Structures and electronic properties of $Mo_{2n}N_n$ (n=1–5): a density functional study*

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The lowest-energy structures and the electronic properties of $Mo_{2n}N_n$ (n=1–5) clusters have been studied by using the density functional theory (DFT) simulating package DMol^3 in the generalized gradient approximation (GGA). The resulting equilibrium geometries show that the lowest-energy structures are dominated by central cores which correspond to the ground states of Mo_n (n = 2, 4, 6, 8, 10) clusters and nitrogen atoms which surround these cores. The average binding energy, the adiabatic electron affinity (AEA), the vertical electron affinity (VEA), the adiabatic ionization potential (AIP) and the vertical ionization potential (VIP) of $Mo_{2n}N_n$ (n=1–5) clusters have been estimated. The HOMO–LUMO gaps reveal that the clusters have strong chemical activities. An analysis of Mulliken charge distribution shows that charge-transfer moves from Mo atoms to N atoms and increases with cluster size.

Keywords: $Mo_{2n}N_n$ clusters, density functional theory, equilibrium structures, electronic properties

PACC: 3640, 3640B, 7115M

1. Introduction

Transition metal nitrides are interesting materials due to their promising properties of high hardness, high melting point, good electrical conductivity, exceptional chemical stability and catalytic activity, which lead them to be used in cutting tools, structural materials, electric components and superconducting devices.[1−7] As an important candidate for transition metal nitrides, molybdenum nitride (Mo_2N) has been demonstrated to have superior catalytic properties in many catalytic reactions, such as hydrodenitrogenation (HDN), hydrodesulfurization (HDS), NH_3 synthesis, alkane isomerization, in the reaction of cyclohexene with hydrogen and so on.[8−13] In addition, many researches have shown that Mo_2N has electronic structures and catalytic properties similar to those of noble-metal. For these reasons, Mo_2N, as an economical alternative to noble-metal catalyst, has attracted much attention.[14−17] There have been numerous theoretical and experimental studies on molybdenum nitride. In theory,[18−21] Martínez *et al.*[18] studied how a Mo atom reacts with N_2 using density functional theory (DFT); Bérces *et al.*[19] obtained most stable geometrical conformations and lowest electronic states of molybdenum and niobium atoms, dimers, trimers, and tetramers and their adducts with dinitrogen by gradient-corrected density functional calculations; Shim and Gingerich[20] investigated the low lying electronic states of the molecule MoN by performing all electron *ab initio* multi-configuration self-consistent-field calculations; Liu and Rodriguez[21] employed the DFT to study the catalytic properties of molybdenum nitrides. In experiment,[8,17,22−31] Shen *et al.*[23] prepared nanocrystalline γ-Mo_2N with average size 5 nm by the direct-current arc discharge method in N_2 gas; Gajbhiye and Nigthoujam[28] prepared nanocrystalline γ-Mo_2N phases by chemical route, which showed a superconducting transition temperature of 3.8 K; recently, Kadono *et al.*[30] synthesized highly dispersed Mo nitride clusters having a composition of Mo_2N in zeolite pores by means of a chemical vapour deposition (CVD) method through using $Mo(CO)_6$ as a precursor; Lightstone *et al.*[31] synthesized molybdenum nitride clusters via laser ablation in the presence of dilute and neat reactive carrier gases.

Although there have been several theoretical and experimental studies recently, a detailed knowledge of the structures, stabilities, and electronic properties of

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the Mo_2N clusters is still unclear. As we know, to understand the catalytic properties of Mo_2N at molecular level, the structures and electronic properties of Mo_2N clusters should be clarified first.[32,33] Herein, we focus on stoichiometric $Mo_{2n}N_n$ (n=1–5) clusters using DFT method. In this study, we aim to answer the following questions. First, what structure is the most stable structure for each cluster size? Second, are there any relationships between pure molybdenum clusters and molybdenum nitride clusters in ground-state structure? Third, how does the binding energy change with cluster size? Fourth, what kind of bond is formed between Mo atoms and N atoms in the $Mo_{2n}N_n$ (n=1–5) clusters? Finally, how are the electronic properties in the clusters, such as IP, EA, HOMO–LUMO energy gaps?

The rest of this paper is organized as follows. The computational details are given in Section 2. The presentation and the discussion of the results are presented in Section 3. Finally, we summarize our findings and conclusions in Section 4.

2. Computational details

All structural optimizations and electronic structure calculations were performed by using the DFT within the generalized gradient approximation (GGA) though employing the Perdew–Wang exchange–correlation functional (PW91)[35] as implemented in the Dmol^3 code.[36] The double numerical basis set including d-polarization functions (DND) was utilized to describe the valence electrons, with the core electrons described by effective core potential. In the geometry optimizations, the convergence thresholds were set to be 0.04 Hartree/nm for the forces, 0.0005 nm for the displacement, and 2×10^{-5} Hartree for the energy change. Self-consistent field calculations were done with a convergence criterion of 10^{-5} Hartree for the total energy. To obtain more accurate calculations, we chose an octupole scheme in the multipolar representation of the charge density and Coulomb potential. The direct inversion in an iterative subspace (DIIS) approach was used to speed up SCF convergence. The charge density and the magnetic moments were evaluated via the Mulliken population analysis. All the geometry structures were optimized without any symmetry constraint. Considering the open-shell of this system, we chose spin-unrestricted DFT for all initial structures. In order to obtain the global minimum structures of $Mo_{2n}N_n$ (n=1–5) clusters, different spin multiplicities were calculated for all geometries.

It is well known that initial cluster geometry plays an important role in obtaining the lowest-energy structure. We considered all possible sites of Mo_{2n} cluster and added nN atoms to it. In addition, we also replaced nMo atoms with nN atoms in Mo_{3n} cluster. In order to reduce the computational time, the initial calculations were done with low quality. The geometric optimizations were then repeated with medium quality for obtaining the lowest-energy structures of $Mo_{2n}N_n$ (n=1–5) clusters.

