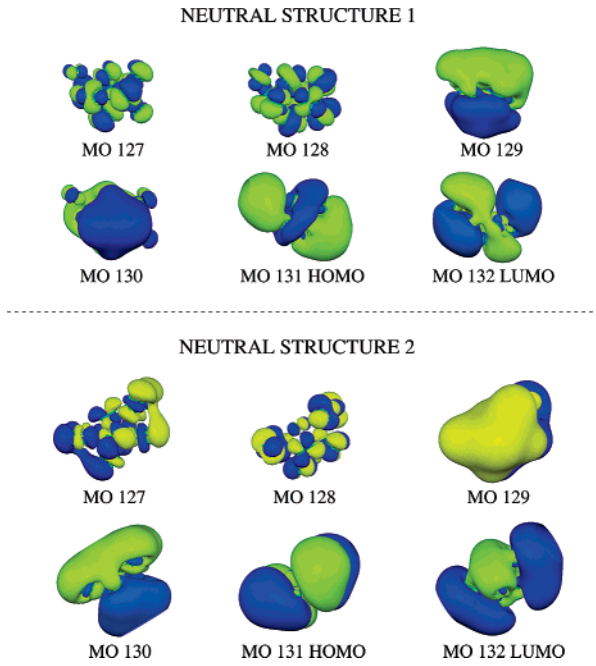

Figure 3. Selected molecular orbitals of the ground-state and first low-lying structure of the neutral copper cluster nonamer.

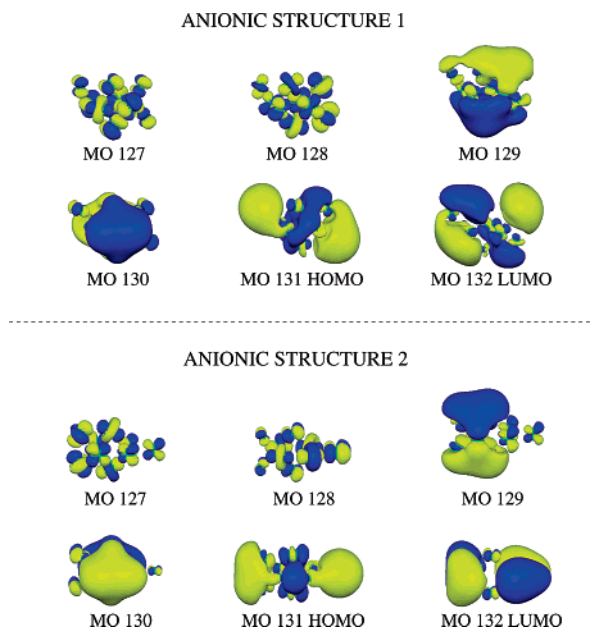

Figure 4. Selected molecular orbitals of the ground-state and first low-lying structure of the anionic copper cluster nonamer.

the neutral and anionic, ground-state structures, as Figures 3 and 4 show. The HOMO of the first low-lying neutral structure (structure 2 of Figures 1 and 3) is a d-type orbital similar to the one found in a previous theoretical work.[76] A more detailed analysis reveals that the mixing between the 3*d* and 4*s* atomic orbitals is slightly larger in the anionic clusters.

4. Conclusions

In this work we have reported LCGTO-DFT local and GGA first principle all-electron calculations for the structural and spectroscopic properties of neutral and anionic copper nonamers. Several topological structures on different PES

were investigated for the neutral cluster as well as for the ionic system. We believe that this work represents the most extended study ever reported for the neutral and the anionic copper nonamer cluster. New ground-state structures have been found for both neutral and anionic systems. All found minima were characterized by a vibrational analysis in order to guide future experiments, which we hope will be forthcoming. The inclusion of gradient corrections is important for the relative stability energy of different low-lying isomers. Adiabatic and vertical electron affinity have been reported. The obtained results are in good agreement with the available experimental data. This indicates that the newly suggested ground-state structures for Cu_9 and Cu_9^- are most likely the ones observed in the vertical detachment experiments. Experimental vibrational resolved photoelectron spectra would be very important in order to assign unequivocally the ground-state structures of these systems. The analysis of the MOs shows that the orbitals at the HOMO−LUMO gap possesses shapes according to the shell model.

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References

(1) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer: Berlin, Germany, 1995.

