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Unraveling the Apparent Dimerization Tendency in Small Mo_n Clusters with $n = 3-10$

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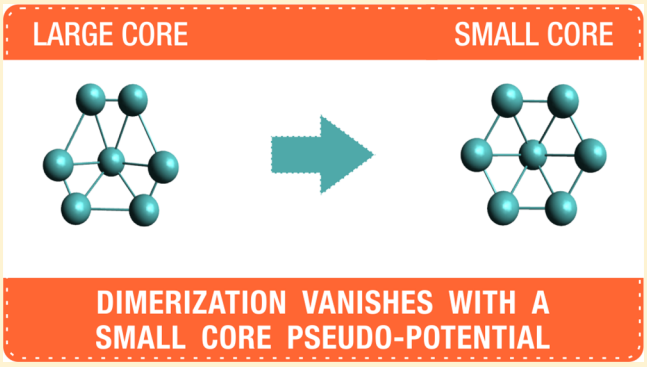
ABSTRACT: The geometric, electronic, and magnetic properties of Mo_n clusters, with $n = 3-10$, are investigated from a computational point of view. Calculations are carried out using gradient-corrected density functional theory, a small core pseudopotential to represent inner electrons, and a triple-ζ basis set to describe the 4s, 4p, 4d, and 5s valence atomic orbitals. The geometries of the ground states for every cluster size are distorted versions of the familiar structures adopted by transition metal aggregates. Both the average interatomic distance and the atomization energy show a monotonic increase. In most cases metallic aggregates exhibit closed-shell electronic configurations. Only Mo_3, Mo_8, and Mo_{10} show open-shell electronic structures. However, several isomers are found to lie within 60 meV/at above the corresponding ground state for all cluster sizes. The apparent tendency to form dimers observed by some authors in small molybdenum clusters from the dimer to the heptamer is revisited using the present methodology. In all cases an important geometrical distortion is undergone by the original clusters leading to new equilibrium geometries in which dimerization is completely absent. It is then concluded that using small core pseudopotentials is essential to obtain realistic geometries for small molydenum clusters.



INTRODUCTION

Transition metal (TM) clusters have been studied for a long time, with a variety of methods and approaches, because of their importance in diverse fields such as nanotechnology, material science, and catalysis.[1] Despite all those efforts some features of small TM clusters, as the equilibrium geometry at some cluster sizes, are still a matter of debate.

Two of the most recent and systematic studies of Mo clusters are the works of Zhang et al.[2] (ZH) and Aguilera-Granja and co-workers[3] (AG). The first work presents results for Mo clusters from the dimer up to Mo_{55} obtained with density functional theory (DFT) using a plane-wave basis set and a valence space that includes the $4d^5\ 5s^1$ electrons only. Interestingly, the authors also carried out some calculations including the $4p^6$ electrons in the valence space, but they claim that although the smaller core provides better results for the dimer, results for bulk Mo are more satisfactory when the larger core is used. Thus, the remaining clusters are studied using the larger core to represent inner electrons. AG performed periodic DFT calculations on small molybdenum clusters containing up to 13 atoms using a linear combination of pseudoatomic orbitals for the $4d^5\ 5s^1$ valence electrons. In that work no additional tests with a smaller core were accomplished. The most striking finding reported in those references is the tendency shown by the smaller clusters to form both linear and planar structures with alternate short and long bond lengths, the short ones being very similar to the bond length found in Mo_2. Such an alternation in bond lengths leads to a natural stabilization of structures with an even number of atoms, and in some cases, linear and planar structures are reported to be the ground state for given cluster sizes. ZH, for example, found that the ground state of Mo_4 is a parallelogram, but a linear isomer formed by two dimers separated by a distance of 3.18 Å is reported to be relatively close in energy. AG, on the other hand, found that both Mo_3 and Mo_4 are characterized by linear ground states with a clear tendency to form short bonds, whereas planar ground states are reported for Mo_5, Mo_6, and Mo_7, in which the tendency to form dimers is also exhibited. More surprising, the authors report stable, planar isomers for Mo_8, Mo_9, and Mo_{10} that compete in energy with the most stable 3D isomers for that cluster sizes.