To test the suitability of DFT method and basis sets in our systems, the values of bond length (R_e/nm) and vibration frequency (ω/cm^{-1}) of MoN, Mo_2 and N_2 were calculated and listed in Table 1. It is obvious that the results obtained by the PW91 exchange–correlation functional[35] are in good agreement with the reported experimental values.[37–41]

Table 1. Calculated results and experimental values of bond length (R_e/nm) and vibration frequency (ω/cm^{-1}) for MoN, Mo_2 and N_2.

		MoN	Mo_2	N_2
R_e/nm	this work	0.1641	0.1986	0.1107
	experimental	0.1636[37]	0.194[38]	0.1098[40]
ω/cm^{-1}	this work	1105	523	2355
	experimental	1075±30[39]	477[41]	2358[40]

3. Results and discussion

3.1. Equilibrium geometries and stabilities of $Mo_{2n}N_n$ (n=1–5) clusters

In this section, we present the equilibrium structures and stabilities of $Mo_{2n}N_n$ (n=1–5) clusters. Figure 1 shows the most stable structures and other low-lying isomers of $Mo_{2n}N_n$ (n=1–5) clusters. For each size, several isomers are placed in descending order of stability. The results of symmetries, spin multiplicities, average

binding energies (E_b), HOMO–LUMO gaps, magnetic moments and average charge of N atoms for $Mo_{2n}N_n$ (n=1–5) are listed in Table 2. One can see from Fig. 1 that for each size, the lowest-energy structure prefers to form a core of metal atoms, which is capped by nitrogen atoms. In other words, nitrogen atoms are adsorbed on the surface of molybdenum clusters. By comparison with the pure Mo clusters, we find that the cores of metal atoms have the ground-state structures of Mo_n (n = 2, 4, 6, 8, 10) clusters, which are calculated by the same calculational method as that in Section 2. The geometries of the lowest-energy structures of Mo_n clusters with n = 2, 4, 6, 8, 10 are shown in Fig. 2.

Table 2. Symmetries, spin multiplicities, values of average binding energy E_b (eV), HOMO–LUMO gap E_g (eV), magnetic moment $M(\mu_B)$ and average charge Q_N of N atom of $Mo_{2n}N_n$ (n=1–5) clusters for all equilibrium geometries.

cluster	symmetry	E_b	spin	E_g	M	Q_N
Mo_2N	C_{2v}	2.278	2	1.230	1	–0.454
	C_{2v}	2.431	8	0.884	7	–0.360
	$D_{\infty h}$	2.362	8	0.286	7	–0.327
Mo_4N_2	D_{2d}	3.806	1	0.949	0	–0.428
	C_1	3.625	3	0.482	2	–0.440
	C_2	3.622	3	0.413	2	–0.535
	C_1	3.463	1	0.690	0	–0.067
	C_s	3.352	5	0.079	4	–0.049
Mo_6N_3	C_1	4.194	2	0.384	1	–0.545
	C_2	4.170	2	0.500	1	–0.504
	C_s	4.143	2	0.300	1	–0.490
	C_1	3.926	2	0.378	1	–0.443
	D_{3h}	3.921	2	0.243	1	–0.434
Mo_8N_4	C_1	4.417	5	0.344	4	–0.392
	C_i	4.313	5	0.206	4	–0.484
	C_1	4.237	3	0.027	2	–0.631
	C_{2h}	4.150	1	0.293	0	–0.492
	D_{2h}	4.139	3	0.297	2	–0.359
	D_{4h}	4.060	1	0.270	0	–0.628
$Mo_{10}N_5$	C_s	4.633	2	0.229	1	–0.641
	C_1	4.475	8	0.013	7	–0.599
	C_s	4.403	2	0.349	1	–0.327
	C_{2v}	4.292	4	0.178	3	–0.178

For the Mo_2N cluster, we have optimized three isomers, which are derived from Mo_2 cluster by capping an N atom at terminal site, edge site and inserting an N atom between the two Mo atoms, respectively. The calculated lowest-energy structure with different bond lengths of Mo–N (R_{23} = 0.1786 nm, R_{31} = 0.2147 nm) has a doublet state, while the other two (C_{2v}, $D_{\infty h}$) have octet states. To elucidate the difference between the two Mo–N bonds in the ground state, the net charges on different molybdenums have been obtained by Mulliken population analysis. The positive charges present on Mo1 (0.195 a.u.) are apparently less than that present on Mo2 (0.259 a.u.). It indicates that the strength of Mo–N bond is related to transformation of the charges from molybdenum to nitride in Mo_2N cluster. Besides, the E_b of Mo_2N^- (2.813 eV/atom) is larger than the E_b of neutral Mo_2N (2.728 eV/atom), while the E_b of Mo_2N^+ (0.510 eV/atom) is much less stable than that of Mo_2N. For the Mo_2N^-, the reason is that the electron added to Mo_2N occupies the LUMO. For the Mo_2N^+, what leads to the less stable structure is the ionized electron coming from a deeper bonding orbital of the neutral Mo_2N.