(2) Bonin, K. D.; Kresin, V. V. *Electric-Dipole Polarizabilities of Atoms, Molecules and Clusters*; World Scientific: Singapore, Singapore, 1997; Chapter 3, pp 64−81.

(3) Green, S. M. E.; Alex, S.; Fleischer, N. L.; Millam, E. L.; Marcy, T. P.; Leopold, D. G. Negative ion photoelectron spectroscopy of the group 5 metal trimer monoxides V_3O, Nb_3O, and Ta_3O. *J. Chem. Phys.* **2001**, *114*, 2653.

(4) Martìnez, A.; Köster, A. M.; Calaminici, P.; Salahub, D. R. Bonding in Nb_3O, Nb_3S and Nb_3Se: A topological analysis of the electrostatic potential. *J. Chem. Phys.* **2001**, *114*, 819.

(5) Chrétien, S.; Salahub, D. R. Kohn-Sham density-functional study of low-lying states of the iron clusters $Fe_n^+/Fe_n/Fe_n^-$ (n=1−4). *Phys. Rev. B* **2002**, *66*, 155425.

(6) Gutsev, G. L.; Bauschlicher, C. W., Jr. Electron affinities, ionization energies, and fragmentation energies of Fe_n clusters (n=2−6): A density functional theory study. *J. Phys. Chem. A* **2003**, *107*, 7013.

(7) Calaminici, P.; Köster, A. M. Structures and vibrations of V_3O and V_3O^-: A density functional study. *Int. J. Quantum Chem.* **2003**, *91*, 317.

(8) Calaminici, P.; Köster, A. M.; Salahub, D. R. Negative ion photoelectron spectra simulation of V_3O from a density functional study. *J. Chem. Phys.* **2003**, *118*, 4913.

(9) Calaminici, P.; Flores−Moreno, R.; Köster, A. M. Structures and vibrations of Nb_3O and Nb_3O^-: A density functional study. *J. Chem. Phys.* **2004**, *121*, 3558.

(10) Calaminici, P. Polarizability of Fe_n (n ≤ 4) clusters: an all-electron density functional study. *Chem. Phys. Lett.* **2004**, *387*, 253.

(11) Koutecký, J.; Fantucci, P. Theoretical Aspects of Metal Atom Clusters. *Chem. Rev.* **1986**, *86*, 539.

(12) Morse, M. D. Clusters of Transition-Metal Atoms. *Chem. Rev.* **1986**, *86*, 1049, and references therein.

(13) Flad, J.; Igel-Mann, G.; Preuss, H.; Stoll, H. A Combination Of Pseudopotentials And Density Functionals - Results for Cu_n, Cu_n^+, Ag_n, and Ag_n^+ Clusters. *Chem. Phys.* **1984**, *90*, 257.

(14) Amos, A. T.; Brook, P. A.; Moir, S. A. Extended Hückel Calculations On Copper Clusters. *J. Phys. Chem.* **1988**, *92*, 733.

(15) Calaminici, P.; Köster, A. M.; Russo, N.; Salahub, D. R. A Density Functional Study of Small Copper Clusters Cu_n (n≤5). *J. Chem. Phys.* **1996**, *105*, 9546.

(16) Jackson, K. A. First-Principles Study of the Structural and Electronic-Properies of Cu Clusters. *Phys. Rev. B* **1993**, *47*, 9715.

(17) Tatewaki, H.; Miyoshi, E.; Nakamura, T. Electronic-Structure of Small Copper Clusters. *J. Chem. Phys.* **1982**, *76*, 5073.

(18) Miyoshi, E.; Tatewaki, H.; Nakamura, T. Electronic-Structure of Small Copper Clusters. *Int. J. Quantum Chem.* **1983**, *23*, 1201.

(19) Bachmann, C.; Demuynck, J.; Veillard, A. *Faraday Symp. Chem. Soc.* **1980**, *14*, 170.

(20) Richtsmeier, S. C.; Dixon, D. A.; Gole, J. L. Structure of Group 1B Metal-Clusters, M_n, n=4−6. *J. Phys. Chem.* **1982**, *86*, 3937.

(21) Bauschlicher, C. W.; Langhoff, S. R.; Patrige, H. Theoretical-Study of the Homonuclear Tetramers and Pentamers of the Group-IB Metals (Cu, Ag, and Au). *J. Chem. Phys.* **1990**, *93*, 8133.

