

Bonding in Cu, Ag, and Au Clusters: Relativistic Effects, Trends, and Surprises

Hannu Häkkinen,¹ Michael Moseler,² and Uzi Landman¹

¹*School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430*

²*Theoretische Quantendynamik, Fakultät für Physik, Universität Freiburg, 79106 Freiburg, Germany*

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Electronic structure and bonding in anionic coinage metal clusters are investigated via density-functional calculations, focusing on an extensive set of isomers of Cu_7^- , Ag_7^- , and Au_7^- . While the ground states of Cu_7^- and Ag_7^- are three dimensional (3D), that of Au_7^- is planar, separated from the optimal 3D isomer by 0.5 eV. The simulated thermally weighted photoabsorption spectrum of Au_7^- is dominated by planar structures, and it agrees well with the measured one. The propensity of Au_N^- clusters to favor planar structures (with N as large as 13) is correlated with strong hybridization of the atomic $5d$ and $6s$ orbitals due to relativistic effects.

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The atomic electronic structure of Cu, Ag, and Au, featuring a filled d shell and a singly occupied s shell [$nd^{10}(n+1)s^1$, with $n = 3, 4,$ and 5 for Cu, Ag, and Au], suggests that the properties of these metals could be treated to first approximation within a “simple metal” framework—that is, as s^1 -electron systems perturbed, with increasing strength from Cu to Au, by the underlying filled d shell. However, the above view may be oversimplified since this series contains Au which exhibits very strong relativistic effects [1].

Recently, there has been a surge of interest in the properties of finite nanoscale gold systems serving as building blocks of nanostructured materials and electronic devices [2–6], as well as novel nanocatalytic systems [7,8]. In light of the observed extreme size sensitivity of the properties of small gold aggregates, it is imperative that a fundamental understanding of the electronic and geometric structures of gold clusters be gained and put in context within the coinage metal group (for pertinent studies of coinage metal clusters, see Refs. [9–16]). Added motivation for such studies derives from theoretical predictions [4] of a transition from two-dimensional (2D) to 3D optimal structures of neutral gold clusters and their anions (Au_N and Au_N^-) for $N \geq 8$ and $N \geq 7$, respectively, and recent gas-phase mobility experiments [15] where evidence has been found for 2D structures of Au_N^- with N extending to unusually large sizes, i.e., up to 9–11 atoms.

Here we show through an extensive density-functional study, focusing on Cu_7^- , Ag_7^- , and Au_7^- [17], that relativistic effects on bonding and structures in small gold clusters lead to quite remarkable results. In particular, the structures of the ground state and the close-lying first isomer of Au_7^- are found to be planar, separated by a large energy gap (0.47 eV, equivalent to an internal vibrational temperature [18] of 730 K) from the lowest-lying 3D isomer. Furthermore, the propensity of anionic gold clusters to favor planar structures continues up to surprisingly large sizes, at least up to 13 atoms. This trend

correlates with a relativistically enhanced stronger sd hybridization and $d-d$ interaction in gold than in Ag and Cu, where for the latter elements the 2D \rightarrow 3D structural transition occurs for smaller clusters.

The electronic and geometric structures (optimized without any symmetry constraints) were obtained through Born-Oppenheimer density-functional calculations [19] employing norm-conserving scalar-relativistic pseudopotentials [20] and including self-consistent gradient corrections (PBE-GGA) [21].

For each of the metals we show in Fig. 1a the calculated energetic ordering of nine optimized cluster structures (given in Fig. 1b and described in the caption). While Cu_7^- and Ag_7^- clearly favor 3D structures, similar to Na_7^- that we included for comparison, the ground-state structure of Au_7^- is 2D (edge-capped square: ECS) with a close-lying planar structure (edge-capped rhombus, ECR) as the first isomer (separated by about 50 K in vibrational temperature; see the scale on the right-hand side of Fig. 1a). The lowest-lying 3D structure of Au_7^- (edge-capped pyramid, ECP) is separated from the 2D ground state by 730 K, and it differs from the optimal 3D structures of the Cu, Ag (and Na) clusters. The surprisingly clear tendency of Au_7^- to favor planar structures is due to relativistic effects, as verified directly via comparison of the (3D) capped octahedral (COh) and (2D) ECS structures reoptimized with a nonrelativistic gold pseudopotential (employing the core radii given in Ref. [20]); see element AuNR in Fig. 1a. The nonrelativistic AuNR $_7^-$ favors 3D structures, and the energy difference between its COh and ECS isomers is very similar to that of Ag_7^- .