In the case of Mo_4N_2, the D_{2d} symmetry structure (2A) with a singlet state is found to be the most stable structure, which is derived from the tetrahedron of Mo_4 by capping two N atoms on edge sites. The energy of the second lowest conformation (2B) is 1.09 eV higher than that of the ground-state, while it is taken as the ground-state by Berces *et al.*[19] The conformation (2C) is the structure capping two N atoms on two adjacent

faces of Mo_4 tetramer. Its energy is 1.11 eV higher than that of the ground-state. In addition, we have obtained two conformers (2D, 2E) which consist of Mo_4 tetramer and dinitrogen, but they are 2.06 eV and 2.73 eV higher in energy than the ground-state, respectively. For the conformers 2D and 2E, the lengths of N–N bonds prolong by 0.0025 nm and 0.0037 nm respectively, compared with the N_2 molecular (0.1098 nm).[40]

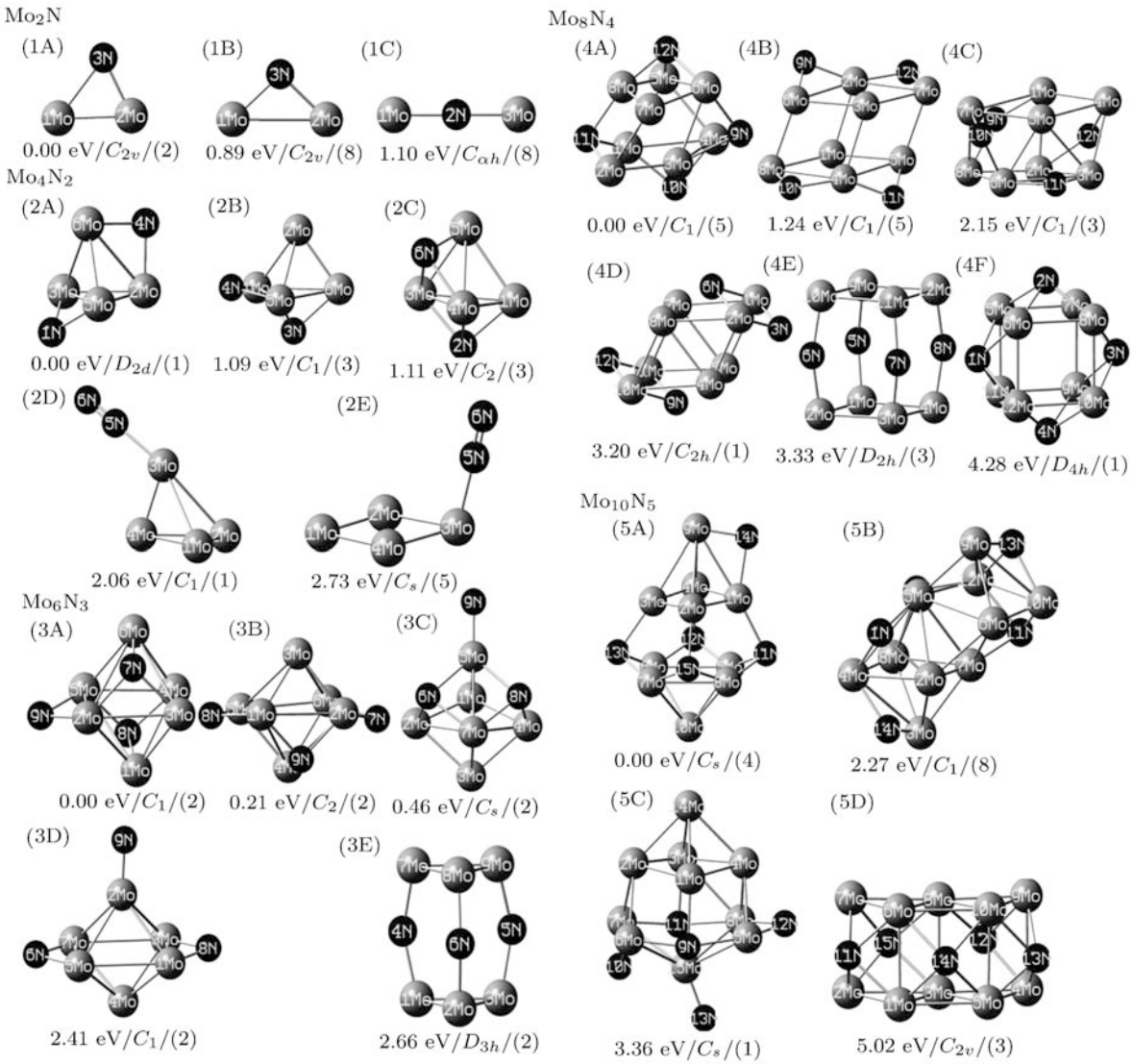


Fig. 1. Equilibrium geometries, point groups and values of relative energy (ΔE/eV) of $Mo_{2n}N_n$ (n=1–5) clusters. Isomers are placed in descending order of stability.

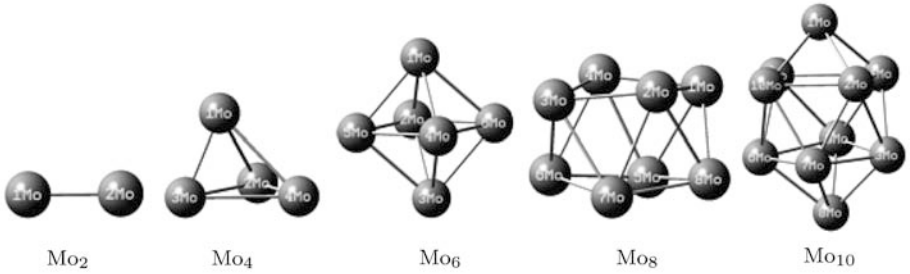


Fig. 2. Geometries of the lowest-energy structures of Mo_n (n = 2, 4, 6, 8, 10) clusters.

For Mo_6N_3, all the equilibrium structures obtained here each have a spin doublet state. Except the sandwich structure (3E), they are all formed by octahedron structure covered by three N atoms at different sites (face,

edge and terminal). During the process of optimization, we also find the N atoms prefer capping on Mo_6 cluster to inserting into it. Moreover, Mulliken population analysis (in Table 2) indicates that the number of charges transferring from Mo atoms to the N atoms decreases as the energy of Mo_6N_3 increases.