More recently, Min studied small Mo clusters from the dimer to the octamer by means of periodic DFT calculations using a projector augmented wave pseudopotential and a $4d^5\ 5s^1$ valence configuration.[4] The 4s and 4p subshells were considered as semicore states. The author shows that the inclusion of semicore states reduces considerably the tendency to form dimers, and as a consequence, the even−odd alternation in the atomization energy is almost nonexistent. Such an alternation was not observed in a previous work of one of us in which nonperiodic DFT calculations using the frozen-

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core approximation were utilized to study Mo clusters up to the tetramer.[5]

To shed light on the apparent tendency to form dimers observed in small molybdenum clusters, a systematic study on Mo_n clusters, with n = 3−10, is accomplished in the present work using tools from the gradient-corrected DFT and a small-core pseudopotential to represent 28 inner electrons. Moreover, the linear and planar ground states reported by AG are revised using the present calculation method to verify whether the dimerization tendency and the even−odd alternation persist when a small-core pseudopotential is used.

COMPUTATIONAL DETAILS

The geometric structures of Mo_n clusters, with n = 3−10, are studied using the exchange−correlation density functional due to Perdew, Burke, and Ernzerhof (PBE)[6] within the context of the generalized gradient approximation to the density functional theory.[7−9] A variety of 2D and 3D starting geometries are used for geometry optimization. They are described in detail in the next section for every cluster size. No symmetry constraints are imposed during optimization, which is considered complete when the maximum element of the gradient vector of the total electronic energy with respect to the atomic coordinates falls below a threshold of 3×10^{-4} atomic units. In addition, the total electronic energy is also minimized with respect to the electron spin multiplicity, which is kept fixed during a given geometry optimization. When geometric structures become optimized the Hessian matrix of the total electronic energy with respect to the atomic coordinates is constructed and diagonalized. This way the eigenvalues of the Hessian matrix are used to check whether the geometry found is a local minimum on the potential energy surface of the given cluster. When one or more negative eigenvalues of the Hessian matrix are found, the corresponding eigenvectors are utilized to distort the previously optimized geometry to obtain a new starting geometry, which is then reoptimized. The procedure is repeated until a local minimum is found.

The Def2-TZVP basis set is used for the $4s^2\ 4p^6\ 4d^5\ 5s^1$ valence electrons,[10] whereas a pseudopotential is utilized to mimic the effect of 28 inner electrons.[11] It is important to stress that the choice of the PBE exchange−correlation density functional is due to the fact that both AG and Min utilize the same functional in their works. Moreover, ZH use the PW91 exchange−correlation density functional,[12] which is a relative of PBE in which more boundary conditions are satisfied. In this way, the quality of the pseudopotential is the only variable when the four works are compared.

To accelerate the calculations, the resolution of identity is exploited in the RI-J version using an auxiliary basis set to fit the electron density during the calculation of the Coulomb repulsion.[13] All calculations are accomplished with the ORCA program.[14]

The atomization energies reported in this work are calculated as follows

$$E_{at}(Mo_n) = \frac{n \times E(Mo) - E(Mo_n)}{n} \quad (1)$$

where $E(Mo_n)$ is the total electronic energy of the cluster with n atoms and $E(Mo)$ is the total electronic energy of the molybdenum atom in its ^7S ground state.

RESULTS AND DISCUSSION

Mo_n Clusters, with n = 3−10. Mo_2 is studied mainly to validate the methodology used throughout the present work. Table 1 compares the most recent theoretical results for the molybdenum dimer with experimental values. It can be seen from the table that atomization energies are much better described by those methods that use a large core to represent inner electrons. However, equilibrium distances obtained with those methods are consistently shorter than experimental values. On the other hand, small-core methods provide equilibrium distances which are in excellent agreement with experimental measures. Nevertheless, atomization energies are underestimated in those cases. It is then expected that both good geometries and underestimated atomization energies will be obtained with the present methodology.