We analyze the Kohn-Sham (KS) orbitals [$\phi_i(\mathbf{r}), i = 1 \dots N_e$] of the COh and ECS structures by calculating the weights $w_{\ell m, i}^{(I)} = \int_0^R | \int Y_{\ell m, i}^{(I)}(r) \phi_i(r) d\Omega |^2 dr$. The $w_{\ell m, i}^{(I)}$ are the coefficients in the spherical harmonics decomposition of the local (partial) charge, associated with the i th KS orbital, around each atom (I); the integration is performed in a sphere of radius R , taken to be about half of the average bond length in the cluster. The total charge included in

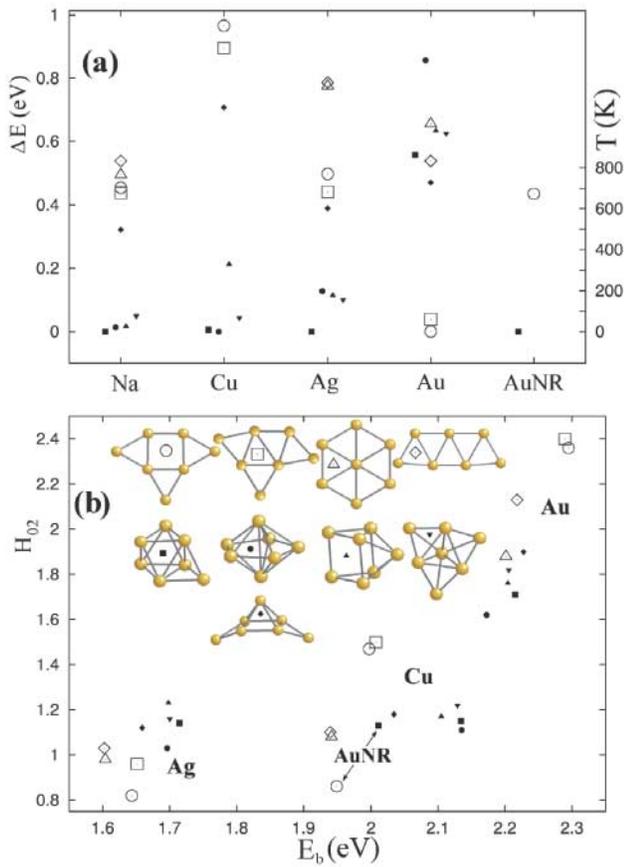


FIG. 1 (color online). (a): Differences in total energy between the isomers and the ground-state structures of Na_7^- , Cu_7^- , Ag_7^- , and Au_7^- . Open and filled symbols denote 2D and 3D structures, respectively. The considered structures (nine per element) and assigned symbols are shown in (b) and are named (from left to right) edge-capped “square” (ECS, C_{2v} , open circle), edge-capped rhombus (ECR, C_s , open square), hexagon (HEX, D_{6h} , open triangle), “W-like structure” (W, C_{2v} , open diamond), capped “octahedron” (COh, C_{3v} , filled square), pentagonal bipyramid (PBP, D_{5h} , filled circle), capped prism (CP, C_{2v} , filled up-triangle), tricapped tetrahedron (TCT, T_d , filled down-triangle), and edge-capped pyramid (ECP, C_{2v} , filled diamond). “AuNR” denotes “nonrelativistic gold.” (b) Correlation between the sd hybridization index H_{02} and the binding energy per atom; a larger value of H_{02} indicates stronger sd hybridization. Note the clear correlation between the sd hybridization (favoring 2D structures) and the strong binding in Au_7^- , and the similarity of H_{02} between AuNR_7^- and Ag_7^- .

this analysis encompasses typically over 85% of the total charge of the cluster. We further define a hybridization index $H_{kl} = \sum_{i=1}^{N_e} h_{kl,i}$, where $h_{kl,i} = \sum_{l,m,m'} w_{km,i}^{(l)} w_{lm',i}^{(l)}$.

