# Large adsorption energies for CO on $Sc_n$ ($n$ = 2–8, 13) nanoclusters*

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In order to seek a transition metal cluster with high ability to adsorb CO molecule, the author performs a density function theory calculation on $COSc_n$ ($n$ = 2–8, 13) clusters. The results demonstrate that $COSc_n$ ($n$ = 2–8, 13) clusters have the large adsorption energies of which the values are over 3.6 eV, and the elongations of C–O bond length exceed 20% in most calculated sizes. Adsorbing CO contributes to the improvement of the chemical activity, but reduces the magnetic moment of corresponding $Sc_n$ cluster.

**Keywords:** $Sc_n$ clusters, CO adsorption, structures, electronic properties

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## 1. Introduction

Transition metal (TM) cluster always possesses complex surface- and large surface-to-volume ratios, so it can be used more easily as a favorable catalysis than corresponding bulk. Therefore, the study of the electronic properties for small molecule adsorbed on the TM nanocluster has aroused great interest of researchers in recent years.[1–5]

Among all of the clusters of 3d series, small scandium (Sc) clusters ($Sc_2$–$Sc_{20}$) have been main subject of studying the dependence of magnetic moments on cluster size during the past years.[6–9] Like the exploration of the variation of magnetism of the pure Sc cluster, theoretical researches of the complexes such as $Sc_nAl$, $Sc_nMn$, $Sc_nFe$, etc. also focused on the effect on the magnetic moment from the doping atoms (Al, Mn, Fe, etc.). These studies have come to the universal conclusion that all of the doping atoms, from an overall perspective, tend toreduce the magnetic moments of corresponding Sc clusters.[9–11]

As is well known, Sc atom has not only a large atomic radius in 3d series, but also surface effect in nanocluster-size, these characteristics mean that Sc cluster should have a high adsorption efficiency in the process of adsorbing small molecules. However, no report on such an adsorption behavior is available to date. By contrast, there are a wide variety of studies about the interaction between other TM clusters (such as Mn, Au, Ni, Pd) with certain small molecules,such as carbon monoxide (CO).[12–15] According to these earlier investigations, studies of the electronic and magnetic properties of the CO–$X_n$ ($n$ = Mn, Au, Ni, Pd, etc.) complexes have beena critical focus area. It is worth noting that, however, the adsorption energies of CO adsorbed on these TM clusters are rather small in most sizes, and the biggest value of them is generally no more than 2 eV. Such an exhibition suggests the relatively low adsorption efficiency of CO molecule. A special case is the adsorption of CO on yttrium (Y) clusters, a series of large values of adsorption energies was theoretically given as the size of $Y_nCO$ cluster varies, in which the values are above 3 eV in most cases.[16] Nevertheless, the application of Y in a variety of experiments is very limited no matter whether it is cluster or bulk. Although Y clusters exhibit high adsorption efficiency in adsorbing CO, NO,[16,17] it is merely of theoretical significance in a certain sense. In comparison to Y, the bulk of Sc is widely used in various experiments relating to the new materials preparation. Therefore, it has practical significance to investigate the interaction between small molecule and Sc nanoclusters. Given this, the electronic properties of $COSc_n$ ($n$ = 1–8, 13) clusters can be studied in detail. The calculated adsorption energies of $COSc_n$ complexes are beyond 3.5 eV in most cluster sizes, showing the favorable efficiency of the catalytic performance of Sc nanoclusters. It is hoped that our findings could be useful for some relevant experiments in seeking the new kind catalyst with high performance.

## 2. Computational method

All calculations were performed by employing density functional theory (DFT) implemented in the DMOL3 package.[18] The exchange–correlation interaction was treated within the generalized gradient approximation (GGA) by using Perdew–Burke–Ernzerhof (PBE) function.[19] The treatment of electrons-core was based on the employment of the DFT-based semi-core pseudopotential (DSPP),[20] and a double numerical basis including d-polarization function (DND) were chosen.

