Theoretical study of small Mo clusters and molecular nitrogen adsorption on Mo clusters*

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This paper studies the small molybdenum clusters of Mo_n (n=2–8) and their adsorption of N_2 molecule by using the density functional theory (DFT) with the generalized gradient approximation. The optimized structures of Mo_n clusters show the onset of a structural transition from a close-packed structure towards a body-centred cubic structure occurred at $n = 7$. An analysis of adsorption energies suggests that the Mo_2 is of high inertness and Mo_6 cluster is of high activity against the adsorption of N_2. Calculated results indicate that the N_2 molecule prefers end-on mode by forming a linear or quasi-linear structure Mo–N–N, and the adsorption of nitrogen on molybdenum clusters is molecular adsorption with slightly elongated N–N bond. The electron density of highest occupied molecular orbital and lowest unoccupied molecular orbital, and the partial density of states of representative cluster are also used to characterize the adsorption properties of N_2 on the sized Mo_n clusters.

Keywords: density functional theory, molybdenum clusters, adsorption property, N_2 molecule

PACC: 7115M, 3640B, 6845B

1. Introduction

Many kinds of atomic clusters of transition metals have been theoretically and experimentally studied, mainly because of their potential applications as building blocks for functional nanostructure materials, electronic devices, and nanocatalysts.[1,2] In particular, the good catalytic properties to various reactions were found, such as the oxidation of CO and reduction of NO.[3] As one of the key factors to understanding the catalytic mechanism, adsorption behaviours of gas molecules on metal clusters have been studied widely both theoretically and experimentally.[4−15] It was found that the adsorption properties changed strongly with increasing cluster size for many systems, such as H_2 on Fe[4] clusters, O_2 on Au clusters,[7] N_2 on W anion clusters,[11] and so on. The comparative studies for the gas molecules adsorption on metal clusters can be expected to provide information to gain a basic understanding of catalytic process and play an important role for unveiling molecular-level mechanisms of various catalytic reactions on nanomaterials.

Molybdenum atom, a typical 5d transition metal, has a special electronic configuration of $4d^55s^1$, in which d shell and s shell are all half-filled. Pis Diez[16] studied small molybdenum clusters up to the tetramer within the framework of density functional theory (DFT), he found that the Mo_2 with equilibrium bond distances of 0.197 nm characterized $^1\Sigma_g^+$ electronic state, the Mo_3 and Mo_4 corresponding to obtuse triangle (C_{2v}) and the distorted tetrahedron (D_{2d}) structures were $^3A_1$ and $^1A_1$ electronic states respectively. Min *et al.*[17] suggested that the onset of structural transition from a close-packed structure towards a body-centered cubic (bcc) structure appears at Mo_6 and Mo_8. Zhang *et al.*[18] indicated that the linear and planar molybdenum clusters have a strong tendency to form dimers and exhibit significant nonmetallic characteristics. Aguilera-Granja *et al.*[19] reported that all Mo_N (N=2–13) clusters have a strong tendency to form dimers, and the binding energies of pure molybdenum clusters exhibit an odd–even effect in all dimensionalities. The N_2 molecule is not only the main and aimed product of the reduction of nitrogen oxides, but also the most important component in atmosphere. The desorption and adsorption of N_2 molecules on the surfaces of various metal are generally thought to be quite important for understanding the mechanism of the reaction with the surfaces of metal. Therefore, the geometric and electronic

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structures of adsorbed N_2 molecules on various metal surfaces have been extensively examined for a long time.[9,13−15] Experimental studies by a fast-flow reactor equipped with a laser vaporization cluster source and laser ionization time-of-flight mass spectrometer give structural transitions occurred in molybdenum clusters in the size range 13–20 metal atoms, and cluster reaction products have nitrogen bound in both atomic and molecular forms.[14] From theoretical side, using DFT Attila *et al.* reported, however, an observation that the N_2 is dissociative on molybdenum clusters with partially broken (0.12–0.14 nm) and fully broken (0.27 nm) N–N bonds.[9]

From these studies we can see that the microscopic features of geometric and electronic structures of molybdenum clusters and their adsorption of N_2 molecule are still an issue, particularly with respect to the structural transition size range in molybdenum clusters and adsorption pattern of N_2 molecule (such as molecular adsorption or dissociative chemisorption). Moreover, it is very important to confirm the adsorption pattern for the understanding of the catalytic process, so further theoretical studies are still necessary. In this paper, we will perform a systematic study on the adsorption properties of N_2 molecule on Mo_n (n=2–8) clusters. We hope that this study can help people understand the small molybdenum clusters and catalytic mechanism better. In the following section we will present the computational details. Our results and discussion are presented in Section 3. Finally, the summary of our findings and conclusions are given in Section 4.