Table 1. Atomization Energies (E_{at}, in eV/at) and Equilibrium Bond Lengths (R_e, in Angstroms) for Mo_2[a]

	E_{at}	R_e
Zhang et al.[2]	2.54	1.80
Aguilera-Granja et al.[3]	2.23	1.65
Min[4]	1.89	1.94
this work	1.95	1.93
experimental[15]	2.06 ± 0.38	1.93
experimental[16]		1.94
experimental[17]	2.24 ± 0.01	

[a]All calculated states are singlet electronic states.

Three starting geometries are constructed for the trimer, namely, the equilateral triangle, an acute triangle, and an obtuse triangle. No linear geometries are explored as possible conformations for Mo_3. The Mo_3 GS (GS) was found to be characterized by a triplet electronic state and an acute triangular geometry with an atomization energy of 2.11 eV/at. An equilateral triangle with the same multiplicity and with almost the same atomization energy as the GS was also found. Table 2 lists the relevant properties of Mo_3 found in the present work and their comparison with the values reported by other authors. Figure 1 shows the equilibrium geometries of the stable isomers of Mo_3 found in this work. Both ZH and Min also found an acute triangle to be the GS for Mo_3. Also, a linear structure is reported to be a stable isomer in ref 2, being 290 meV/at above the triangular GS and exhibiting a short bond length of 1.80 Å and a longer one of 2.92 Å. AG, on the other hand, found a linear structure to be the GS for the molybdenum trimer with a short bond length of 1.61 Å and a long bond length of 2.89 Å.

Both 2D and 3D starting geometries are constructed in the case of Mo_4. In particular, a square geometry and a rhombic geometry were constructed as 2D models, whereas a tetrahedron and a rhombus that is slightly out of plane were used as models for 3D structures. It is shown in Table 2 that the GS was found to be the out-of-plane rhombus, characterized by a singlet electronic state and an atomization energy of 2.66 eV/at. A strongly distorted tetrahedron, also characterized by a singlet electronic state, was found 50 meV/at above the GS. See Figure 1 for the equilibrium geometries of the stable Mo_4 isomers found in this work. Min reports a planar, distorted square structure with bond lengths of about 2.20 Å to be the GS of Mo_4. AG reported the GS of Mo_4 to be a linear tetramer with two short bond lengths of 1.59 Å and a long one of 2.95 Å. ZH report a parallelogram as the GS of the molybdenum tetramer with two short bond lengths of 1.83 Å.

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Table 2. Atomization Energies (E_{at}, in eV/at), Electronic Spin Multiplicity ($M = 2S + 1$), and Equilibrium Bond Lengths (R_e, in Angstroms, the shorter bond length, longer bond length, and average bond length, respectively, are indicated) for the Stable Mo_n, with $n = 3-10$, Isomers Found in the Present Work[a]

isomer	E_{at}	M	R_e	isomer	E_{at}	M	R_e
3−1	2.11	3	2.165, 2.413, 2.250	7−1	3.42	1	2.342, 2.796, 2.485
3−2	2.11	3	2.218, 2.219, 2.218	7−2	3.41	3	2.241, 2.882, 2.541
ZH[b]	2.25	3	2.04, 2.34, 2.14	7−3	3.41	1	2.248, 2.953, 2.546
AG[c]	1.96	7	1.61, 2.89, 2.25	7−4	3.40	5	2.321, 2.941, 2.545
Min[d]	2.08	3	2.17, 2.42, 2.25	ZH[b]	3.30	3	2.00, 3.24, 2.56
4−1	2.66	1	2.224, 2.993, 2.480	AG[c]	2.95	3	1.71, 2.91, 2.49
4−2	2.61	1	2.074, 2.668, 2.469	Min[d]	3.37	1	2.34, 2.80, 2.48
ZH[b]	2.84	1	1.83, 3.09, 2.52	8−1	3.55	5	2.282, 2.918, 2.561
AG[c]	2.71	1	1.59, 2.95, 2.04	8−2	3.54	3	2.329, 2.939, 2.549
Min[d]	2.61	1	2.17, 2.42, 2.25	8−3	3.53	1	2.405, 2.868, 2.559
5−1	2.96	1	2.251, 2.843, 2.488	8−4	3.53	3	2.295, 2.750, 2.507
5−2	2.93	3	2.269, 2.866, 2.482	ZH[b]	3.39	1	2.02, 2.88, 2.54
5−3	2.93	1	2.324, 2.811, 2.486	AG[c]	3.31	1	1.62, 3.03, 2.68
ZH[b]	2.84	1	2.26, 2.77, 2.43	Min[d]	3.41	1	2.21, 2.86, 2.56
AG[c]	2.50	5	1.68, 2.88, 2.50	9−1	3.66	1	2.393, 2.984, 2.549
Min[d]	2.92	1	2.25, 2.84, 2.49	9−2	3.60	1	2.153, 2.871, 2.563
6−1	3.29	1	2.194, 2.798, 2.509	ZH[b]	3.50	3	2.34, 2.73, 2.48
6−2	3.25	3	2.292, 2.797, 2.506	AG[c]	3.19	3	1.63, 3.15, 2.68
6−3	3.25	3	2.261, 2.929, 2.520	10−1	3.73	3	2.224, 2.853, 2.548
ZH[b]	3.16	1	1.86, 2.97, 2.57	10−2	3.71	1	2.201, 2.910, 2.545
AG[c]	2.99	1	1.62, 2.94, 2.28	10−3	3.71	3	2.312, 2.910, 2.561
Min[d]	3.25	1	2.19, 2.79, 2.59	ZH[b]	3.59	9	2.31, 2.85, 2.55
				AG[c]	3.40	1	1.62, 3.31, 2.72