The accuracy of the way described above was tested by

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the computations on small $Sc_2$ dimer and CO molecule. For $Sc_2$, the quintet state is energetically the lowest among all spin multiplicities in this calculation, which is in good consistence with other theoretical results[7,8] and the experimental ones.[21,22] For CO, the bond length 1.142 Å and vibrational frequency 2096.29 $cm^{-1}$ are all in accordance with the experimental values of 1.128 Å and 2143.2 $cm^{-1}$,[23] respectively. This suggests that our method used here is suitable to studying the small $COSc_n$ ($n = 2$–8, 13) clusters.

## 3. Results and discussion

### 3.1. Ground state structures

The ground state geometries of the pure $Sc_n$ ($n = 2$–8, 13) clusters, which are in good consistence with other theoretical calculations,[8] are first optimized as shown in Fig. 1. On the basis of the optimized $Sc_n$ geometries, different adsorption sites of CO molecule for determining the different-sized $COSc_n$ isomers, i.e., top site, bridge site, and face site, are taken into account. For all isomers of each cluster, the local minima of the potential energy surface are guaranteed by the harmonic vibrational frequencies without imaginary mode. In addition, the initial structures in different spin states are optimized. Among all of the calculated results, the lowest energy structures of $COSc_n$ isomers ($n = 2$–8, 13) are chosen and regarded as the ground state structures, which are also plotted in Fig. 1.

All of the ground state structures of $COSc_n$ ($n = 2$, 3, 4, 6, 8, and 13) complexes are viewed as C atom adsorbed on face position of corresponding $Sc_n$ cluster (except for $n = 2$). Meanwhile, the O atom prefers to bond with neighboring Sc atoms, covering another face laterally. An important feature of this evolution is that the basic framework of corresponding $Sc_n$ cluster, within the range of $n = 2$, 3, 4, 6, 8, and 13, is not modified even though CO is adsorbed on the face position. However, essentially structural change occurs at $n = 5$, 7. One can see that the triangular bipyramid structure of $Sc_5$ transforms into a square pyramid with C atom nearly in the center of the bottom. Meanwhile, O atom still shows the tendency to unite with other two Sc atoms by occupying the bridge site. Similarly, the adsorption of CO leads to the fundamental alteration of the host $Sc_7$ cluster, accompanied by the alike adsorption model as $n = 5$.

Such evolution behaviors are basically similar to those of $COY_n$ complexes,[16] but different from those of CO on Ni, Pd, Au, and Mn clusters where the C atom of CO tends to occupy the bridge site (Mn, Ni), or top position (Mn, Au, Pd) of corresponding cluster.[12–15] Apparently, the adsorption model of face site easily makes more Sc atoms bond with C atom, giving rise to the enhancement of adsorption strength.