2. Computational details

Fully geometric optimizations and electronic structure calculations were performed by using the spin polarized DFT implemented in the Dmol3 package.[20] As we know, the reactions between molybdenum clusters and N_2 molecule may yield a large variety of geometrical structures, and each structure may exist in various spin states. So, in order to obtain the global lowest energy structures of Mo_nN_2 clusters, first a considerable amount of possible isomers of pure Mo_n clusters were considered as initial candidates and optimized at different spin multiplicities, and then N_2 molecule adsorbing at all possible sites of bare Mo_n clusters with the lowest-energy structures is taken into account. Here, each system with different spin multiplicities was treated.

In the geometrical optimizations, the exchange–correlation interaction was treated within the generalized gradient approximation (GGA) using the PW91 functional.[21] The converge threshold were set to 2.0×10^{-5} for energy change, 0.04 Hartree/nm for the forces and 5.0×10^{-4} nm for the displacement. In the electronic structure calculations, the double numerical basis set including d-polarization function (DND) was utilized to describe the valence electrons and the core electrons were described with effective core potential. Self-consistent field calculations were done with a convergence criterion of 10^{-5} Hartree on the total energy. The density mixing criterion for charge and spin were 0.02 and 0.05, respectively. The Direct Inversion in an Iterative Subspace (DIIS) approach was used to speed up SCF convergence. A 5.0×10^{-4}-Hartree of smearing was applied to the orbital occupation. For the accurate calculations, we chose an octupole scheme in the multipolar expansion of the charge density and Coulomb potential. A global orbital cutoff of 0.44 nm was used. The charge density and the magnetic moments were evaluated via the Mulliken population analysis.[22] All the geometrical structures were optimized without any symmetry constraint and using spin unrestricted.

To check the reliability of the methods and basis sets used in our calculations, the bond lengths (R_e/nm) and the vibration frequencies (ω/cm^{-1}) of MoN dimer, Mo_2 and N_2 molecules were calculated, as listed in Table 1. It is obvious that our calculated results are in good agreement with the reported values from experiments.[23−26]

Table 1. The calculated results and experimental values of bond lengths and vibration frequencies of MoN, Mo_2 and N_2.

		MoN	Mo_2	N_2
R_e/nm	this work	0.1641	0.198	0.1107
	experiment	0.1636[23]	0.194[24]	0.1098[26]
ω/cm^{-1}	this work	1105	523	2355
	experiment	1075±30[25]	477[24]	2358[26]

3. Results and discussion

3.1. The properties of Mo_n (n=2–8) clusters

Before discussing the reaction products of Mo_nN_2 clusters, we first describe the bare molybdenum clusters. The optimized lowest-energy structures of molybdenum molecules are shown in Fig. 1, where the main bond lengths are also labeled. As can be seen from Fig. 1, for Mo_2 dimer, our calculated distance of 0.198 nm between the Mo atoms is in the range of other theoretical results (0.163–0.198 nm),[16−18,27−32] but is slightly larger than those of experimental values (0.193–0.194 nm).[24,33,34] For Mo_3, the ground-state structure features equilateral triangle with bond length 0.229 nm, which can be built up by adding one edge-capped atom on Mo_2 molecule. This ground-state structure accords with the result in Ref. [16], but does not accord with the ground-state structure obtained by Min *et al.*,[17] Zhang *et al.*[18] and Aguilera-Granja *et al.*[19] respectively, in which the ground-state structure characterized the isosceles triangle feature. Our calculations show that such a ground-state structure having isosceles triangle (not shown in Fig. 1) is higher by 0.333 eV than the ground-state equilateral triangle structure. For $n = 4$ and 5, the ground-state structures are the distorted tetrahedron and the trigonal bipyramidal structure respectively. We have optimized three stable Mo_4 structures: the distorted tetrahedral geometry, the linear structure and the plane structure (not shown in Fig. 1), one-dimensional (1D) linear structure and two-dimensional (2D) plane structure are 0.301 eV and 2.081 eV higher in energy than that of 3D distorted tetrahedron, which is the same result as that in Refs. [18] and [19]. Four stable Mo_5 structures have been considered: the linear structure, the toothed structure, the pentagonal structure (not shown in Fig. 1) and the trigonal bipyramid structure. Our calculations show that the trigonal bipyramid structure is the lowest-energy structure, which agrees with that in Refs. [17] and [18]. Generally, the high symmetrical polyhedrons such as the octahedron O_h are expected to be the ground state of many TM clusters. For the Mo_6 cluster, our calculations show that an octahedral structure with high symmetry O_h is the lowest-energy geometry, which consists with the result in Ref. [17]. In the case of Mo_7, we found that the ground-state is the pseudo pentagonal bipyramid C_s (see Fig. 1), which can be taken as the onset of a structural transition from a close-packed structure towards a bcc structure. As for $n = 8$, we find that the distorted square-prism is an energetically favourable structure among optimized seven stable Mo_8 structures, this agrees with the result of Ref. [17], not the bicapped tetragonal bipyramid structure in Refs. [18] and [19]. The multiplicities, the symmetry, the HOMO (highest occupied molecular orbital)–LUMO (lowest unoccupied molecular orbital) gap, and the calculated electronic properties of the lowest-energy Mo_n clusters are all listed in Table 2. As seen in Table 2, the multiplicities of Mo_n clusters are all spin singlet states except for Mo_3 with spin triplet state. Namely, the total magnetic moments are quenched except for $n = 3$, which may relate to the electronic configuration of the isolated Mo atom ($4d^5 5s^1$). For the Mo_3 cluster, total magnetic moment is 2.0 μ_B, which accords with the value of 0.67 μ_B/atom reported in the previous literatures.[16,19]