[a]Lower-lying excited states up to 60 meV/at above the ground state are also shown. See Figure 1 for labels. Results obtained by other authors are also shown for comparison. [b]Reference 2. [c]Reference 3. [d]Reference 4.

The authors also show a distorted tetrahedron with two short bond lengths of 1.86 Å and four longer ones at about 10 meV/at above the GS.

In the case of the pentamer, the starting geometries are the pentagon, the trigonal bipyramid, the square pyramid, and a derivative of the tetramer GS in which the fifth Mo atom is located on top of the out-of-plane rhombus. Interestingly, the GS is found to be a distorted version of the capped out-of-plane rhombus characterized by a singlet electronic state, bond lengths in a range from 2.25 to 2.84 Å, and an atomization energy of 2.96 eV/at, see Table 2 and Figure 1. Another distorted, capped out-of-plane rhombus characterized by a triplet electronic state and a trigonal bipyramid showing a singlet electronic state were found to lie about 30 meV/at above the GS. Min found a GS structure that is remarkably similar to the one found in the present work, with almost identical bond distances and an atomization energy of 2.92 eV/at. AG report a deformed pentagon with two short bond lengths of 1.68 Å to be the GS of Mo_5. A 3D isomer with two short bond lengths is also reported by those authors to lie about 70 meV/at above the GS. Interestingly, ZH report a trigonal bipyramid without short bond lengths to be the GS of the pentamer. Another 3D isomer with two short bond lengths was found by those authors lying only 20 meV/at above the GS.

Starting geometries for Mo_6 are the hexagon, the octahedron, and the pentagonal pyramid. As can be seen from Table 2 the GS of the hexamer was found to be a singlet electronic state in a slightly deformed octahedral geometry with an average bond length of 2.51 Å and an E_{at} of 3.29 eV/at, see also Figure 1. Two quasi-degenerate distorted octahedra characterized by a triplet electronic state are found to be only 40 meV/at above the GS. Min reports a very similar distorted octahedron as the GS of Mo_6. ZH find a sort of capped trigonal bipyramid with three short bond lengths to be the GS of the hexamer. Moreover, those authors also found a 2D isomer formed by two parallelograms sharing an edge that is only 80 meV/at above the GS. AG report a planar structure with three short bond lengths of about 1.70 Å as the GS of Mo_6. Another 3D isomer with three short bond lengths was found by those authors at about 70 meV/at above the GS.