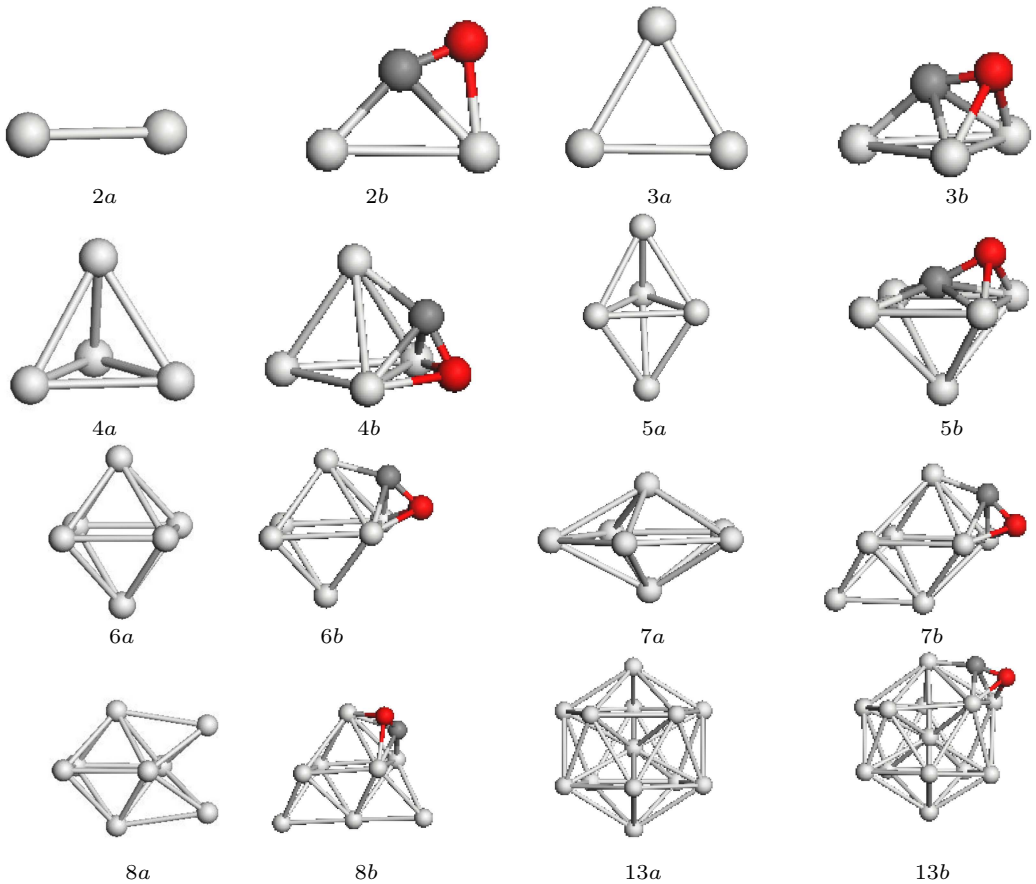



**Fig. 1.** (color online) Ground state structures of pure $Sc_n$ and $COSc_n$ clusters. The red and gray balls represent O and C atoms, respectively.

### 3.2. Adsorption strength and electronic properties

The adsorption strength between cluster and small molecule can generally be reflected by the adsorption energy which is defined as

$$E_{\text{ads}} = -\left[E(\text{COSc}_n) - E(\text{Sc}_n) - E(\text{CO})\right],$$

where $E(n)$ is the total energy of the relaxed $\text{Sc}_n$, CO, and $\text{COSc}_n$.

Figure 2 shows the plot of the calculated adsorption energy versus cluster size. It is seen that the adsorption energy follows the tendency of oscillational increase in the size range of $n = 2$–5, exhibiting the largest value of 4.43 eV at $n = 5$. Then, the variation of this value basically is in the range from 3.8 eV to 3.9 eV at $n = 6$, 7, 8, and 13. Obviously, the adsorption energies calculated here are significantly larger than those of $X_n\text{CO}$ series ($X$ = Mn, Au, Ni, and Pd), in which the values are not beyond 2 eV in most cases.[12–14] Even though $\text{Y}_n$ exhibits favorable performance in the sense of adsorbing CO molecule, the value of adsorption energy is still less than those of $\text{COSc}_n$ complexes in most sizes as shown above. Namely, our calculated results suggest that Sc exhibits a bigger value of adsorption energy in regard to adsorbing CO molecule in most sizes than those of other TM clusters.

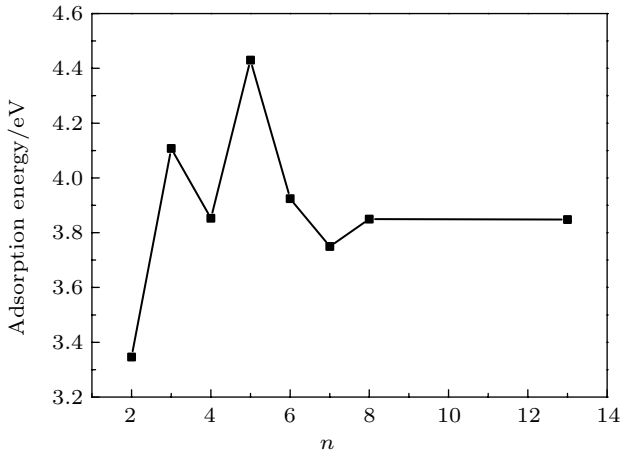



**Fig. 2.** Adsorption energies of $\text{COSc}_n$ ($n = 2$–8, 13) clusters.

A necessary step of analyzing the catalytic ability is to explore the variation of bond length and vibrational frequency of small molecule adsorbed on cluster. Hence, we present the calculated C–O bond lengths and vibrational frequencies of CO for corresponding $\text{COSc}_n$ ($n = 2$–8) clusters in Fig. 3. In comparison with the bond length of 1.142 Å of free CO molecule, the bond length of C–O, when CO is adsorbed on $\text{Sc}_n$ cluster, becomes longer in all of the sizes, and the value of elongation are beyond 20% except for $n = 2$. Specially, the outstanding peak of 1.529 Å at $n = 5$ indicates that the interaction between C and O is so weak that the C–O bond appears to be faint.