(22) Post, D.; Baerends, E. J. On the Hartree-Fock and X-Alpha Descriptions of Small Copper Cluster Electronic-Structures. *Chem. Phys. Lett.* **1982**, *86*, 176.

(23) Taneda, A.; Esfarjani, K.; Hasahi, Y.; Kawazoe, Y. *Similarities and Differences Between Atomic Nuclei and Cluster*; Abe, Y., Arai, I., Lee, S. M., Yabana, Y., Eds.; AIP Conference Proceedings No. 416, American Institute of Physics: New York, United States, 1997; p 471.

(24) Lammers, U.; Borstel, G. Electronic and Geometrical Structure of Noble-Metal Clusters. *Phys. Rev. B* **1993**, *49*, 17360.

(25) Walch, S. P.; Laskowski, B. C. Calculated Ground-State Potential Surface and Excitation-Energies for the Copper Trimer. *J. Chem. Phys.* **1986**, *84*, 2734.

(26) Langhoff, S. R.; Bauschlicher, C. W.; Walch, S. P.; Laskowskii, B. C. Ab-Initio Study of the Ground-State Surface of Cu_3. *J. Chem. Phys.* **1986**, *85*, 7211.

(27) Akeby, H.; Panas, I.; Pettersson, L. G. M.; Siegbahn, P.; Wahlgren, U. Electronic and Geometric Structure of the Cu_n Cluster Anion (n≤10). *J. Phys. Chem.* **1993**, *94*, 9715.

(28) Massobrio, C.; Pasquarello, A.; Car, R. Structural and Electronic-Properties of Small Copper Clusters - A First Principle Study. *Chem. Phys. Lett.* **1995**, *238*, 215.

(29) Massobrio, C.; Pasquarello, A.; Car, R. First Principles Study of Photoelectron-Spectra of Cu_n^- Clusters. *Phys. Rev. Lett.* **1995**, *75*, 2104.

(30) Massobrio, C.; Pasquarello, A.; Dal Corso, A. Structural and electronic properties of small Cu-n clusters using generalized-gradient approximations within density functional theory. *J. Chem. Phys.* **1998**, *109*, 6626.

(31) Crispin, X.; Bureau, C.; Geskin, V.; Lazzaroni, R.; Breás, J.-L. Local density functional study of copper clusters: A comparison between real clusters, model surface clusters, and the actual metal surface. *Eur. J. Inorg. Chem.* **1999**, 349.

(32) Calaminici, P.; Köster, A. M.; Vela, A.; Jug, K. Comparison of Static Polarizabilities of Cu_n, Na_n and Li_n. *J. Chem. Phys.* **2000**, *113*, 2199.

(33) Jug, K.; Zimmermann, B.; Calaminici, P.; Köster, A. M. Structure and Stability of Small Copper Clusters Cu_n ($n \leq 10$). *J. Chem. Phys.* **2002**, *116*, 4497.

(34) Jaque, P.; Toro-Labbé, A. The formation of neutral copper clusters from experimental binding energies and reactivity descriptors. *J. Phys. Chem. B* **2004**, *108*, 2568.

(35) Parent, D. C.; Anderson, S. L. Chemistry of Metal and Semimetal Cluster Ions. *Chem. Rev.* **1992**, *92*, 1541.

(36) Jarrold, M. F.; Creegan, K. M. Photodissociation of Copper Clusters, Cu_n^+ ($n = 3-8$), in the 370−710 nm Wavelength Region. *Int. J. Mass Spectrom. Ion Processes* **1990**, *102*, 161.

(37) Powers, D. E.; Hansen, S. G.; Geusic, M. E.; Michalopoulos, D. L.; Smalley, R. E. Supersonic Copper Clusters. *J. Phys. Chem.* **1983**, *78*, 2866.

(38) Knickelbein, M. B. Electronic Shell Structure in the Ionization-Potentials of Copper Clusters. *Chem. Phys. Lett.* **1992**, *192*, 129.

(39) Leopold, D. G.; Ho, J.; Lineberger, W. C. Photoelectron-Spectroscopy of Mass-Selected Metal Cluster Anions. 1. Cu-1−10. *J. Chem. Phys.* **1987**, *86*, 1715.

(40) Taylor, K. J.; Pettiette-Hall, C. L.; Cheshnovsky, O., Smalley, R. E. Ultraviolet Photoelectron-Spectra of Coniage Metal-Clusters. *J. Chem. Phys.* **1992**, *96*, 3319.