The hybridization of atomic s and d states (H_{02}) is particularly interesting since the main relativistic effect in gold is the stabilization of the $6s^1$ orbital and destabilization of the $5d^{10}$ ones, thus bringing them energetically closer [1]. Indeed, the H_{02} index for Au_7^- is on average much larger than for Cu_7^- and Ag_7^- , and for both Ag_7^- and Au_7^- stronger binding correlates with enhanced sd hybridization (Fig. 1b). Furthermore, a strong sd hybridiza-

tion favors planar bonding for Au_7^- (compare open and filled symbols in Fig. 1b). Note that for nonrelativistic Au_7^- (AuNR in Fig. 1), both the binding energy and sd hybridization are reduced compared to the relativistic case, and as aforementioned the ground state reverts to a 3D structure (COh) with a hybridization index similar to Ag_7^- (Fig. 1b) [22].

The relativistic contraction of the Au $6s$ orbital is concomitant with a significant shortening of the interatomic bond distances (typically 0.25 \AA for the Au_7^- isomers studied here) [23] resulting in an increased overlap between the $5d$ orbitals of neighboring atoms. Consequently, in the relativistic Au_7^- clusters the KS molecular orbitals derived from the d electrons are more delocalized over the volume of the cluster than in the AuNR_7^- case, as portrayed in the significantly smaller electronic kinetic energies ($E_K^{(el)}$) calculated with the scalar-relativistic pseudopotentials. Furthermore, in the relativistic case $E_K^{(el)}$ is much smaller for the 2D cluster isomers than for the 3D

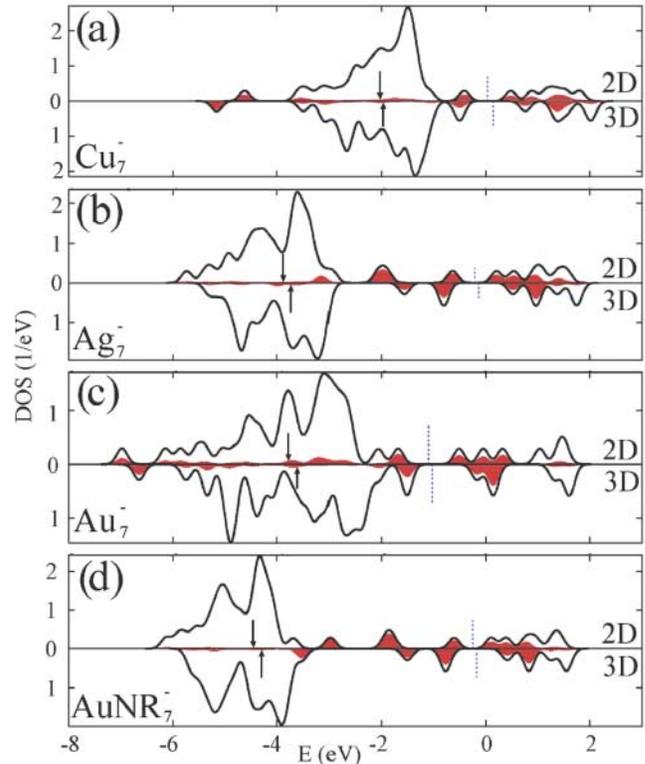


FIG. 2 (color online). (a)–(d) DOS for the 2D ECS and 3D COh structures (up and down curves in each panel, respectively) of Cu_7^- , Ag_7^- , Au_7^- , and AuNR_7^- . The solid lines denote the total DOS, and the s component is shown by the shaded areas. The arrows denote the center of gravity of the DOS, and the vertical dashed lines indicate the Fermi energy E_F . The p contribution to the DOS (not shown) is negligible below E_F and becomes comparable to s only for unoccupied states. Note the large width of the d band of Au compared to that of Cu and Ag, and the similar shape and width of the DOS of AuNR_7^- to those of the DOS of Ag_7^- .

TABLE I. Calculated vertical detachment energies (in eV). The values for the ground-state clusters are in boldface. The experimental values are Cu_7^- : 2.2 eV [11]; Ag_7^- : 2.5 eV [11], and Au_7^- : 3.5 eV [14].