For Mo_7 the starting geometries are the heptagon, the pentagonal bipyramid, a face-capped octahedron, and a buckled version of the previous structure. Table 2 shows that the GS is found to be a distorted face-capped octahedron with an average bond length of 2.53 Å an E_{at} of 3.42 eV/at and characterized by a singlet electronic state. Three distorted pentagonal bipyramid isomers lie between 10 and 20 meV/at above the GS and present singlet, triplet, and quintet electronic states, respectively. Their geometries are shown in Figure 1. The GS reported by Min for Mo_7 is again very similar to the one found in the present work. AG found a 2D isomer with three short bond lengths to be the GS of the molybdenum heptamer and a 3D structure also with three short bond lengths at about 100 meV/at above the 2D isomer. The GS found by ZH for the heptamer is a face-capped octahedron with two short bond lengths. The authors also reported another 3D isomer with three short bond lengths which lies only 70 meV/at above the GS.

A variety of 2D and 3D starting geometries were constructed for Mo_8. In the case of the 2D structures, the starting geometries are the octagon, a heptagon with the eighth atom at the center, and two opposite linear segments formed by four atoms giving place to a sort of *ladder*. Initial 3D structures include the cube, a cube that undergoes a sort of monoclinic

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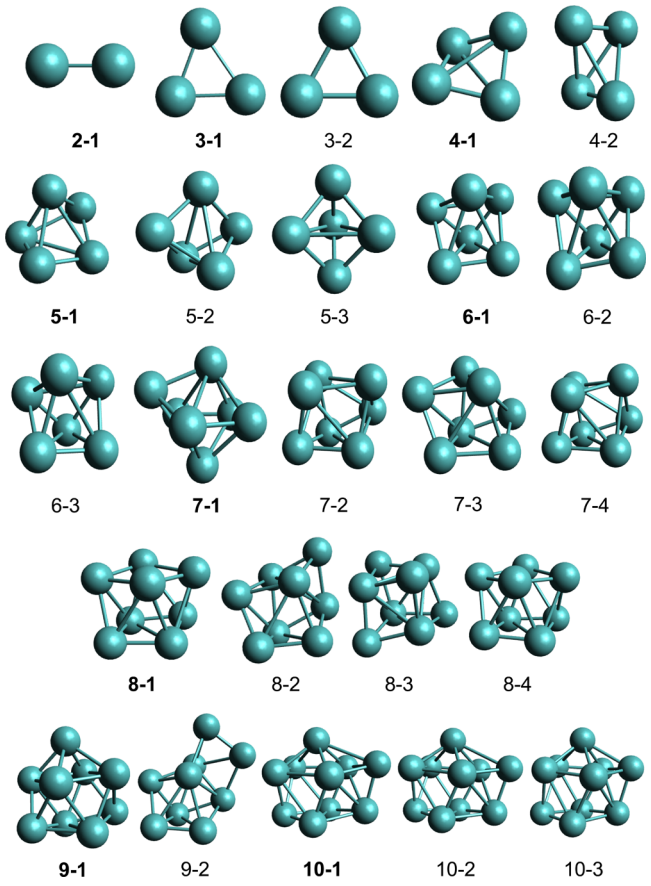

Figure 1. Equilibrium geometries of the stable Mo_n, n = 3−10, isomers found in the present work. Lower lying excited isomers up to 60 meV/at above the ground state are also shown.

distortion, and a series of bicapped octahedra in which the two capping atoms are located at the center of different faces. The GS becomes an octahedron in which the two capping atoms are located at two adjacent faces with an E_{at} of 3.55 eV/at and characterized by a quintet electronic state, see Table 2 and Figure 1. Three isomers were found to lie between 10 and 20 meV/at above the GS. Two of them are strongly distorted cubes characterized by a singlet electronic state and a triplet electronic state, respectively, whereas the third isomer is similar in geometry to the GS but exhibits a triplet electronic state. Interestingly, Min reports for the GS an equilibrium geometry very similar to the one found in the present work but characterized by a singlet electronic state instead of the quintet one mentioned above. ZH also found a bicapped octahedron to be the GS of Mo_8 characterized by a singlet electronic state and four short bond lengths. Furthermore, the authors found two other isomers lying only 20 meV/at above the GS and without short bond lengths. AG report a very distorted bicapped octahedron as the GS for the octamer, also characterized by a singlet electronic state and four short bond lengths.