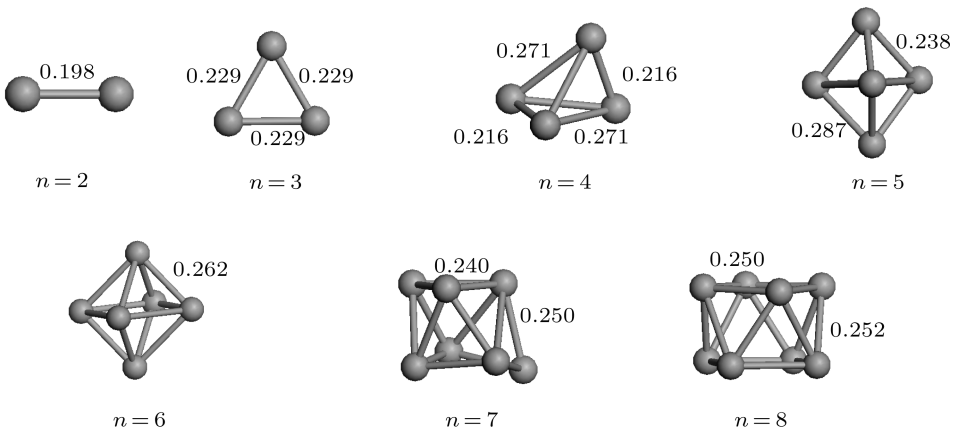


Fig. 1. The calculated lowest-energy structure of Mo_n clusters and main bond lengths (unit in nm).

To discuss the relative stabilities of Mo_n clusters, we have calculated the atomic averaged binding energy (E_b), the fragmentation energy $D(n, n-1)$, and the second-order difference of total energies ($\Delta_2 E_n$) for the lowest-energy structures of the Mo_n clusters by using the following formulas:

$$E_b(Mo_n) = [E(Mo_n) - nE(Mo)]/n,$$
$$D(n, n-1) = E(Mo_{n-1}) + E(Mo) - E(Mo_n),$$
$$\Delta_2 E_n = E(Mo_{n+1}) + E(Mo_{n-1}) - 2E(Mo_n),$$

where $E(Mo)$ represents the atomic energy of Mo, $E(Mo_n)$, $E(Mo_{n-1})$ and $E(Mo_{n+1})$ represent the total energies of the ground-state of Mo_n, Mo_{n-1} and Mo_{n+1}, respectively. The calculated atomic averaged binding energy, fragmentation energy, and the second difference of total energies are plotted in Figs. 2(a)–2(c). As can be seen from Fig. 2(a), the atomic averaged binding energy of the Mo_n clusters increases monotonically with the increasing cluster size, indicating that the clusters can continuously gain energy during successively adding Mo atoms and the clusters become increasingly stabilized. In cluster physics, the fragmentation energies and the second-order difference of total energies are sensitive quantities to reflect the relative stability of clusters. Figure 2(b) and 2(c) show the size dependence of the fragmentation energies and the second-order difference of total energies. Local peak is found at $n = 5$ corresponding to the trigonal bipyramid structure in both curves, indicating that the Mo_5 cluster is more stable than its neighbouring clusters.

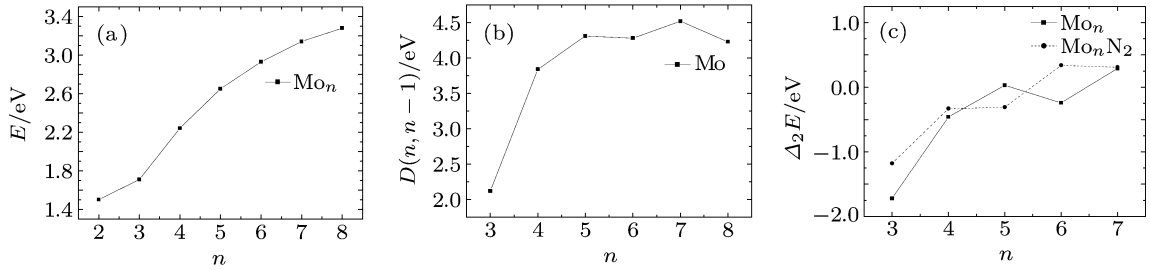


Fig. 2. The average binding energies $E_b(n)$ (a), the fragmentation energy $D(n, n-1)$ (b), the second-order difference of total energies $\Delta_2 E_n$ (c) of the lowest-energy Mo_n clusters.