	COh	PBP	TCT	CP	ECP	HEX	ECR	W	ECS
Cu_7^-	2.41	2.09	2.19	2.45	2.50	1.77	2.14	2.26	2.17
Ag_7^-	2.60	2.16	2.34	2.62	2.67	1.89	2.35	2.40	2.29
Au_7^-	3.41	3.04	3.22	3.46	3.57	2.75	3.32	3.43	3.46
AuNR_7^-	2.47								2.16

ones, while in the AuNR_7^- case the $E_K^{(el)}$ values are comparable for the two dimensionalities [for the relativistic Au_7^- $\Delta_K^{(el)} = E_K^{(el)}(3\text{D}) - E_K^{(el)}(2\text{D}) = 12.85$ eV, while for AuNR_7^- $\Delta_K^{(el)} = 0.56$ eV]. The $E_K^{(el)}$ term is counterbalanced by the potential energy contributions (electronic, and ion-ion repulsion [19]) which always favor higher coordination, i.e., 3D structures, and it is this energy balance that underlies the lower dimensionality of smaller clusters ($N \leq 13$) and the transition to 3D clusters for larger sizes.

The strong sd hybridization and $d-d$ interaction in Au_7^- leads to a rather large d -band width compared to the Cu_7^- and Ag_7^- clusters [see the density of states (DOS) plotted for the 3D COh and 2D ECS structures in Fig. 2]; note that the bandwidth and the shape of the DOS of the AuNR_7^- are very similar to that of Ag_7^- [24]. Through comparisons between the measured photoelectron spectra [including the vertical electron detachment energy (vDE)] and those calculated for specific atomic arrangements, one may obtain valuable information about the cluster geometries. While the large gap between the 2D and 3D isomers of Au_7^- (corresponding to a vibrational temperature of 730 K) suggests that cluster beams consisting mainly of planar ground-state clusters may be formed and detected, comparison of the calculated vDEs (Table I) to the measured one [14] indicates that a definite determination of the structure of Au_7^- cannot be made based solely on this observable. We note, however, that the shape of the low-energy region of the calculated DOS of the ground-state 2D ECS structure (i.e., the two peaks corresponding to the highest occupied states above the steep d -band edge; see the top curve in Fig. 2c between $E = -2.3$ eV and E_F) agrees rather well with the early PES spectra [9], as well as with a recent high-resolution experiment [14,25].

Another method commonly used for probing the electronic and geometric structures of clusters (through comparisons with simulated spectra) is optical absorption (photodepletion) spectroscopy. The optical absorption oscillator strengths, calculated via the time-dependent local density approximation (TDLDA) [26,27], for the ground-state planar ECS structure and the lowest-energy 3D ECP isomer are shown in Figs. 3a and 3b, respectively. The measured [15] spectrum of Au_7Xe^- shows a strong transition at 2.5 eV, followed by weaker ones at 2.6, 2.8, and 3.2 eV (the transition energies are denoted by the

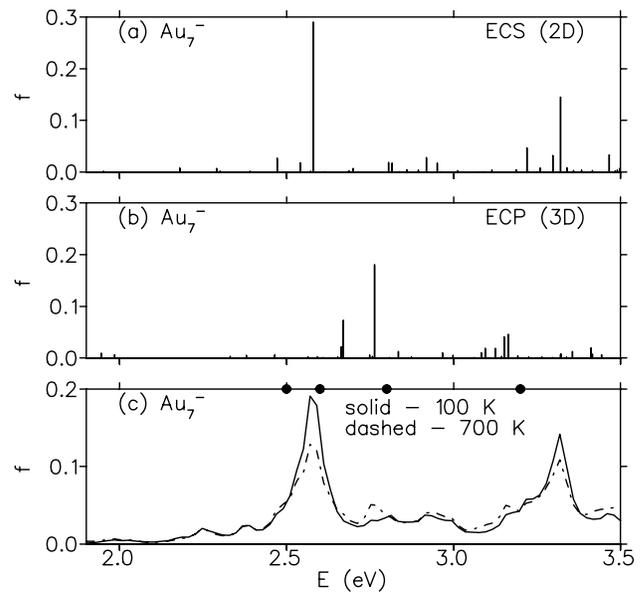


FIG. 3. Calculated TDLDA oscillator strengths of optical transitions for the 2D ground-state structure ECS (a) and the optimal 3D structure ECP (b). Comparison to experiment [15] is given in (c), displaying a calculated thermally weighted spectrum consisting of the two lowest-energy 2D and 3D structures (2D: ECS, ECR; 3D: ECP, and COh; see Fig. 1b) broadened by Lorentzian function (width of 0.05 eV). The energies of the main experimental transitions are denoted by filled dots on the upper abscissa. The theoretical spectra are plotted without any shifts of the transition energies.

filled dots on the upper abscissa of Fig. 3c). To facilitate comparison to the experiment, we show in Fig. 3c the thermally (Boltzmann) weighted TDLDA spectrum for “low” (100 K) and “high” (700 K) temperatures. The spectrum, and particularly the first peak at 2.6 eV, is dominated by the ground-state features, and thus it provides strong support for the high abundance of planar structures in the measured beam of Au_7^- clusters.