(41) Begemann, W.; Hector, R.; Liu, Y. Y.; Tiggersbäumker, J.; Meiwes-Broer, K. H.; Lutz, H. O. Sputtered Metal and Silicon Cluster IOns - Collision-Induced Fragmentation and Neutralization. *Z. Phys. D: At., Mol. Clusters* **1989**, *12*, 229.

(42) Begemann, W.; Meiwes-Broer, K. H.; Lutz, H. O. Unimolecular Decomposition of Sputtered Al^+, Cn^+ and Si^+ Clusters. *Phys. Rev. Lett.* **1986**, *56*, 2248.

(43) Hilpert, K., Gingerich, K. A. Atomization Enthalpies of the Molecules Cu_3, Ag_3 and Au_3. *Ber. Bunsenges, Phys. Chem.* **1980**, *84*, 739.

(44) Moskovits, M.; Hulse, J. E. Ultraviolet-Visible Spectra of Diatomic, Triatomic, and Higher Nickel Clusters. *J. Chem. Phys.* **1977**, *66*, 3988.

(45) Morse, M. D.; Hopkins, J. P.; Langridge-Smith, P. R. R.; Smalley, R. E. Spectroscopic Studies of the Jet-Cooled Copper Trimer. *J. Chem. Phys.* **1983**, *79*, 5316.

(46) Ozin, G. A.; Mitchell, S. A.; Macintosh, D. F.; Mattar, S. M.; Garcia-Prieto, J. Copper Atoms and Copper Clusters in Solid Xenon - Special Atom and Dimer Sites and Covalently Bound Clusters with 3 to 5 Atoms. *J. Phys. Chem.* **1983**, *87*, 4651.

(47) DiLella, D. P.; Raylor, K. V.; Moskovits, M. Tricopper - A Fluxional Molecule. *J. Phys. Chem.* **1983**, *87*, 525.

(48) Howard, J. A.; Preston, K. F.; Sutcliffe, R.; Mile, B. Electron-Spin Resonance-Spectrum of Matrix-Isolated Cu_3. *J. Phys. Chem.* **1983**, *87*, 536.

(49) Howard, J. A.; Sutcliffe, R.; Tse, J. S.; Mile, B. Electron-Spin Resonance-Spectrum of Cu_5, A trigonal Bipyramidal Copper Cluster. *Chem. Phys. Lett.* **1983**, *94*, 561.

(50) Ingólfsson, O.; Takeo, H.; Nonose, S. Energy-resolved collision-induced dissociation of Al_n^+ clusters ($n=2-11$) in the center of mass energy range from few hundred meV to 10. *J. Chem. Phys.* **1999**, *110*, 4382.

(51) Pettiette, C. L.; Yang, S. H.; Craycraft, M. J.; Conceicao, J.; Laaksonen, R. T.; Cheshnovsky, O.; Smalley, R. E. Ultraviolet Photoelectron-Spectroscopy of Copper Clusters. *J. Chem. Phys.* **1988**, *88*, 5377.

(52) Cha, C. Y.; Ganteför, G.; Eberhardt, W. Photoelectron-Spectroscopy of Cu_n^- Clusters - Comparison With Jellium Model Predictions. *J. Chem. Phys.* **1993**, *99*, 6308.

(53) Howard, J. A.; Sutcliffe, R.; Miles, B. Cryochemical Studies .7. Electron-Spin Resonance-Spectrum of Ag_5. *J. Phys. Chem.* **1983**, *87*, 2268.

(54) Howard, J. A.; Sutcliffe, R.; Mile, B. The Geometric and Electronic-Structures of Small Metal-Clusters of Group-1B Metals. *Surf. Sci.* **1985**, *156*, 214.

(55) Cheshnovsky, O.; Taylor, K. J.; Conceicao, J.; Smalley, R. E. Ultraviolet Photoelectron-Spectra of Mass-Selected Copper Clusters - Evolution of the 3d Band. *Phys. Rev. Lett.* **1990**, *64*, 1785.

(56) Yang, M.; Jackson, K. A.; Koehler, C.; Frauenheim, T.; Jellinek, J. Structure and shape variations in intermediate-size copper clusters. *J. Chem. Phys.* **2006**, *124*, 024308.