The ionization potential and electron affinity, and the HOMO–LUMO gap are the most important quantities which can be used to signal the onset of metallic characteristics in the metal clusters. So we calculated the vertical ionization potential (VIP) and vertical electron affinity (VEA) of Mo_n clusters according to

$$VIP_n = E[Mo_n^+] - E[Mo_n],$$
$$VEA_n = E[Mo_n] - E[Mo_n^-],$$

where $E(Mo_n^+)$ and $E(Mo_n^-)$ represent the total energies of ionic clusters at the neutral optimized geometry. Figure 3(a) indicates that the VIP of small Mo clusters generally decreases as the cluster size increases and thus becomes easier to oxidize, and reaches a local maxima at $n = 5$. For the Mo_5 cluster, all electrons are paired, giving a closed shell electronic structure, so it is difficult to remove an electron from the Mo_5 cluster, again indicating that the Mo_5 cluster is more stable than other clusters. Figure 3(b) shows that the VEA values of the Mo_n clusters are generally small and increase with the increase of the number of Mo atoms except for $n = 4$ with a local minimum. It is interesting to point out that the large-sized clusters usually have smaller VIP and larger VEA in comparison with the small-sized clusters, implying that it is much more difficult to ionize the smaller clusters than the larger ones but much easier to attach an electron to the smaller clusters than to the larger ones.

The values of the HOMO–LUMO gap of the lowest-energy Mo_n clusters as a function of the cluster sizes are plotted in Fig. 4(a). Overall, the HOMO–LUMO gap oscillates with the cluster size and decreases to 0.36 eV at $n = 7$ and 0.37 eV at $n = 8$. The local peak is found at $n = 5$, implying that the Mo_5 cluster is more stable and has lower chemical reactivity than other clusters. The values of HOMO–LUMO gap for the lowest-energy Mo_n clusters (listed in Table 2) range from 0.36 eV to 1.90 eV, indicating that these clusters are of semiconducting feature. According to the above discussion, we can safely conclude that the Mo_5 cluster is a magic cluster.

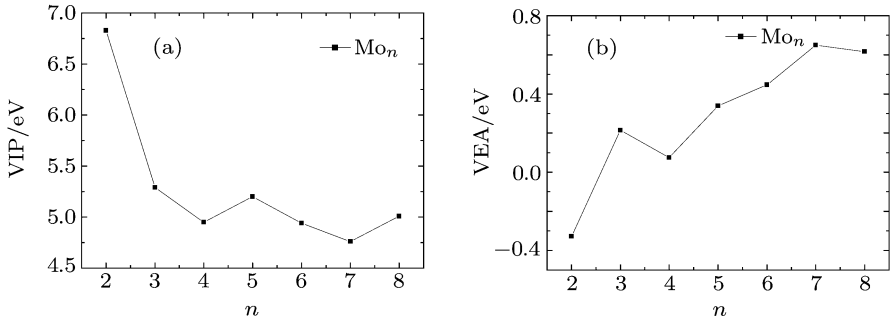


Fig. 3. Size dependence of VIP (a) and VEA (b) of the lowest-energy Mo_n clusters.

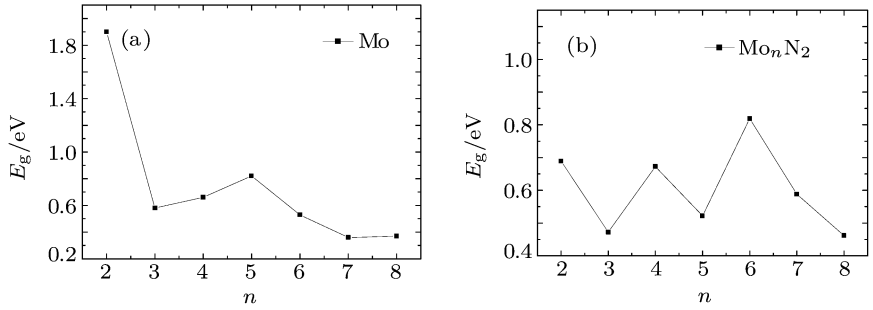


Fig. 4. The HOMO–LUMO gaps of Mo_n (a) and Mo_nN_2 (b) clusters.