Finally, we note that our calculations predict that the tendency of Au_N^- clusters to prefer planar structures extends to surprisingly large sizes; that is, our results indicate that planar structures are energetically favorable up to at least $N = 13$ [28], correlating with recent measurements and related quantum-chemical calculations [15]. This unique behavior, that has been shown here to be an added manifestation of the strong relativistic effects in gold [1,29,30], is likely to influence the gas-phase reactivity and catalytic activity of small gold clusters, e.g., with O_2 [8] and CO [31].

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- [1] P. Pyykkö, *Chem. Rev.* **88**, 563 (1988).
- [2] U. Landman *et al.*, *Science* **248**, 454 (1990).
- [3] H. Häkkinen *et al.*, *J. Phys. Chem. B* **104**, 9063 (2000), and references therein.
- [4] H. Häkkinen and U. Landman, *Phys. Rev. B* **62**, R2287 (2000).
- [5] C. L. Cleveland *et al.*, *Phys. Rev. Lett.* **79**, 1873 (1997).
- [6] H. Häkkinen *et al.*, *Phys. Rev. Lett.* **82**, 3264 (1999).
- [7] A. Sanchez *et al.*, *J. Phys. Chem. A* **103**, 9573 (1999).
- [8] H. Häkkinen and U. Landman, *J. Am. Chem. Phys.* **123**, 9704 (2001).
- [9] K. J. Taylor *et al.*, *J. Chem. Phys.* **96**, 3319 (1992).
- [10] H. Handschuh *et al.*, *J. Chem. Phys.* **100**, 7093 (1994).
- [11] H. Handschuh *et al.*, *J. Chem. Phys.* **102**, 6406 (1995).
- [12] V. Bonacić-Koutecký *et al.*, *J. Chem. Phys.* **100**, 490 (1994).
- [13] C. Massobrio *et al.*, *Phys. Rev. Lett.* **75**, 2104 (1995).
- [14] S. Burkart, Ph.D. thesis, University of Konstanz, 2000; G. Ganteför (private communication).
- [15] S. Gilb, Ph.D. thesis, University of Karlsruhe, 2001; F. Furche *et al.* (to be published).
- [16] R. Fournier, *J. Chem. Phys.* **115**, 2165 (2001).
- [17] In light of recent mobility and optical experiments on Au_N^- clusters (Ref. [15]), we performed here a more extensive search for structural isomers than in Ref. [4], leading to the discovery of the new planar structures for $N \geq 7$.
- [18] The energy difference in terms of temperature is calculated as $T = 2\Delta E/(3N - 6)k_B$.
- [19] R. N. Barnett and U. Landman, *Phys. Rev. B* **48**, 2081 (1993). We have verified by GGA local-spin-density calculation that the spin singlet ($S = 0$) is the ground state for the low-energy structures of the metal anionic heptamer clusters.
- [20] N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991). The core radii (in units of a_0) are as follows: Cu: $s(2.08)$, $p(2.3)$, $d(2.0)$; Ag: $s(2.5)$, $p(2.6)$, $d(2.2)$; and Au: $s(2.5)$, $p(3.0)$, $d(2.0)$, with s as the local component. The plane wave cutoff energy is 90.6 Ry for Cu and 61.7 Ry for Ag and Au. For further information about the scalar-relativistic pseudopotentials that we used, see citation 11 in Ref. [6] and citation 14 in Ref. [4] of this Letter. For Cu_2 (Ag_2), the calculated bond length and dissociation energy are 2.28 Å (2.63 Å) and 2.02 eV (1.70 eV), compared to experimental values of 2.22 Å (2.53 Å) and 1.97 eV (1.62 eV). For experimental values, see *AIP Handbook* (McGraw-Hill, New York, NY, 1972), for Cu_2 , Ref. [16] for Ag_2 , and Ref. [8] for Au_2 . Comparison of the results for Au_4 given in [4], with a full relativistic four-component approach [S. Varga *et al.*, *Eur. Phys. J. D* **16**, 29 (2001)], verified the accuracy of our scalar-relativistic calculations.
- [21] J. P. Perdew *et al.*, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [22] For the Cu_7^- clusters the highest value of H_{02} is found for the 2D ECR and ECS isomers (see empty circle and square in Fig. 1b). However, the highest binding energies are found for 3D structures with lower values of H_{02} . Apparently in this case other contributions to the energetics of the cluster (e.g., electronic and ionic repulsion, and electronic kinetic energy) dominate the subtle energy balance that governs the structural dimensionality.