As for Mo_8N_4 cluster, the four N atoms are added to terminal, edge, and face capping sites for octamer, which is clearly demonstrated in Fig. 1. The results indicate that the lowest-energy structure with a low symmetry is a structure capping four N atoms on different faces of the ground-state of Mo_8 cluster. Mo_8 cluster is composed of two twisted parallelograms. However, there is a high symmetrical conformer (4F), which is 4.28 eV higher in energy than the ground-state.

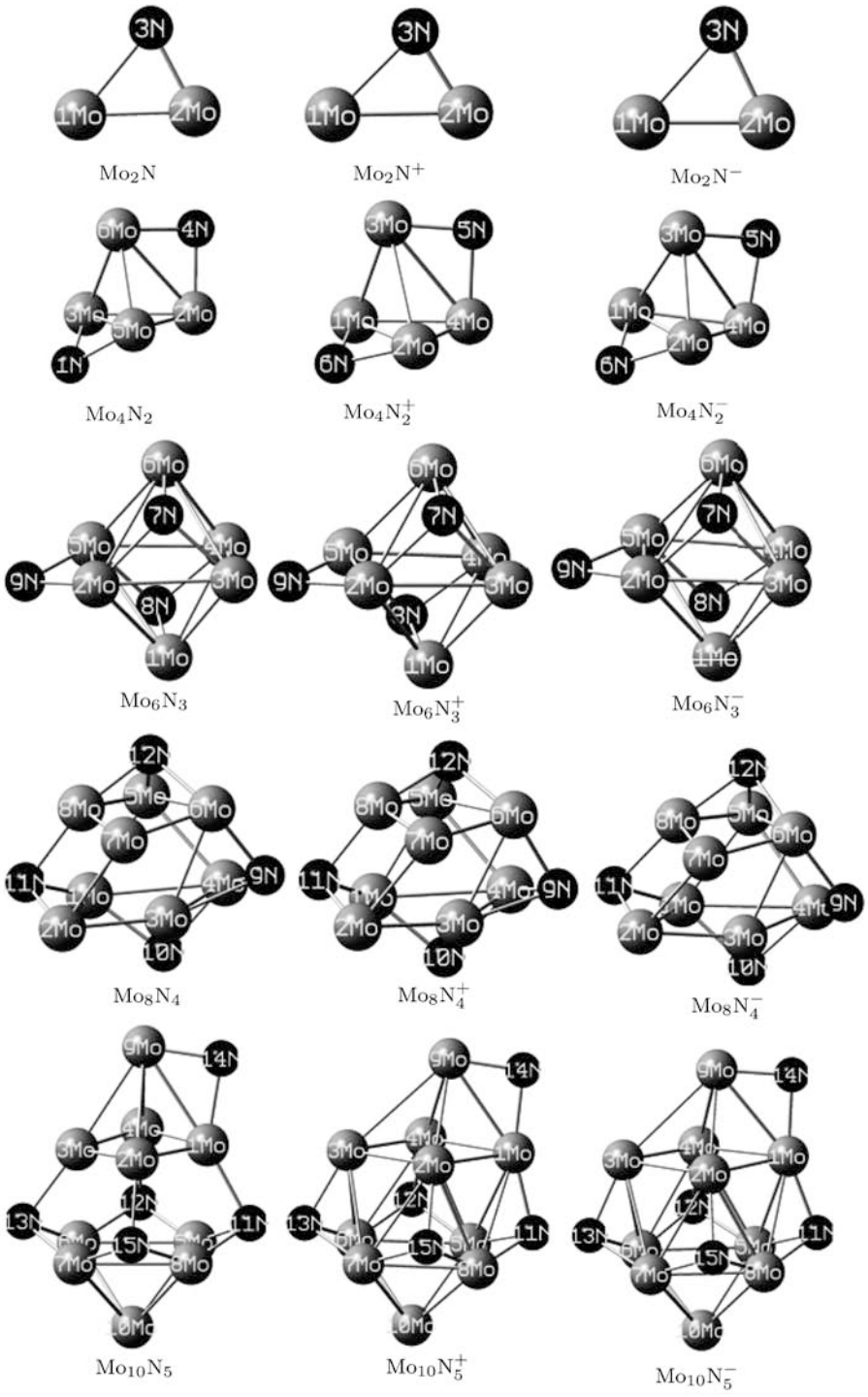


Fig. 3. Ground-state structures of cationic and anionic $Mo_{2n}N_n$ (n=1–5) clusters.

The optimized geometries indicate that the possible $Mo_{10}N_5$ isomers with high symmetries are not the stable structures. As shown in Fig. 1, the 5D isomer, which is formed by capping five N atoms on side faces of two parallel isosceles trapezoids, is 5.11 eV higher in total energy than the lowest-energy 5A isomer. In order to obtain more details about $Mo_{10}N_5$ clusters, we perform the Mulliken population analysis on $Mo_{10}N_5$ clusters. From Table 2, we find that the amount of charge-transfer increases with relative stability. As a result, we speculate that the stability of $Mo_{10}N_5$ cluster would be related to charge-transfer.

From our calculation, all the ground-state structures of cationic and anionic $Mo_{2n}N_n$ (n=1–5) clusters (in Fig. 3) have similar structures to those of neutral clusters. In order to understand the relative stability of the most stable $Mo_{2n}N_n$ (n=1–5) neutral and ionic clusters, it is significant to calculate the average binding energy E_b, which is defined as

$$E_b = \frac{2nE(\mathrm{Mo}) + nE(\mathrm{N}) - E(\mathrm{Mo}_{2n}\mathrm{N}_n)}{3n}, \qquad (1)$$

where E(Mo), E(N) and $E(Mo_{2n}N_n)$ denote the total energies of the Mo, N, and $Mo_{2n}N_n$ clusters, respectively.