Table 2. The calculation results for Mo_n clusters (in unit eV).

Mo_n	S	Sym.	gap	E_b	$\Delta_2 E$	VIP	VEA	$D(n, n-1)$
n=2	1	$D_{\infty h}$	1.90	1.50		6.38	–0.33	
$n=3$	3	D_{3h}	0.58	1.71	–1.72	5.29	0.22	2.12
$n=4$	1	D_{2d}	0.66	2.24	–0.46	4.95	0.07	3.84
$n=5$	1	D_{3h}	0.82	2.65	0.03	5.20	0.34	4.31
$n=6$	1	O_h	0.53	2.92	–0.24	4.94	0.45	4.28
$n=7$	1	C_s	0.36	3.15	0.29	4.76	0.65	4.52
$n=8$	1	D_{4d}	0.37	3.29		5.01	0.62	4.23

3.2. Adsorption of N_2 on the Mo_nN_2 (n=2–8) clusters

The main aim of our current work is to investigate nitrogen molecule adsorption on the small molybdenum clusters. We performed an exhaustive minimum energy structural search for N_2 molecule adsorption on the optimized bare Mo_n (n=2–8) clusters with the lowest-energy structures. The lowest-energy structures of Mo_nN_2 (n=2–8) clusters are displayed in Fig. 5, where the bent Mo–N–N angles, the N–N bond lengths and N–Mo bond lengths are also labeled. The coordination modes of the N_2 molecule on metal surface are adopted end-on and side-on.[12] As seen in Fig. 5, for all the Mo_nN_2 clusters, the N_2 molecule prefers end-on mode. We also find the N–N bond length of adsorbed N_2 molecule becomes slight larger (0.002–0.004 nm) than that of the calculated value 0.111 nm of free N_2 molecule. The distance of Mo–N bond is also elongated by 0.032–0.055 nm in comparison with the MoN dimer. Apparently from Fig. 5, the Mo–N–N structures are linear or quasi-linear. Additionally, it is clearly seen that the adsorption of nitrogen on the molybdenum clusters is the molecular adsorption with unbroken N–N bond, not the dissociative chemisorption,[9] which may result from different calculated methods. This result is incomplete in agreement with the experimental result,[14] which can be explained by the discrepancy of molybdenum cluster surfaces which is caused by different sizes. The calculated electronic and geometrical properties of the lowest-energy Mo_nN_2 clusters are all listed in Table 3. Table 3 shows that the multiplicities of Mo_nN_2 clusters are all spin singlet states. In other words, the total magnetic moments are quenched after adsorption N_2 molecule, which is due to the closed-shell electronic configuration.

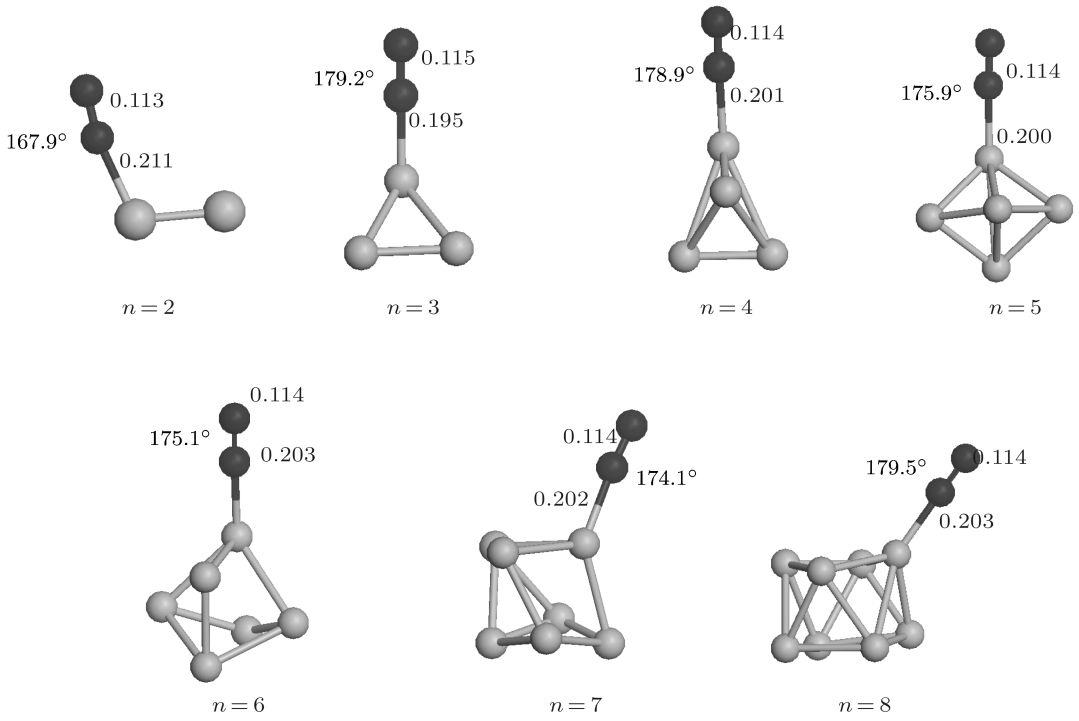


Fig. 5. The calculated lowest-energy structures of Mo_nN_2 clusters, the bond lengths (in unit nm) of N–N and N–Mo, and the Mo–N–N angles (in unit degree).

