

Density functional study on the structural, frontier orbital, electronic, and magnetic properties of the transitional metal clusters $\text{Pd}_5(\text{CO})_n$ ($n = 1$ to 6)

Chun-Mei Tang*, Hui Wang, Wei-Hua Zhu, Ming-Yi Liu, Ai-Mei Zhang, Jiang-Feng Gong, Hua Zou, and Wei Guo

College of Science, Hohai University, Nanjing 210098 China

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Abstract. The generalized gradient approximation based on density functional theory is used to analyze the structural, electronic, and magnetic properties of the transition metal clusters $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6). For Pd_5CO , the most stable isomer is the singlet state structure with C atom adsorbed on the hollow site in the form of CO molecule, as same as the conclusion reported by Zanti *et al* (Eur. J. Inorg. Chem. 2009, 3904). In the most stable isomers of $\text{Pd}_5(\text{CO})_2$ and $\text{Pd}_5(\text{CO})_3$, the first CO molecule is adsorbed on the hollow site, while the second and the third CO molecules are adsorbed on the bridge sites, whereas, for the most stable $\text{Pd}_5(\text{CO})_n$ ($n=4,5,6$), all CO molecules are adsorbed on the bridge sites. It is known from the adsorption energy that $\text{Pd}_5(\text{CO})_2$ should be the most possible adsorption product. The energy gap indicates that $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6) have the enhanced dynamical stability compared to Pd_5 , and $\text{Pd}_5(\text{CO})_3$ should be most dynamically stable of all. The chemisorptions of CO molecules onto the Pd_5 cluster are non-dissociative and the strength of C-O bond becomes weaker while more CO molecules are adsorbed. Along with the increase of the CO molecules in $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6), the ability for detaching electrons is weakened and that for obtaining electrons is improved. The magnetic moment of Pd_5 is $2\mu_B$, however, $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6) have no magnetic moment.

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Key words: Pd_5 , Pd_5CO , $\text{Pd}_5(\text{CO})_n$, density functional theory, geometric structure, electronic properties

1 Introduction

Because of the closed-shell configuration and unusual magnetic property of the Pd atom, Palladium clusters have become a kind of very important catalytic materials, which have

*Corresponding author. *Email address:* tcmnj@163.com (C. -M. Tang)

been widely researched. Experimentally, Judai *et al.*[1] have reported that the small Pd_n ($n < 31$) clusters not only could tune a catalytic process by changing the cluster size, but also could catalyze chemical reactions at low temperature. Theoretically, Ni *et al.*[2] have explored that H_2 was either physically adsorbed to the Pd atom in some cases, or chemically dissociated to be H atoms in other cases. Endou *et al.*[3] have found that when NO is adsorbed on Pd_2 , there exists charge transfer between NO and Pd_2 , leading to the increase of the strength of the N-O bond. Qiu *et al.*[4] have reported the high stabilities and narrowing of the HOMO-LUMO energy gaps for the Pd_nS ($n = 3, 5, 7$) clusters. Dufaur *et al.*[5] have discovered that the strength of the N-O bond is dramatically weakened when the molecule is adsorbed on the small Pd_n clusters due essentially to an electrostatic repulsion between N and O.

As is known, the adsorption mechanism of CO molecules on the transitional metal clusters surface has become a hot research topic. For example, Tian *et al.*[6] have found that the CO molecule are adsorbed on the atop site of the Pd_n clusters for $n = 2, 4, 7, 8$ and on the bridge site for $n = 3, 5, 6$. Zanti *et al.*[7] have explored the most stable structure of Pd_5 is a trigonal bipyramid with the D_{3h} symmetry, moreover, the Pd_5CO isomer with C atom adsorbed on the hollow site in the CO molecule form is the most stable, as same as the conclusion gotten by us, but the detailed analysis about the electronic structure have not been paid attention to. Ge *et al.*[8] have shown that the Pd_5CO cluster with O atom adsorbed on the atop site in the CO molecule form should be the most stable. Kalita *et al.*[9] have reported that the C atom of CO adsorbed on the top site in the lowest energy structure of Pd_5CO , which did not accord with our results. Therefore, in order to explicitly know the adsorption position and adsorption manner of CO in the most stable Pd_5CO structure, this article intends to study the geometric structure and electronic properties of Pd_5CO in detail. Furthermore, there have been no research reported for $\text{Pd}_5(\text{CO})_n$ ($n = 2$ to 6) clusters until now, so this article will continue to study the geometric, electronic, and magnetic properties of $\text{Pd}_5(\text{CO})_n$ ($n = 2$ to 6) molecules.