Two 2D starting structures are considered for the study of Mo_9, namely, the regular nonagon and an octagon with the ninth atom at the center of the structure. On the other hand, the 3D starting geometries include a variety of bicapped pentagonal bipyramids, a capped cube and a buckled version of it, a cube with the ninth atom in its center, and a nonamer formed by a pentagon located on top of a square. The resulting GS was found to be a distorted bicapped pentagonal bipyramid with an average bond distance of 2.55 Å and an atomization energy of 3.66 eV/at as can be observed in Table 2 and Figure 1. Another bicapped pentagonal bipyramid is found to be only 60 meV/at above the GS. Both isomers are characterized by a singlet electronic state. ZH indicate that the GS of Mo_9 is a derivative of two twisted squares and shows a triplet electronic state. No reference to the presence of short bond lengths in that isomer is made by the authors. AG report a GS for the molybdenum nonamer, which is very similar to the one found in the present work. That structure is characterized by a triplet electronic state and exhibits three short bond lengths. Those authors also found a stable 2D isomer about 60 meV/at above the GS and with four short bond lenghts.

Finally, several starting structures were constructed for Mo_{10}. 2D structures include the regular decagon and a nonagon in which the 10th atom is located at its center. For the 3D case, starting structures comprise two square pyramids connected by their bases and a buckled version of it, two pentagons one atop the other and a distorted version of it, and a hexagon with the seventh atom located at its center and an equilateral triangle on top of it. According to results shown in Table 2 the GS corresponds to the buckled version of the two square pyramids connected by their bases with an average bond length of 2.60 Å and an E_{at} of 3.73 eV/at. That GS is characterized by a triplet electronic state. Two other isomers are found to lie 20 meV/at above the GS. They exhibit a geometry very similar to the one presented by the GS and are characterized by a singlet electronic state and a triplet electronic state, respectively, see Figure 1. AG report a singlet electronic state with five short bond lengths as the GS. Interestingly, a structure very similar to the GS found in the present work is mentioned by those authors to be about 300 meV/at above in energy with respect to the GS. ZH, on the other hand, found a GS for Mo_{10} with the same structure as the one reported in the present work. The electronic state of that GS, however, is characterized by eight unpaired electrons.

The atomization energies of the GS found in the present work for Mo_n, with n = 3−10, are shown in Figure 2 and are compared with the corresponding energies reported by ZH, AG, and Min, respectively. The zigzag behavior presented by the atomization energies obtained by AG and, to a lesser extent, by ZH are evident from the figure. That behavior clearly favors those aggregates with an even number of atoms due to the dimerization tendency found by those authors. On the other hand, the present results are very similar to the ones reported by Min. It is important to recall that the investigations made by ZH and AG involve pseudopotentials that include $4d^5$ $5s^1$ electrons only. Min, on the other hand, considered the 4s and 4p subshells as semicore states, whereas the present calculations include those subshells explicitly into the valence space. These facts seem to suggest that the inclusion of 4s and 4p subshells either as semicore states or as valence states is extremely important to describe adequately the geometric features of small molybdenum clusters. The next subsection shows a deeper study on the dimerization tendency reported by ZH and AG.

Dimerization Tendency Revisited. According to present results, the dimerization tendency shown by the smaller molybdenum clusters and reported both by ZH and by AG seems to be an artifact caused by the use of large pseudopotentials to mimic inner electrons. To shed light on the effect of pseudopotential size on the structural features of small molybdenum clusters the geometries of Mo_2−Mo_7 found