Based on the optimized geometries, the adsorption energies of N_2 molecule adsorption on neutral molybdenum clusters were calculated by using the following equation:

$$E_{\rm ad} = E(\mathrm{Mo}_n) + E(\mathrm{N}_2) - E(\mathrm{Mo}_n\mathrm{N}_2),$$

where $E(\mathrm{Mo}_n)$, $E(\mathrm{N}_2)$ and $E(\mathrm{Mo}_n\mathrm{N}_2)$ are the calculated lowest energies of the Mo_n clusters, N_2 molecule and $\mathrm{Mo}_n\mathrm{N}_2$ clusters, respectively. It is well known that the adsorption energies can be used to quantitatively describe the reactivity of N_2 molecule on the Mo_n clusters. The calculated adsorption energies ($E_{\rm ad}$) corresponding to the most energetically favourable adsorption site are shown in Fig. 6, which has a strong dependence on the clusters size and increases rapidly from 0.56 eV at $n = 2$ to 1.23 eV at $n = 3$, then increases slowly until 1.73 eV at $n = 6$. The curve attains the local maximum at $n = 6$, and then decreases to the lower value of 1.25 eV at $n = 8$. The present results show that the Mo_2 is of high inertness while Mo_6 cluster is of high activity with respect to the N_2 adsorption. In all the cases, our calculations show that all the molybdenum clusters can adsorb one N_2 molecule with the adsorption energies about 0.56–1.73 eV, by forming a linear or quasi-linear Mo–N–N structures.

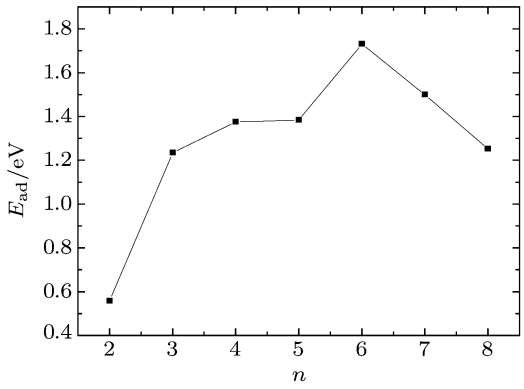


Fig. 6. The adsorption energy of N_2 on Mo_n as a function of the cluster size.

To further study the relative stability of clusters after adsorbing N_2 molecule, we have calculated the second-order difference of total energies for the lowest-energy $\mathrm{Mo}_n\mathrm{N}_2$ clusters defined by

$$\Delta_2 E_n = E(\mathrm{Mo}_{n-1}\mathrm{N}_2) + E(\mathrm{Mo}_{n+1}\mathrm{N}_2) - 2E(\mathrm{Mo}_n\mathrm{N}_2),$$

where $E(\mathrm{Mo}_{n-1}\mathrm{N}_2)$, $E(\mathrm{Mo}_{n+1}\mathrm{N}_2)$ and $E(\mathrm{Mo}_n\mathrm{N}_2)$ are the total energies of the ground-state of $\mathrm{Mo}_{n+1}\mathrm{N}_2$, $\mathrm{Mo}_{n-1}\mathrm{N}_2$ and $\mathrm{Mo}_n\mathrm{N}_2$ clusters, respectively. The second-order difference of total energies for the lowest-energy $\mathrm{Mo}_n\mathrm{N}_2$ and Mo_n clusters for comparison are

plotted in Fig. 2(c). For Mo_nN_2 clusters, the local maximum is found at $n = 6$, indicating that the Mo_6N_2 cluster possesses higher stability than their neighbours. By comparing the values of Δ_2E_n for the Mo_nN_2 and Mo_n clusters, it is found that for $n = 3$, 4, 6, the values of Δ_2E_n become higher after nitrogen adsorption. In contrast, the values of Δ_2E_n become smaller at $n = 5$. For $n = 7$, the values of Δ_2E_n for the Mo_nN_2 and Mo_n clusters are close to each other. Thus, the Mo_3N_2, Mo_4N_2, and Mo_6N_2 clusters enhance their stability, and yet the Mo_5N_2 cluster reduces its stability after nitrogen adsorption, which may relate to the fact that Mo_5 cluster is a magic cluster. However, the stability of Mo_7N_2 cluster has little effect after nitrogen adsorption.