This paper chose the Pd_5 cluster for research for two main reasons. On one hand, the Pd_5 cluster was found very active [10]. Generally, the reaction is more likely occurred between the most active molecules. For example, the Mn_n ($n=3,6,8$) clusters have strong activity, and their corresponding CO complexes possess high adsorption ability [6]. Moreover, the most stable $\text{La}_2@C_{72}$ was formed by doping the most active C_{72} isomer with two La atoms [11]. On the other hand, the most stable structure of Pd_5 is a trigonal bipyramid with the high symmetry [1-10], therefore, the isomers for the Pd_5CO clusters will be relatively less. This paper mainly focuses on the following three specific issues:

- (1) What is the most stable structure of Pd_5 ?
- (2) What are the most stable structures of $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6)?
- (3) What are the electronic properties and magnetic properties of the most stable structures of $\text{Pd}_5(\text{CO})_n$ ($n = 1$ to 6)?

2 Computational details

The DFT approach, due to its significant character of high accuracy and low cost, has become one of the most popular calculation routines for large systems [12]. It has been found that the GGA is more accurate than the local density approximation (LDA) in the calculations of the bond length and binding energy [13]. Therefore, GGA [13] based on DFT [12] is adopted in this paper. The calculations are performed with the DFT implemented in Dmol³ package [12]. The spin-unrestricted treatment [14] is carried out with double numerical plus polarization basis set (DNP) [12] and GGA with Perdew-Burke-Ernzerhof (PBE) functional [15]. The core electrons are described with the DFT semi-core pseudopotentials (DSPP). Self-consistent field procedures were carried out with a convergence criterion of 10^{-6} a.u. on the energy and electron density. Geometry optimizations were performed with a convergence criterion of 10^{-3} a.u. on the displacement and 10^{-5} a.u. on the energy. In order to test the accuracy of the methods, we have calculated the bond lengths and binding energies of the Pd₂, CO, and Pd₂CO molecules respectively. For CO, the bond length is 1.127 Å and the binding energy (BE) is 11.2 eV, which are in agreement with the experimental results (the bond length is 1.128 Å, binding energy is 11.2 eV [16]). For Pd₂, the bond length of 2.49 Å and BE of 0.84 eV are close to the experimental results (the bond length is 2.48 Å and BE is 0.74 ± 0.26 eV [17]). This indicates that the method is reliable for the present studied systems.

3 Results and discussion

3.1 The structure and stability of Pd₅CO

In order to be compared with the previous conclusion concluded by other researchers, this paper will firstly find out the most stable structure of Pd₅. There are seven possible isomers presented according to the number of atoms, as shown in Fig. 1, which displays (1) seven initial structures and (2) seven optimized structures of Pd₂. These seven initial structures are classified as line style, face style and body style, but all optimized structures are changed into (h) triangular bipyramid or (i) tetragonal pyramid. The triangular bipyramid is made up of an isosceles triangle in the middle and two tapers, which has three unequal sides, so the triangular bipyramid is highly symmetric above and below. The tetragonal pyramid is made up of the isosceles quadrangle in the bottom and the four isosceles sides in the above. All isomers are optimized with possible spin states. The ground-state structures of both triangular bipyramid and tetragonal pyramid are singlet state, and the minimum frequencies are respectively 52.84 and 33.07 cm⁻¹, proving that these two structures correspond to the minima on the respective potential energy surfaces. The BE is defined as the absolute value of the difference between the total energy of the whole molecule and the energy sum of all the free atoms constituting the molecule. The larger of the BE, the more stable of the structure [18]. The calculated BE of the singlet-state triangular bipyramid is 0.03 eV larger than the singlet state tetragonal pyramid, so

the most stable structure of Pd₅ clusters is the singlet state triangular bipyramid, and the metastable structure of Pd₅ clusters is the singlet state tetragonal pyramid, which is in consistent with the previous conclusion [1-10].