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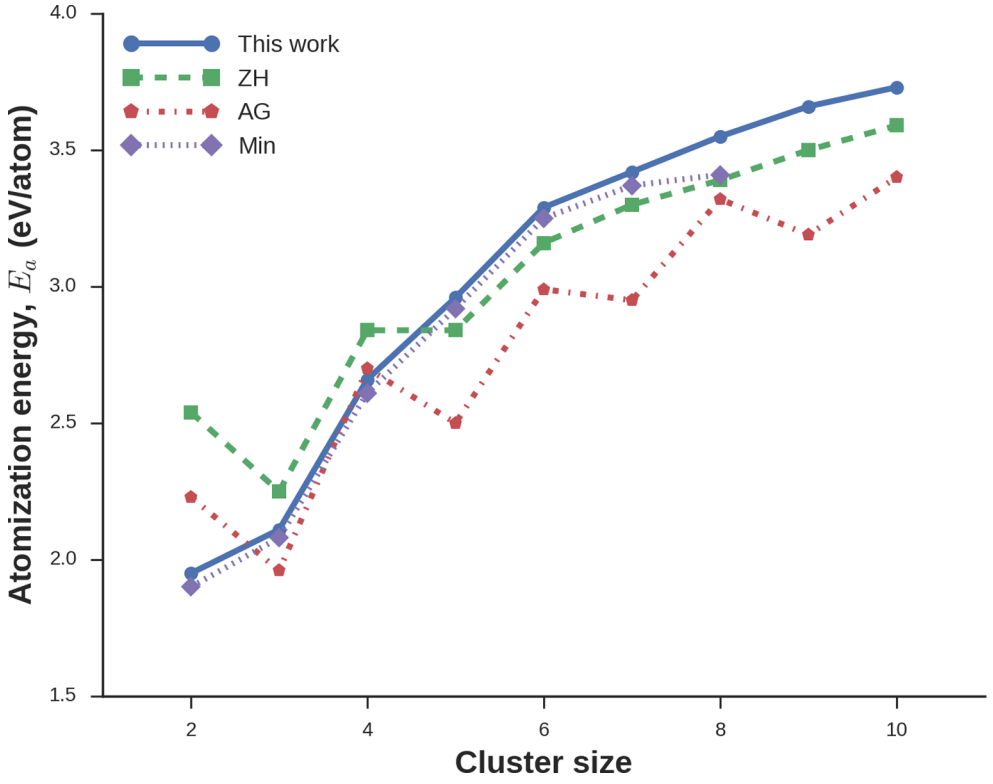

Figure 2. Atomization energy of the ground states of Mo_n clusters, with n = 2−10, found in the present work. Results obtained by other authors are also shown. See text for labels.

by AG are reoptimized using the present methodology. The electron spin multiplicity, however, is kept fixed to the value informed by AG. The result of reoptimizations is summarized in Figure 3.

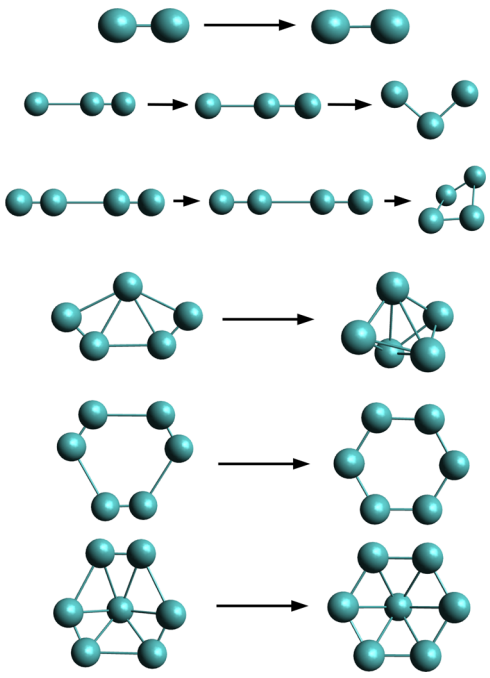

Figure 3. Dimerization tendency exhibited by Mo_n clusters, with n = 2−7, revisited with the present methodology. Original clusters are on the left side; reoptimized aggregates are on the right side. See text for those cases in which three structures are shown.

For Mo_2 the bond length increases from the original value of 1.65 to 1.93 Å, whereas the final atomization energy becomes 1.95 eV/at.

For Mo_3 the linear isomer reported by AG with a short bond of 1.61 Å and a longer one of 2.89 Å remains linear after optimization with bond lengths of 1.98 and 2.82 Å and an E_{at} of 1.62 eV/at. Nevertheless, that linear isomer becomes a saddle point on the potential energy surface on the trimer since the Hessian matrix of the total electronic energy with respect to the atomic coordinates exhibits a negative eigenvalue. The eigenvector of the negative eigenvalue is used as a perturbation to the geometry, which after reoptimization leads to a triangular structure with two bond lengths of 2.195 Å, an angle of 96.6°, and an E_{at} of 1.94 eV/at.