We have also computed the values of the HOMO–LUMO gap of the lowest-energy Mo_nN_2 clusters, as shown in Fig. 4(b). The local peaks are found at $n = 4$ and 6, indicating that Mo_4N_2 and Mo_6N_2 clusters are more stable. Especially for the Mo_6N_2 cluster, the highest value of the HOMO–LUMO energy gap again indicates that it is highly stable.

In order to further explain the above calculated results, we investigate the orbital interaction of N–Mo in Mo_nN_2 clusters after adsorption of N_2 molecule by examining the electron density isosurface of the molecular orbitals. The distribution of electron density of HOMO and LUMO states of the lowest-energy structures of all Mo_nN_2 clusters are plotted in Fig. 7.

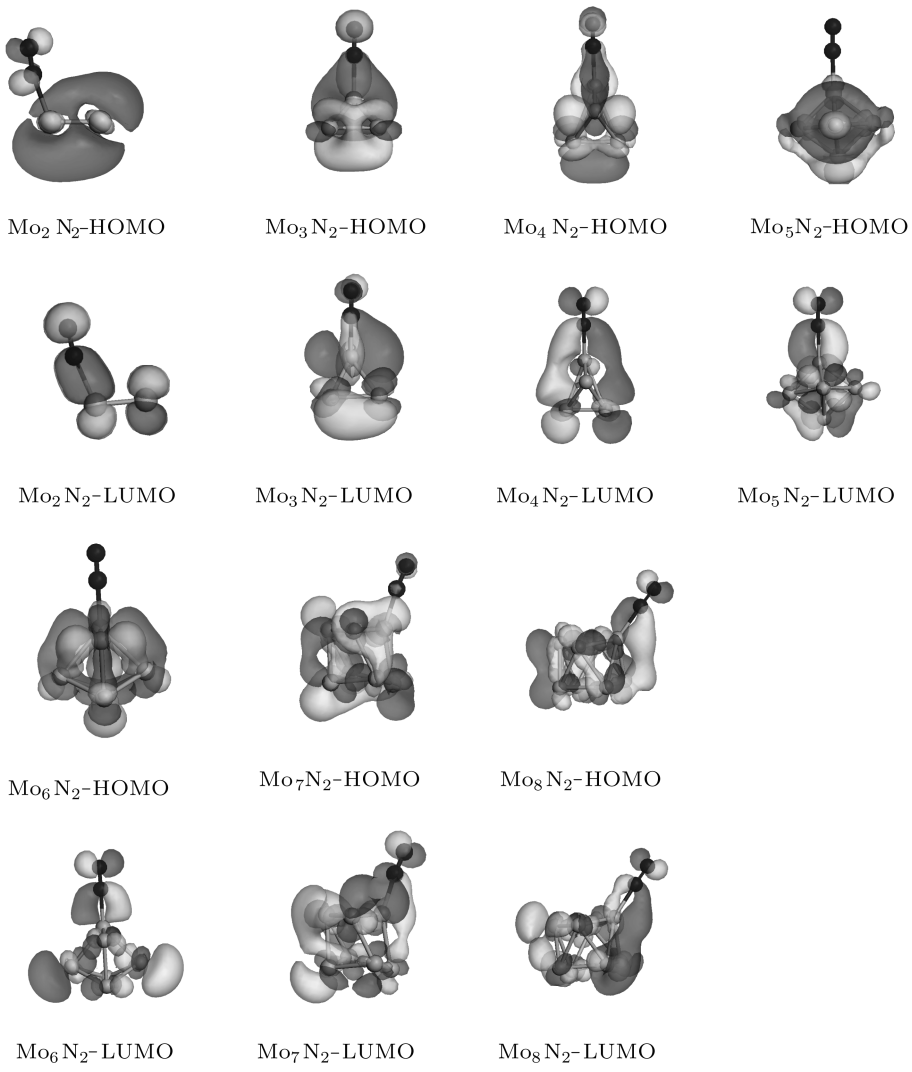


Fig. 7. The HOMO and LUMO of calculated lowest-energy structures of Mo_nN_2 clusters.

Our results indicate that most of the HOMO and LUMO states have delocalized behaviour. Such as Mo_6N_2 cluster, for the HOMO, the electron density is almost delocalized among Mo atoms, there is scarcely any distribution between N atoms. But in the case of the LUMO, the electron density is delocalized among both Mo atoms and N atoms. There is π bond between the Mo atom and the N atom, indicating that the 4d orbital of Mo interacts with the 2p orbital of N. The partial density of states (PDOS) of this representative cluster (Mo_6N_2) is shown in Fig. 8.