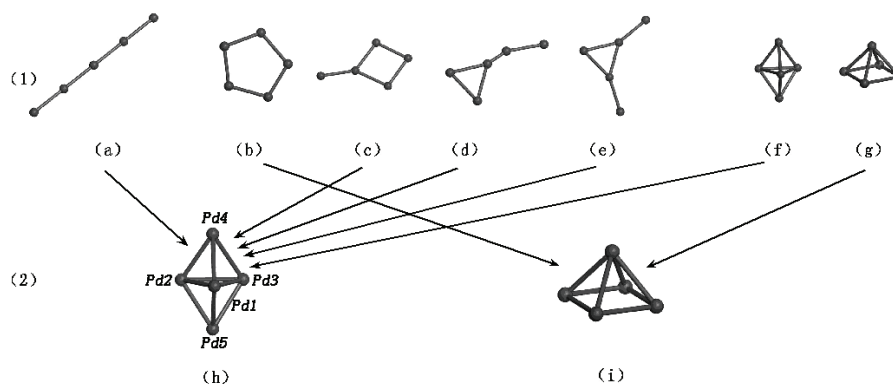


Figure 1: (1) Seven initial structures: (a) the line style, (b), (c), (d) and (e) the face style, (f) and (g) the body style; (2) two optimized structures, respectively are: (h) the triangular bipyramid and (i) the tetragonal pyramid.

According to the geometric knowledge, the adsorption positions of CO on the Pd₅ structure is divided into three categories, which respectively are: (a) the top site (the Pd atom), (b) the bridge site (the center of Pd-Pd bond), and (c) the hollow site (the center of Pd-Pd-Pd face). Moreover, there are three kinds of manners for CO molecules adsorbed on the Pd₅ cluster, and they are respectively: (a) the C atom adsorbed on the Pd₅ cluster in the CO molecular form, (b) the O atom adsorbed on the Pd₅ cluster in the CO molecular form, (c) the C atom and O atom are adsorbed on the Pd₅ cluster in the atomic form. It is summarized that the triangular bipyramid structure contains three kinds of unequal atoms, five kinds of unequal bonds, and three kinds of triangular faces. Therefore, 32 kinds of adsorption structure have been established for Pd₅CO. The optimization of all structures considers all possible spin states. There are mainly three points are summarized in the following. Firstly, the CO molecules on the Pd₅ structure by the O atom adsorbing converted to the C atom adsorbing, validating the structures with C atom adsorbed in the form of CO molecule are most stable. Secondly, the C atom adsorbed on the top site substitutes for the O atom after optimization, which explores that it is more stable when the C atom is adsorbed on the Pd₅ cluster. Thirdly, the C atom adsorbed on the bridge site shifts to the hollow site, showing the hollow site is more stable than the bridge site for adsorption. There is no imaginary frequency for all the structures, indicating all structures are correspond to genuine minima on the respective potential energy surfaces. Fig. 2 presents the BE distributions of the adsorption structures in (a), (b), and (c) respectively and gives out the lowest-energy geometries for three kinds of adsorption mode in (d), where all the most stable structures are singlet state. It is explored from Fig. 2(a) that the C atom adsorption structures should be the most stable. The adsorption