- [23] For all the nine isomers of the anionic heptamers, the average nearest-neighbor distance, \bar{d} , is shortest for Cu and longest for Ag. As a typical example, for the 2D ECS structure $\bar{d}(\text{Cu}) = 2.44$ Å, $\bar{d}(\text{Ag}) = 2.80$ Å, $\bar{d}(\text{Au}) = 2.74$ Å, and $\bar{d}(\text{AuNR}) = 2.97$ Å. For the 3D isomers the average bond lengths are longer by ≤ 0.1 Å.
- [24] We have also found that Cu_7^- , Ag_7^- , and the nonrelativistic Au_7^- possess jelliumlike delocalized states close to the highest occupied molecular orbital (HOMO) of the cluster (i.e., the states that show large s contributions in Figs. 2a, 2b, and 2d). These states exhibit a jelliumlike closed shell s^2p^6 , as expected when Cu, Ag, and Au are considered as monovalent s^1 metals. This is not the case for the relativistic Au_7^- where the strong sd hybridization obliterates the jellium behavior.
- [25] The low-energy two-peak structure of the DOS corresponding to the 3D (COh) ground state of Ag_7^- (see Fig. 2b for $-2 \text{ eV} \leq E \leq E_F$), as well as the expected splitting of the doubly degenerate lowest energy peak (the HOMO level) at finite temperature and the calculated vDE value (2.60 eV, Table I), correlates well with the measured PES (see region $4 \leq E \leq 2 \text{ eV}$ in Fig. 9 of Ref. [11]). On the other hand, Cu_7^- has several low-lying isomers within a small range of 100 K (Fig. 1a), whose contributions are portrayed in the complex structure (relative to Ag_7^-) of the measured low-energy PES [11].
- [26] M. E. Casida, in *Recent Developments and Applications in Modern Density-Functional Theory*, edited by J. M. Seminario (Elsevier, Amsterdam, 1996).
- [27] We have implemented the TDLDA method [26] using the Kohn-Sham states as the basis for building the oscillator matrix. About 1200 particle-hole pairs were used. Varying the size of the particle-hole basis as well as the size of the computational grid shows that the dipole transition energies (locations of the peaks) are converged within 0.1 eV in the energy range shown in Fig. 3. See also M. Moseler *et al.*, *Phys. Rev. Lett.* **87**, 053401 (2001).
- [28] For optimal 2D structures and their symmetries for Au_N^- , $2 \leq N \leq 6$, see Ref. [4]. For $8 \leq N \leq 13$, they are $N = 8$: D_{4h} edge-capped square; $N = 9$: C_{2v} bicapped centered hexagon; $N = 10$: D_{3h} triangular structure; $N = 11$: C_s triangular structure; $N = 12$: C_{3v} triangular structure; and $N = 13$: C_s triangular structure. Many of these clusters have close-lying planar isomers, e.g., for $N = 13$ a D_{6h} six-capped hexagonal “star” lies 0.20 eV above the ground state.
- [29] Motivated by the fact that the relativistic effects for the Pt atom are almost as strong as for Au (Ref. [1]), we carried out a comprehensive study on spin and structure isomers of Pt_7^- . Pt_7^- clearly favors 3D structures with high spin multiplicities (typically $S = 5/2$ or $7/2$).
- [30] For an early study of the strong relativistic effect on the surface reconstruction of gold, see N. Takeuchi *et al.*, *Phys. Rev. B* **43**, 14 363 (1991).
- [31] Our results on the structures and saturation coverages of planar $\text{Au}_N(\text{CO})_M^-$ carbonyls with $7 \leq N \leq 13$ and $4 \leq M \leq 6$ and their correlations with mass spectrometric experiments [W. T. Wallace and R. L. Whetten, *J. Phys. Chem. B* **104**, 10 964 (2000)], as well as their CO binding energies, PES, and vibrational spectra, will be reported elsewhere.