In the case of Mo_4, the lowest energy isomer found by AG is a linear structure with 2 short bond lengths of 1.59 Å and a longer one of 2.95 Å. After optimization with the present methodology the isomer remains linear with two short bond lengths of 1.92 Å and a longer one of 3.19 Å. This structure, however, is a saddlepoint on the potential energy surface of the tetramer according to a negative eigenvalue found after diagonalizing the Hessian matrix. Using the eigenvector of that eigenvalue to reoptimize the geometry, a slightly 3D rhombus is obtained with two bond lengths of 2.03 Å and two others of 2.64 Å. One atom is located 25.5° above the plane formed by the other three atoms, and the atomization energy of the isomer is 2.47 eV/at.

The planar pentamer reported by AG presents two short bond lengths of 1.68 Å and five long bond lengths of 2.88 Å. After reoptimization, a stable, distorted triangular bipyramid with bonds lengths within the range from 2.30 to 2.86 Å and an E_{at} of 2.85 eV/at is found.

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AG reported a deformed hexagon with three short bond lengths of 1.67 Å and three longer ones of around 2.97 Å. Reoptimization leads to a regular hexagon with a bond length of 2.18 Å and an E_{at} 2.75 eV/at.

Finally, the lowest energy structure reported by AG for Mo_7 is a distorted hexagon with the seventh atom in the center of the figure and 35° above the plane. The isomer presents three short bond lengths of 1.76 Å and longer ones of about 2.90 Å. After reoptimization a regular hexagon with the seventh atom located 36° above the plane and bond lengths in the range from 2.20 to 2.69 Å is obtained. The atomization energy of reoptimized Mo_7 is 3.05 eV/at.

In summary, the dimerization tendency found in small molybdenum clusters up to Mo_7 when large core pseudopotentials are used is no longer observed when small core pseudopotentials are utilized. Short bond lengths increase notoriously, and the range of bond distances narrows down. Moreover, 3D structures are favored over linear and planar structures. It is important to emphasize that atomization energies of reoptimized isomers are considerably smaller than the atomization energies found in the present work and reported in the preceding subsection. This finding could be probably due to the fact that the present geometry optimizations were accomplished keeping the electronic multiplicity fixed at the value reported by AG. These results indicate that 4s and 4p electrons play a significant role in bond formation and, consequently, in the shape of small molybdenum clusters.

CONCLUSIONS

The geometric, electronic, and magnetic properties of Mo_n clusters, with n = 3−10, were investigated using gradient-corrected DFT. A small core pseudopotential was used to mimic inner electrons, whereas the 4s, 4p, 4d, and 5s valence atomic orbitals were described by a triple-ζ basis set.

The geometries of the more stable clusters for every size are distorted versions of the most familiar structures adopted by transition metal aggregates. The average interatomic distance shows a smooth enlargement from 2.25 Å in the trimer to 2.55 Å in the Mo_{10}. Atomization energies show a monotonic increase from 2.11 to 3.73 eV/at. The electronic states are characterized in most cases by singlet electronic states. Only Mo_3 and Mo_{10} exhibit a triplet electronic state, whereas Mo_8 shows a quintet electronic state. For all sizes several isomers were found to lie up to 60 meV/at above the corresponding ground state, indicating the complexity of the potential energy surfaces. Mo_8 and Mo_{10}, for example, exhibit singlet electronic states lying only 20 meV/at above the corresponding ground states.

The apparent trend to dimerize observed by some authors in small molybdenum clusters was carefully analyzed using the present methodology. It is shown that the dimerization tendency disappears when a small core pseudopotential is used instead of a large core one. In all cases under study, an important geometrical distortion is undergone by the original clusters leading to new equilibrium geometries in which alternate short and long bond lengths are completely absent. It is then concluded that using small core pseudopotentials is essential to obtain realistic geometries for molydenum clusters.

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