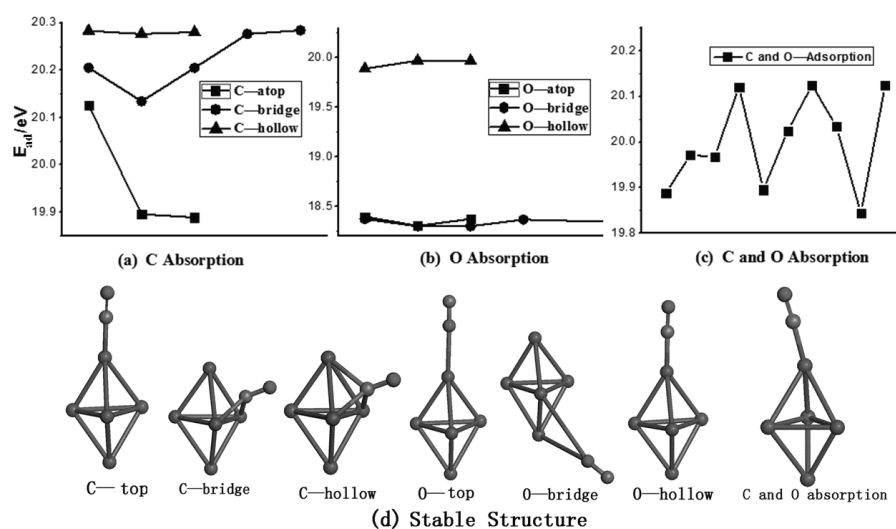


Figure 2: The binding energies (BEs) of all the structures: (a) with C atom adsorbed in the CO molecule, (b) with O atom adsorbed in the CO molecule; (c) with C atom and O atom adsorbed in the atomic form. (d) Gives out the lowest energy geometries of three different adsorption mode. C- and O- respectively indicates the C atom and O adsorption, where, top, bridge, and hollow presents the top site adsorption, bridge sites adsorption, and hollow sites adsorption respectively.

energies (E_{ads}) of seven local stable structures of Pd₅CO have been also calculated from $E_{ads} = E(\text{Pd}_n) + E(\text{CO}) - E(\text{Pd}_n\text{CO})$, where E^* is the total energies of the relaxed Pd_n, CO, and Pd_nCO. The higher E_{ads} indicates the more stability. The E_{ads} is often used to measure the capability of chemical reactivity for the cluster. The calculated E_{ads} of seven different structures of Pd₅CO are 1.91, 1.99, 2.07, 0.19, 0.16, 1.91 and 1.91 eV respectively, therefore, the structure with C atom adsorbed on the hollow site in the form CO molecule should be the most stable, as same as the conclusion reported by Zanti *et al.* [9]. The lengths of C-O bond of all Pd₅CO structures vary from 1.146 to 1.215 Å, longer than that of the free CO molecule bond (1.128 Å), and elongates by 3.55%, 5.32%, 7.71%, 2.13%, 1.60%, 3.55%, and 3.55% respectively, thus, the C-O bond strength of the most stable Pd₅CO structure is mostly influenced.

3.2 The stabilities and geometric structures of Pd₅(CO)_n (n=2 to 6)

It is known from the above analysis that the CO molecule adsorbs on the hollow site binding by the C atom in the most stable structure of Pd₅CO. However, if more CO molecules are adsorbed on the Pd₅ cluster, what are the most stable adsorption sites for the other CO molecules? Therefore, we continue to study the most stable structures of Pd₅(CO)_n (n=2 to 6) in the following. Firstly, we place the second CO molecule in all possible positions of the most stable Pd₅CO structure, and all structures are re-optimized without symmetry restriction. Secondly, the next CO molecule is orderly added to the previous optimized

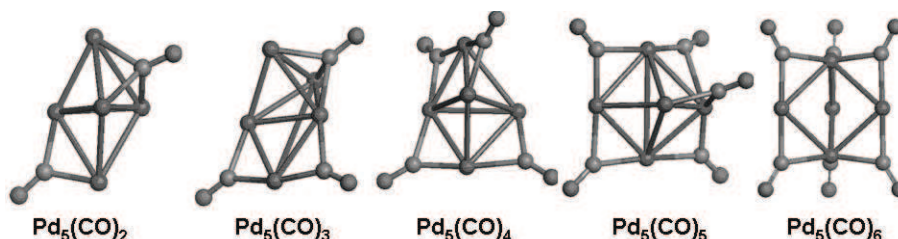


Figure 3: The most stable geometric structures of $\text{Pd}_5(\text{CO})_n$ ($n=2$ to 6).