The average binding energies for $Mo_{2n}N_n$ neutral and ionic clusters versus the number of Mo atom are shown in Fig. 4. For comparison, we have also plotted the E_b curves of Mo_n (n = 2, 4, 6, 8, 10) clusters. It can be seen that the average binding energy generally increases as the size of the neutral and charged $Mo_{2n}N_n$ (n=1–5) clusters and they can continue obtaining energy during the growth. Furthermore, the E_b curves of $Mo_{2n}N_n$ (n=1–5) clusters are generally larger than those of pure Mo_n (n = 2, 4, 6, 8, 10) clusters. In other words, the doping of the N atoms improves the stabilities of Mo_n (n = 2, 4, 6, 8, 10) clusters. The E_b curves of anionic and cationic clusters show that an addition of one electron strengthens the Mo–N interaction, and thus enhances the average binding energy of $Mo_{2n}N_n^-$ as compared with the neutral one, while the removal of one electron decreases the Mo–N interaction which results in low stability for the cationic clusters.

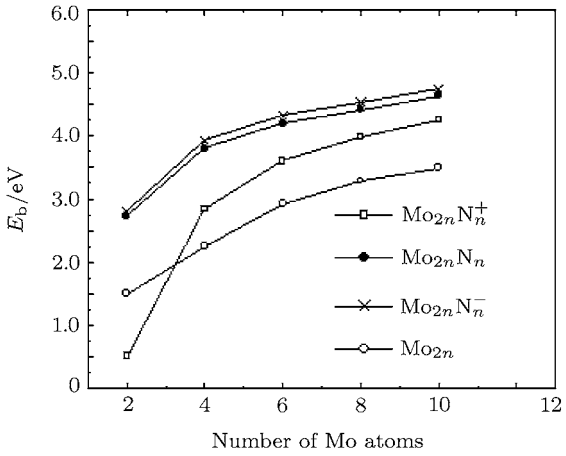


Fig. 4. Curves for average binding energy vs. the number of Mo atoms in the most stable $Mo_{2n}N_n$ clusters, ionic clusters and Mo_{2n} clusters.

3.2. Electronic properties of $Mo_{2n}N_n$ (n=1–5) clusters

Now, we come to discuss the electronic properties. As is well known, ionization potential (IP) and electron affinity (EA) are important for understanding cluster properties, which can provide information about electronic and geometric structure as well as chemical reactivity with other molecules.[42] Therefore, we calculate adiabatic electron affinities (AEAs), vertical electron affinities (VEAs), adiabatic ionization potentials (AIPs) and vertical ionization potentials (VIPs) of $Mo_{2n}N_n$ (n=1–5) clusters. AEA, VEA, AIP and VIP are calculated as defined in the following:

$$\begin{aligned} \mathrm{AEA} &= E(\text{optimized } \mathrm{Mo}_{2n}\mathrm{N}_n) \\ &\quad - E(\text{optimized } \mathrm{Mo}_{2n}\mathrm{N}_n^-), \qquad (2) \\ \mathrm{VEA} &= E(\text{optimized } \mathrm{Mo}_{2n}\mathrm{N}_n) \\ &\quad - E(\text{nonoptimized } \mathrm{Mo}_{2n}\mathrm{N}_n^-), \qquad (3) \\ \mathrm{AIP} &= E(\text{optimized } \mathrm{Mo}_{2n}\mathrm{N}_n^+) \\ &\quad - E(\text{optimized } \mathrm{Mo}_{2n}\mathrm{N}_n), \qquad (4) \\ \mathrm{VIP} &= E(\text{nonoptimized } \mathrm{Mo}_{2n}\mathrm{N}_n^+) \\ &\quad - E(\text{optimized } \mathrm{Mo}_{2n}\mathrm{N}_n). \qquad (5) \end{aligned}$$

In Fig. 5, the curves for AEA and VEA each show a monotonic increase from Mo_2N to $Mo_{10}N_5$. The differences between AEA and the corresponding VEA are 0.01–0.09 eV which are rather small. So the most stable $Mo_{2n}N_n^-$ clusters basically hold the structures that are similar to those of the corresponding most stable neutral clusters. From Fig. 6, it follows that the curves of VIP and AIP have parallel trends. However, the VIP value is about 0.06–0.31 eV larger than

the corresponding AIP value. The small difference between VIP and AIP shows that the removal of an electron from a neutral cluster causes small change for the most stable $Mo_{2n}N_n$ cluster. Figure 3 shows the validation of our results. Moreover, the lowest AIP value of Mo_8N_4 implies that its cationic cluster can be easily obtained experimentally and corresponds to the enhanced abundance observed for this species in mass spectroscopy.

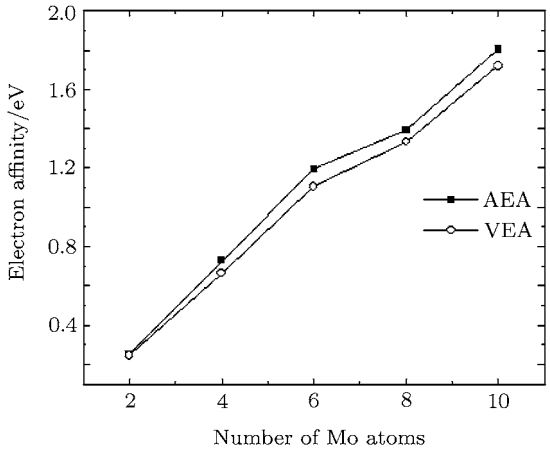


Fig. 5. Size dependences of AEA and VEA for the most stable $Mo_{2n}N_n$ (n=1–5) clusters.