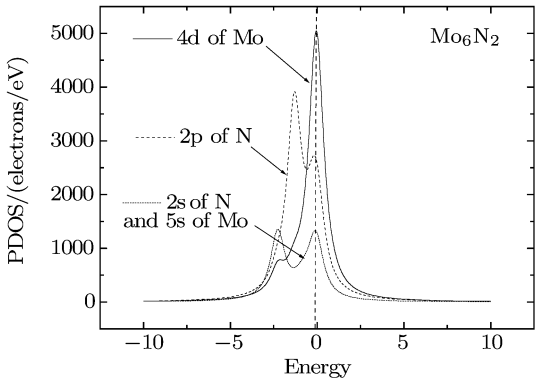


Fig. 8. The s-, d-PDOS of Mo atom and s-, p-PDOS of N atom for the lowest-energy structures of Mo_6N_2 cluster. The dashed line refers to the Fermi level that is shifted to zero.

One can see from Fig. 8 that the electronic states at the vicinity of Fermi surface are mainly come from 4d state of Mo and 2p state of N, and the contribution from 2s of N and 5s of Mo states is very little. Additionally, there is significant overlap of 4d state and 2p state, suggesting that there exists heavy interaction between the 4d state of Mo and the 2p state of N. This fact reveals that the hybrid states are composed of valence orbitals in the cluster. Similar behaviour was observed for all the other sized clusters. Figures 7 and 8 show that the HOMO and LUMO states are composed of Mo 4d, 5s states mixed with N 2s, 2p states. Thus, sp–d hybridization should be responsible for the stability of the adsorption clusters.

To further examine the influence of N_2 by Mo_n clusters, we also list the bond length and the vibration frequency of N_2, and the charge population from Mulliken population analysis on N_2 molecule in Table 3. As can be seen from Table 3, N_2 molecule has certain charge when adsorption on Mo_n clusters, indicating that the interaction between them is remarkable. It is easier for Mo_n clusters which have lower VEA to transfer electron from Mo_n to N_2 molecule. When the charge transfer occurs, π^* antibonding orbital of N_2 will be filled by more electrons, so the N–N bonding will be weakened and as a result the N–N bond length will be elongated and the vibration frequency of N–N bond will be decreased to the extent, which can be seen from Table 3, these results are similar to the N_2 molecule adsorption on W_n clusters.[10]

Table 3. The calculation results for N_2 molecule adsorption on Mo_n clusters.

Mo_nN_2	S	gap/eV	E_{ad}/eV	Δ_2E/eV	R_{N-N}/nm	Q_{N2}/e	ω_{N2}/cm^{-1}
$n=2$	1	0.689	0.558		0.113	–0.034	2113
$n=3$	1	0.472	1.234	–1.184	0.115	–0.149	1967
$n=4$	1	0.673	1.375	–0.329	0.114	–0.134	2016
$n=5$	1	0.522	1.383	–0.310	0.114	–0.133	2049
$n=6$	1	0.819	1.731	0.335	0.114	–0.126	2018
$n=7$	1	0.588	1.500	0.310	0.114	–0.152	2028
$n=8$	1	0.462	1.252		0.114	–0.149	2017

4. Conclusions

The small Mo_n (n=2–8) clusters and their adsorption of N_2 molecule have been studied by using DFT calculations employing Perdew–Wang exchange correlation functional with the GGA. For the bare Mo_n (n=2–8) clusters, the three-dimensional structure starts at $n=4$, and a structural transition from a close-packed structure towards a bcc structure occurs at $n=7$. The multiplicities of the lowest-energy Mo_n clusters are all singlet states except for $n=3$ with triplet state. The calculated fragmentation energies $D(n,n-1)$, the second-order difference of total energies (Δ_2E_n), and the values of HOMO–LUMO gap for the ground states of the Mo_n clusters all indicate that Mo_5 isomer characterizing the trigonal bipyramid structure is the magic cluster.

For N_2 molecule adsorption on Mo_n clusters, we found that the N_2 molecule prefers an end-on mode for all Mo_nN_2 clusters with forming linear or quasi-linear Mo–N–N structures. Additionally, the multiplicities of the lowest-energy Mo_nN_2 clusters are all remain singlet states. The adsorption energies (E_{ad}) show that the Mo_2 is of high inertness and Mo_6 cluster is of high activity against the adsorption of N_2. The calculated second-order difference of total energies ($\Delta_2 E_n$) and the values of HOMO–LUMO gap for the ground states of the Mo_nN_2 clusters show that the Mo_6N_2 cluster is considerably more stable than the other clusters. The adsorption of nitrogen on the molybdenum clusters is the molecular adsorption with slightly elongated N–N bond, not the dissociative chemisorption.

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