structure until six CO molecules are adsorbed. Fig. 3 shows the most stable structures of $\text{Pd}_5(\text{CO})_n$ ($n=2$ to 6). It is found that for $\text{Pd}_5(\text{CO})_2$ and $\text{Pd}_5(\text{CO})_3$, the C atoms of the second and third CO molecules are adsorbed on the bridge sites, but the C atoms of the first CO molecule is still adsorbed on the hollow site. Whereas, for the most stable $\text{Pd}_5(\text{CO})_n$ ($n=4,5,6$), C atoms of all CO molecules are all adsorbed on the bridge sites. Because all the CO molecules are adsorbed in symmetrical positions, so the adsorption structures keep the integrality of the triangular bipyramid. The deformation of $\text{Pd}_5(\text{CO})_3$ is most of all.

The average adsorption energies (E_{ads}/n) for per CO molecule of $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6) are listed in Table 1. The E_{ads}/n is defined as: $E_{ads}/n = [E(\text{Pd}_n) + nE(\text{CO}) - E(\text{Pd}_n\text{CO})]/n$, which is an important indicator to measure the adsorbing capacity of each CO molecule. The positive value of E_{ads}/n indicates the exothermic reaction, and the higher value of the E_{ads}/n indicates the stronger adsorption strength. It is known from Table 1 that the synthesis of $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6) is exothermic, thus, they should be easily isolated in the experiment. Moreover, the E_{ads}/n of $\text{Pd}_5(\text{CO})_n$ ($n=2$ to 6) becomes smaller with the increase of CO molecules, amongst, $\text{Pd}_5(\text{CO})_2$ reaches maximum E_{ads}/n value, thus, $\text{Pd}_5(\text{CO})_2$ should be the most possible product.

3.3 Electronic structure

Table 1 lists the average adsorption energy (E_{ads}/n) of per CO molecule, HOMO-LUMO energy gap (E_g), average bond length of C-O[A(C-O)], average bond length of C-Pd[A(C-Pd)], the average Mulliken charge transference from C atom to Pd atom (AMC), vertical ionization potential(VIP), and vertical electron affinity (VEA) of $\text{Pd}_5(\text{CO})_n$. The E_g can reflect how much energy the excitation electron requires. The higher the E_g is, the harder the molecular is excited and the weaker the activity is. The calculated E_g of Pd_5 is only 0.17eV, while those of $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6) increase 0.31, 1.09, 1.44, 1.34, 1.3, and 1.33eV respectively, illustrating their enhanced dynamical stability compared to Pd_5 , however, $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6) do not display the increasing stability with the increase of the CO molecules. Obviously, $\text{Pd}_5(\text{CO})_3$ has the best dynamical stability amongst of all.

Table 1 also shows that the A(C-O) values of $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6) are longer than that of the free CO molecule(1.128Å), and increased by 7%, 6.2%, 5.31%, 4.42%, and 4.42% respectively, indicating the C-O bond length decrease with the increase of CO molecules,

Table 1: The average adsorption energy (E_{ads}/n) of per CO molecule, E_g , average bond length of C-O[A(C-O)] and C-Pd[A(C-Pd)], the average Mulliken charge transfer from C to Pd[average C-Pd(AMP)], vertical ionization potential(VIP), and vertical electron affinity (VEA) of $Pd_5(CO)_n$.

| | Pd ₅ | Pd ₅ CO | Pd ₅ (CO) ₂ | Pd ₅ (CO) ₃ | Pd ₅ (CO) ₄ | Pd ₅ (CO) ₅ | Pd ₅ (CO) ₆ |
|-----------------|-----------------|--------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| $E + ads/n(eV)$ | — | 1.96 | 2.10 | 1.92 | 1.83 | 1.68 | 1.63 |
| $E_g(eV)$ | 0.17 | 0.48 | 1.26 | 1.61 | 1.51 | 1.47 | 1.50 |
| A(C-O)(Å) | — | 1.21 | 1.20 | 1.19 | 1.18 | 1.17 | 1.17 |
| A(C-Pd) (Å) | — | 2.03 | 2.02 | 2.06 | 2.06 | 2.06 | 2.09 |
| C-Pd(AMP) (e) | — | 0.13 | 0.27 | 0.34 | 0.54 | 0.68 | 0.71 |
| VIP(eV) | 6.14 | 6.26 | 6.81 | 7.31 | 7.32 | 7.47 | 7.64 |
| VEA(eV) | 0.87 | 1.07 | 1.15 | 1.35 | 1.77 | 1.91 | 2.42 |