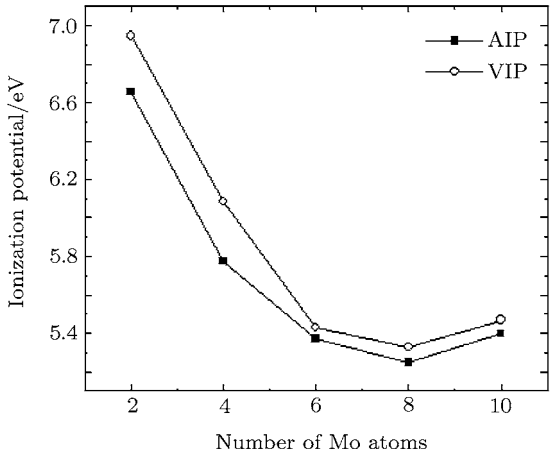


Fig. 6. Size dependences of AIP and VIP for the most stable $Mo_{2n}N_n$ (n=1–5) clusters.

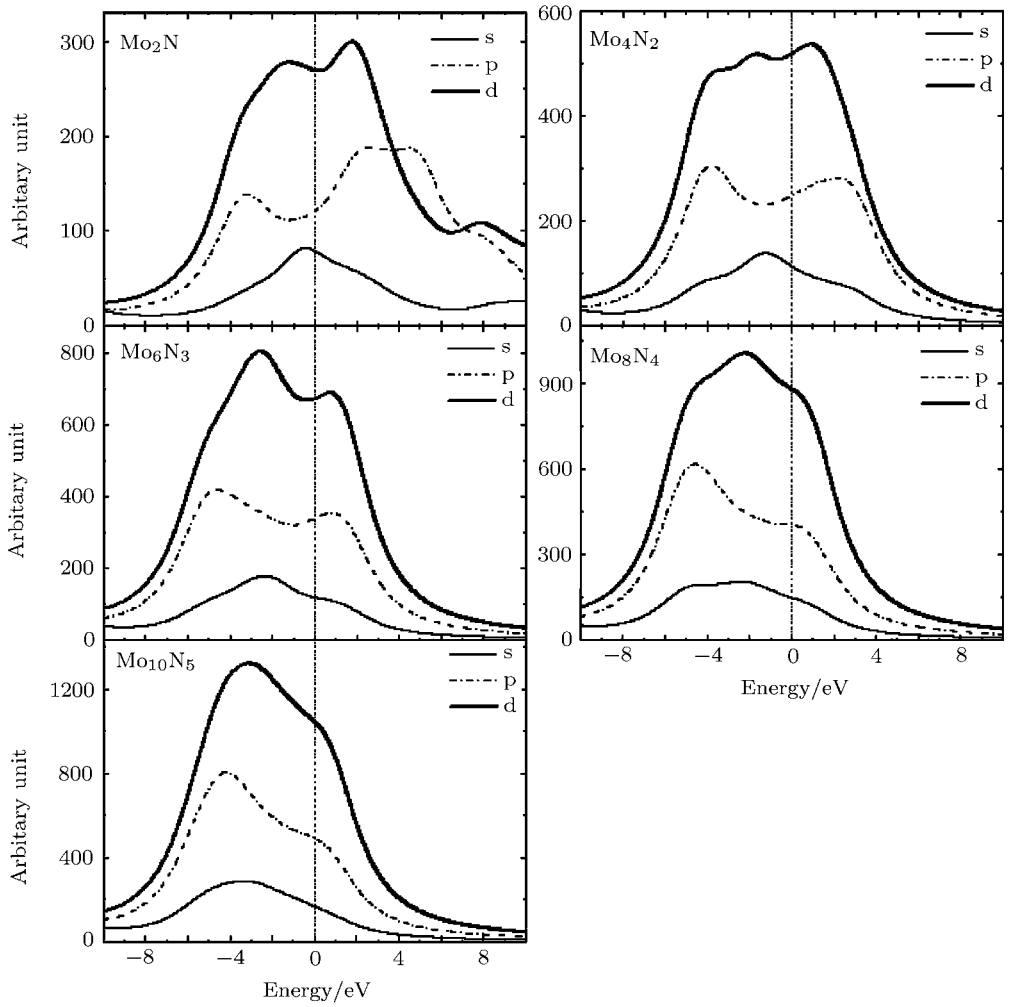


Fig. 7. Partial densities of states for $Mo_{2n}N_n$ (n=1–5) clusters.

To obtain further insight into the bonding behaviour of $Mo_{2n}N_n$ (n=1–5) clusters, the partial densities of states (PDOSs) of $Mo_{2n}N_n$ (n=1–5) clusters are calculated and shown in Fig. 7. From the figure we can find that the density of states on the Fermi surface mainly comes from the contribution of 4d orbital of Mo atoms and that a distinct d–s–p hybrid appears in the vicinity of Fermi level.

Next we focus on the study of HOMO–LUMO gaps of $Mo_{2n}N_n$ (n=1–5) clusters. Based on our results, it can be seen that the gaps for $Mo_{2n}N_n$ (n=1–5) clusters (in Fig. 8) decrease monotonically with cluster size, which indicates that the metallic characteristics are enhanced as cluster size increases.

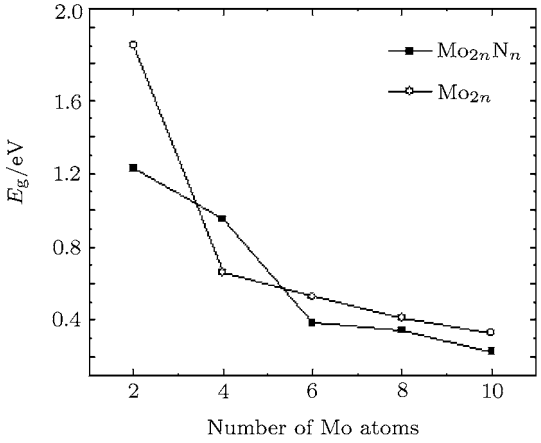


Fig. 8. Size dependences of HOMO–LUMO gaps for the most stable $Mo_{2n}N_n$ (n=1–5) clusters.