(57) *deMon Software*, *deMon-KS Version 3.4*; Casida, M. E.; Daul, C.; Goursot, A.; Köster, A. M.; Pettersson, L. G. M.; Proynov, E.; St-Amant, A.; Salahub, D. R.; Duarte, H.; Guan, J.; Jamorski, C.; Leboeuf, M.; Malkin, V.; Malkina, O.; Sim, F.; Vela, A. Montréal, Canada, 1996.

(58) *AllChem*; Köster, A. M.; Krack, M.; Leboeuf, M.; Zimmermann, B. Universität Hannover, 1998.

(59) Krückeberg, S.; Schweikhard, L.; Ziegler, J.; Dietrich, G.; Lützenkirchen, K.; Walther, C. Decay pathways and dissociation energies of copper clusters, Cu_n^+ ($2 \leq n \leq 25$), Cu_n^{2+} ($15 \leq n \leq 25$). *J. Chem. Phys.* **2001**, *114*, 2955.

(60) Reveles, J. U.; Köster, A. M. Geometry optimization in density functional methods. *J. Comput. Chem.* **2004**, *25*, 1109.

(61) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev. A* **1965**, *140*, 1133.

(62) Köster, A. M.; Calaminici, P.; Casida, M. E.; Flores-Moreno, R.; Geudtner, G.; Goursot, A.; Heine, T.; Ipatov, A.; Janetzko, F.; Martin del Campo, J.; Patchkovskii, S.; Reveles, J. U.; Salahub, D. R.; Vela, A. the deMon Developers, Mexico, 2006.

(63) Köster, A. M.; Flores-Moreno, R.; Reveles, J. U. Efficient and reliable numerical integration of exchange-correlation energies and potentials. *J. Chem. Phys.* **2004**, *121*, 681.

(64) Dunlap, B. I.; Connolly, J. W. D.; Sabin, J. R. First-Row Diatomic-Molecule and Local Density Models. *J. Chem. Phys.* **1979**, *71*, 4993.

(65) Mintmire, J. W.; Dunlap, B. I. Fitting the Coulomb Potential Variationally in Linear-Combination-of-Atomic-Orbitals Density-Functional calculations. *Phys. Rev. A* **1982**, *25*, 88.

(66) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. Optimization of Gaussian-Type Basis-Sets for Local Spin-Density Functional Calculations. 1. Boron Through Neon, Optimization Technique and Validation. *Can. J. Phys.* **1992**, *70*, 560.

(67) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate Spin-Dependent Electron Liquid Correlation Energies for Local Spin-Density Calculations - A Critical Analysis. *Can. J. Phys.* **1980**, *58*, 1200.

(68) Perdew, J. P.; Wang, Y. Accurate and Simple Density Functional for the Electronic Exchange Energy - Generalized Gradient Approximation. *Phys. Rev. B* **1986**, *33*, 8800.

(69) Perdew, J. P. Density-Functional Approximation for the Correlation-Energy of the Inhomogeneous Electron-Gas. *Phys. Rev. B* **1986**, *33*, 8822; **1986**, *34*, 7406.

(70) Ho, J.; Ervin, K. M.; Lineberger, W. C. Photoelectron-Spectroscopy of Metal Cluster Anions - Cu_n, Ag_n and Au_n. *J. Chem. Phys.* **1990**, *93*, 6987.

(71) de Heer, W. A. The Physics of Simple Metal-Clusters - Experimental Aspects and Simple-Models. *Rev. Mod. Phys.* **1993**, *65*, 611.

(72) Knight, W. D.; Clemenger, K.; de Heer, W. A.; Sanders, W. A.; Chou, M. Y.; Cohen, M. L. Electronic Shell Structure and Abundances of Sodium Clusters. *Phys. Rev. Lett.* **1984**, *24*, 2141.

(73) Cohen, M. L.; Knight, W. D. The Physics of Metal-Clusters. *Phys. Today* **1990**, *43*, 42.

(74) Ekardt, W.; Penzar, Z. Self-Consistent Sommerfeld Droplet as a Simple-Model for an accurate Prediction of the Electronic-Properties of Small metal particles. *Phys. Rev. B* **1988**, *38*, 4273.

(75) Khanna, S. N.; Jena, P. Atomic Clusters - Building-Blocks for a Class of Solids. *Phys. Rev. B* **1995**, *51*, 13705.

(76) Jug, K.; Zimmermann, B.; Köster, A. M. Growth pattern and bonding of copper clusters. *Int. J. Quantum. Chem.* **2002**, *90*, 594.

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