so the intensity of the C-O bond is weakened along with the more CO molecules adsorbing. The A(C-Pd) values of $Pd_5(CO)_n$ ($n = 2$ to 6) become larger when more CO molecules are adsorbed. As calculated, the sum of the radius of C and Pd is 2.05Å, which is larger than the A(C-Pd) values of Pd_5CO and $Pd_5(CO)_2$, but is smaller than those of $Pd_5(CO)_n$ ($n=3$ to 6). Furthermore, the charge transfer from C to O is about 0.11e, therefore, the C-O bond is weakened and the CO molecule is activated. The average charge transfer from C to Pd is increased from Pd_5CO to $Pd_5(CO)_6$. Thus, the ionic character of the C-Pd bond of $Pd_5(CO)_n$ ($n=1$ to 6) becomes more and more stronger. Therefore, the chemisorptions of CO molecules onto the Pd₅ cluster should be the non-dissociative adsorption process.

3.4 Frontier orbitals

In quantum chemistry, the reactivity of a molecule can be correlated with its frontier orbitals, vertical ionization potential (VIP), and vertical electron affinity (VEA). Commonly, the atom which contributes more to the HOMO should have the stronger ability for detaching electrons, whereas, the atom which occupies the main component of the LUMO should be easier to gain electrons. The VIP is defined as the total energy difference between the one electron positively charged and neutral clusters. The VEA is defined as the total energy difference between the one electron negatively charged and neutral clusters. Fig. 4 shows the wave functions of the HOMOs and LUMOs of Pd₅ and $Pd_5(CO)_n$ ($n=1$ to 6), where the dark and light grays represent the negative and positive parts of the wave functions. It is discovered from the figure that the HOMO of Pd₅ are mainly distributing on the three Pd atoms of the triangular face in the middle, but the LUMO of Pd₅ are distributing on the five Pd atoms. Furthermore, when the CO molecules are adsorbed onto the Pd₅ cluster, there exists electron transference from C to Pd known from the Mulliken charge analysis. Therefore, five Pd atoms have the ability to gain electrons. The wave functions of HOMO and LUMO of Pd₅ present the character of 4s orbital from the shape of the electron cloud, which explores the five Pd atoms of Pd₅ possess some unpaired electrons which lead to net magnetic moments. For $Pd_5(CO)_n$, the HOMO and LUMO are hardly occupied on the CO molecules, thus, the CO molecules contribute lit-

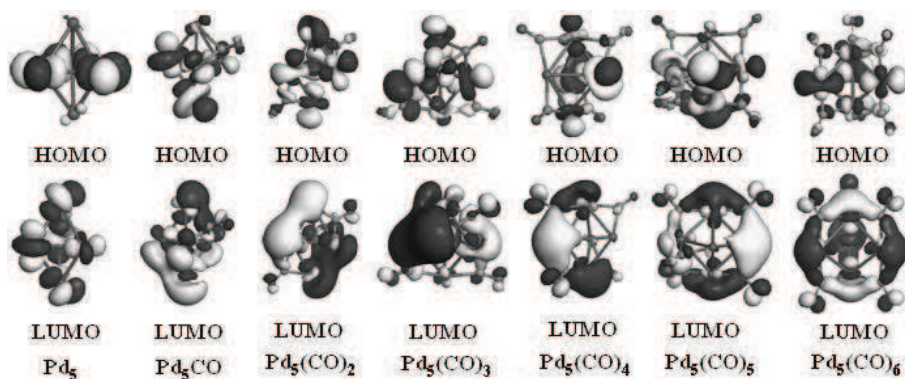


Figure 4: The wavefunctions of the HOMOs and LUMOs of Pd_5 and $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6).

tle to HOMO and LUMO. The 4s orbit of the Pd_5 clusters is rearranged after adsorbing CO molecules, which cause the redistribution of the HOMO and LOMO component. The calculated VIP and VEA of Pd_5 respectively are 6.14eV and 0.87eV, however, those of $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6) are become larger with the increase of the CO molecules. Therefore, along with the increase of CO molecules, the ability for detaching electrons of the cluster is weakened and the ability for obtaining electrons is improved.