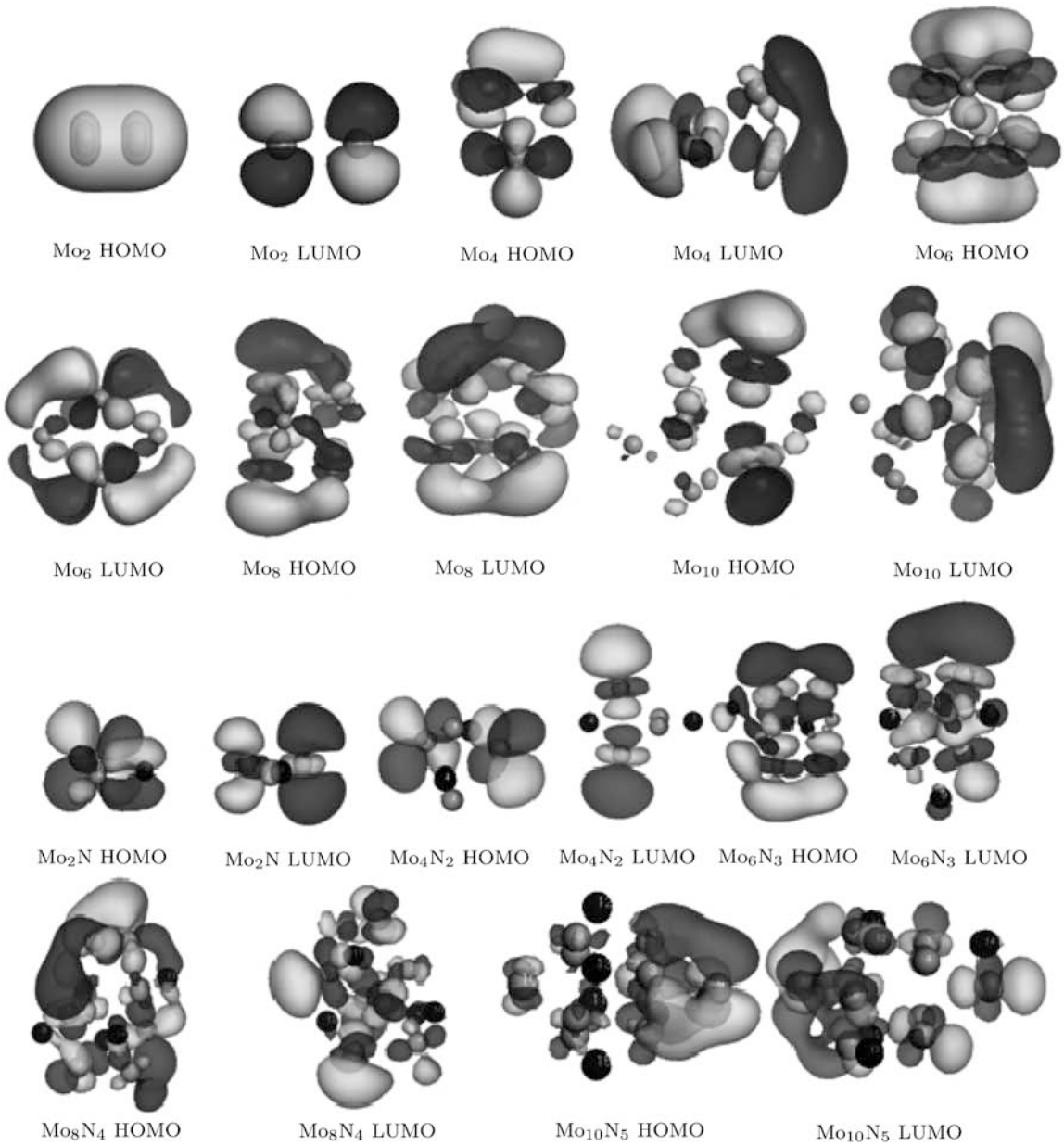


Fig. 9. Charge densities of HOMO and LUMO for $Mo_{2n}N_n$ (n=1–5) clusters.

In contrast with the gaps of corresponding Mo_n (n = 2, 4, 6, 8, 10) clusters, the gaps of $Mo_{2n}N_n$ (n=1–5) clusters are found to be smaller than those of the pure clusters (except that of Mo_4N_2). It suggests that chemical activity strengthens when the N atoms are added to Mo_n clusters. To further investigate the reasons why the HOMO–LUMO gaps of $Mo_{2n}N_n$ clusters are lower than those of corresponding Mo_n clusters, we perform a detailed analysis by inspecting the electron densities of the HOMO states and the LUMO states in the most stable structures (see Fig. 9). From this figure, it follows that the HOMO and the LUMO are composed principally of 4d orbital of Mo atoms and 2p orbital of N atoms. It implies that there is a d–p hybrid between Mo atom and N atom, which leads the HOMO–LUMO gaps for the most stable $Mo_{2n}N_n$ (n=1–5) clusters to be lower than those of the pure Mo_n clusters and also causes the cluster chemical activity to strengthen. It is worth while to point out that the HOMO–LUMO energy gap of Mo_4N_2 is larger than that of Mo_4 cluster, which can be explained as the fact that both N atoms in Mo_4N_2 cluster do not participate in the hybridization.

Listed in Table 2 are the Mulliken atomic net populations for all ground state structures. The results indicate that charge-transfer results in all N atoms with negative charges and Mo atoms with positive charges. The average charge-transfer of N atom versus cluster size is shown in Fig. 10.

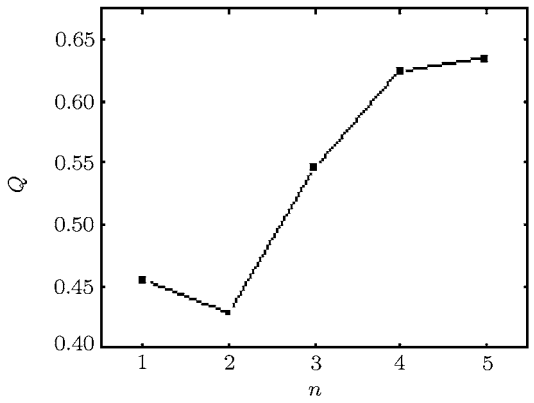


Fig. 10. Size dependences of the average charge transfers for the most stable $Mo_{2n}N_n$ (n=1–5) clusters.

Table 3. Charges of 4d, 5s, 5p states for Mo atom and 2s, 2p, 3d for N atom in $Mo_{2n}N_n$ (n=1–5) clusters.

		4d	5s	5p		2s	2p	3d
1	Mo1	4.757	0.988	0.078	N3	1.829	3.586	0.039
	Mo2	4.645	0.985	0.143				
2	Mo2	4.634	0.961	0.223	N1	1.746	3.645	0.037
	Mo3	4.634	0.960	0.223	N4	1.745	3.645	0.037
	Mo5	4.635	0.961	0.225				
3	Mo1	4.710	0.949	0.163	N7	1.727	3.782	0.035
	Mo2	4.444	0.850	0.274	N8	1.755	3.692	0.038
	Mo3	4.756	0.971	0.163	N9	1.841	3.734	0.032
	Mo4	4.684	0.953	0.205				
	Mo5	4.483	0.780	0.287				
	Mo6	4.774	0.954	0.131				
4	Mo1	4.505	0.841	0.272	N9	1.851	3.788	0.036
	Mo2	4.629	1.037	0.222	N10	1.824	3.716	0.039
	Mo3	4.544	0.685	0.182	N11	1.815	3.799	0.036
	Mo4	4.476	0.813	0.349	N12	1.806	3.766	0.038
	Mo5	4.695	1.016	0.207				
	Mo6	4.466	0.802	0.343				
	Mo7	4.836	1.103	0.155				
	Mo8	4.462	0.780	0.303				
5	Mo1	4.463	0.951	0.222	N11	1.838	3.816	0.035
	Mo2	4.555	0.878	0.268	N12	1.855	3.797	0.036
	Mo3	4.618	1.013	0.192	N13	1.857	3.782	0.039
	Mo4	4.557	0.878	0.264	N14	1.782	3.643	0.035
	Mo5	4.445	0.848	0.280	N15	1.857	3.797	0.036
	Mo6	4.451	0.817	0.287				
	Mo7	4.454	0.812	0.287				
	Mo8	4.443	0.847	0.280				
	Mo9	4.545	1.120	0.286				
	Mo10	4.791	1.123	0.143				

The charges increase with cluster size (except for $n = 2$), which clearly exhibits strong interaction between electrovalent bonds. It should be mentioned that the charge-transfer in Mo_4N_2 cluster becomes smaller than those of other size clusters because both N atoms in Mo_4N_2 cluster do not participate in the hybridization. In addition, some orbital populations of Mo and N atoms of the most stable $Mo_{2n}N_n$ (n=1–5) clusters are summarized at Table 3. The charges in the $Mo_{2n}N_n$ (n=1–5) clusters transfer mainly from 4d and the 5s orbitals to 5p orbital of the Mo atom and from 2s orbital to 2p and 3d orbitals of the N atom. However, the lost electrons of 4d and 5s orbitals are larger than those of 5p orbital attains. It suggests that the electrons of 4d and 5s orbitals transfer not only to 5p orbital but also to 2p orbital, which induces the d–s–p hybridization in Mo atom and the d–p hybridization between Mo atom and N atom.

4. Summary and conclusions

The $Mo_{2n}N_n$ (n=1–5) clusters have been studied by utilizing the PW91 method with the DND basis sets. The average binding energies, the equilibrium geometries, the stabilities, and the electronic properties of $Mo_{2n}N_n$ (n=1–5) clusters, together with AEAs, VEAs, AIPs, VIPs, PDOSs, HOMO–LUMO gaps and population analyses are presented and discussed. The results can be summarized as follows. (i) The most stable $Mo_{2n}N_n$ (n=1–5) clusters each feature a central core which corresponds to the ground states of Mo_n (n = 2, 4, 6, 8, 10) clusters and the nitrogen atoms cap on it. (ii) The ground-state structures of anionic and cationic $Mo_{2n}N_n$ (n=1–5) clusters basically maintain the frames that are parallel to those of the corresponding neutral clusters. (iii) In terms of calculated E_b, the results show that E_b generally increases with cluster size. A comparison among stabilities of Mo_n (n = 2, 4, 6, 8, 10) clusters shows that the doping of the N atoms can enhance the stabilities of Mo_n (n = 2, 4, 6, 8, 10) clusters. (iv) The AEA, VEA, AIP and VIP indicate that there exist not noticeable differences in structure between neutral and ionic configurations of $Mo_{2n}N_n$ (n=1–5) clusters. (v) The HOMO–LUMO gaps reveal that $Mo_{2n}N_n$ (n=1–5) clusters each have a stronger chemical activity than the pure molybdenum clusters. (vi) Population analysis indicates that the charges in $Mo_{2n}N_n$ (n=1–5) clusters transfer mainly from Mo atoms to N atoms and the clusters present d–s–p hybridization on Mo atom and d–p hybridization between Mo atom and N atom.

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