3.5 Magnetic moment

The Mulliken charge of the two Pd atoms at the top of the triangular bipyramid structure of Pd_5 are -0.03e, and that of the three Pd atoms of triangular face in the middle are 0.015, 0.015, 0.03e respectively, so the net magnetic moment of Pd_5 is $2\mu_B$. For $\text{Pd}_5(\text{CO})_n$, the electrons transfer from C to Pd is become larger when more CO molecules are adsorbed, however, $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6) have no magnetic moment. Next, we discuss the reason for the question why $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6) are nonmagnetic. The ground state of Pd atom has a closed-shell configuration of $[\text{Kr}]4d^{10}$, thus it has no magnetic moment. For Pd_5 , the Mulliken charge analysis shows that the configuration of five Pd atoms are $4d^{0.521}5s^{-0.016}5p^{0.000}$, $4d^{0.389}5s^{-0.009}5p^{-0.004}$, $4d^{0.389}5s^{-0.010}5p^{-0.004}$, $4d^{0.376}5s^{-0.012}5p^{0.008}$, $4d^{0.377}5s^{-0.012}5p^{0.008}$, respectively, here, the superscript is the net spin. It is clear that each Pd atom possesses some unpaired electrons and the magnetic moment of Pd_5 is $2\mu_B$. While, the configurations of five Pd atoms of $\text{Pd}_5(\text{CO})_n$ are all $4d^{0.000}5s^{0.000}5p^{0.000}$, there are maybe two reasons, on one hand, the CO molecules provide electrons to the Pd_5 cluster, on the other hand, the orbital hybridization and charge arrangement happened again between five Pd atoms, causing the isolated electrons to be paired, thus, $\text{Pd}_5(\text{CO})_n$ ($n=1$ to 6) have no magnetic moment, as same as the case of Pd_2CO [7]. For example, Zanti *et al.* [7] explored that the configuration of each Pd atom of the Pd_2 cluster is $4d^{10-x}5s^x$, but becomes $4d^{10}$ for Pd_2CO .

4 Conclusion

In this paper, there are six main conclusions are summarized as follows:

(1) For Pd₅CO, the singlet state structure with C atom adsorbed on the hollow site in the form of CO molecule is the most stable in the 32 isomers considered, as same as the conclusion reported by Zanti *et al.*

(2) For Pd₅(CO)₂ and Pd₅(CO)₃, the first CO molecule is adsorbed on the hollow site, the second and third CO molecules are adsorbed on the bridge sites, but for the most stable Pd₅(CO)_n (*n*=4,5,6), all CO molecules are adsorbed on the bridge sites.

(3) Pd₅(CO)_n (*n*=1 to 6) should have the enhanced dynamical stability compared to Pd₅, amongst of all, Pd₅(CO)₂ should be the most possible adsorption product known from the adsorption energy, and Pd₅(CO)₃ has the best dynamical stability indicated by its largest E_g .

(4) The chemisorptions of CO molecules on the Pd₅ cluster surface is a non-dissociative adsorption process and the strength of C-O bond became weaker when more CO molecules are adsorbed.

(5) The CO molecules contribute little to the component of HOMO and LUMO, and cause the redistribution of the component of HOMO and LUMO. For Pd₅(CO)_n (*n*=1 to 6), the abilities of detaching electrons are weakened and the abilities of obtaining electrons are improved along with the increase of the CO molecules.

(6) The magnetic moment of Pd₅ is $2\mu_B$, however, Pd₅(CO)_n (*n*=1 to 6) have no magnetic moment.

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