Such an extension amount is far more than those in CO adsorbed on Mn, Ni, Pd, and Au clusters, in which the C–O bond length is roughly 1.1 Å.[12–15] It is noted that the variation tendency of bond length of C–O in $\text{COY}_n$ complexes is coincident with $\text{COSc}_n$ clusters in the same size with the exception of $n = 8$.[16] In contrast to the molecular adsorptions of $\text{CO}X_n$ ($X$ = Mn ,Ni, Pd, and Au ) complexes, which correspond to a really small elongation of C–O bond length, the adsorption of CO on $\text{Sc}_n$ cluster could be regarded as dissociated adsorption according to the size of C–O bond length.

As far as the vibrational frequency is concerned, the calculated results show a trend opposite to the variation of bond length. As displayed in Fig. 3, $\text{COSc}_2$ has the largest value of 1254.51 $\text{cm}^{-1}$ whereas smallest dip is found at $n = 5$ (717.8 $\text{cm}^{-1}$). In addition to these, an invariable trend of vibrational frequency can be observed in other range, in which the value is almost aconstant of about 1050 $\text{cm}^{-1}$. In fact, all of the C–O vibrational frequencies are evidently smaller than 2096.29 $\text{cm}^{-1}$ of the free CO molecule. Such behaviors imply that a large red shift occurs under the interaction of Sc atoms, and the red shift reaches 50% at least.

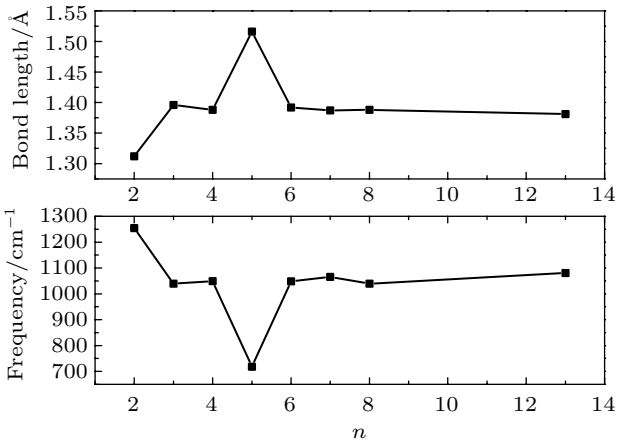



**Fig. 3.** CO bond lengths (above) and vibrational frequencies (below) of $\text{COSc}_n$ ($n = 2$–8, 13) clusters.

According to the discussion above, we easily learn that $\text{COSc}_5$ is in possession of the large adsorption energy and weakened interaction between C and O atom in comparison to the structures of other sizes. This could be attributed to the unusual structure as discussed in Section 1, in which the C atom contributes to bond with four Sc atoms instead of adopting the pattern as done by the structures with other sizes. As is well known, the electronic configuration of an isolated C atom is $2s^2 2p^2$, which will redistribute to $sp^3$ hybridization to form four equivalent C–Sc bonds as C approaches four Sc atoms. This behavior is actually in favour of the stability of the corresponding cluster. In this case, the O atom has more chances to bond with near Sc atoms to form stronger Sc–O bonds which can be mirrored by the shortest Sc–O bong length as displayed in Table 1, leading to the improvement of the stability of $\text{COSc}_5$ cluster.

The energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is a commonly used measure of the ability for cluster to undergo activated chemical reactions with small molecule,

so we analyze the variation tendencies of the HOMO–LUMO gaps for $Sc_n$ and $COSc_n$ clusters.

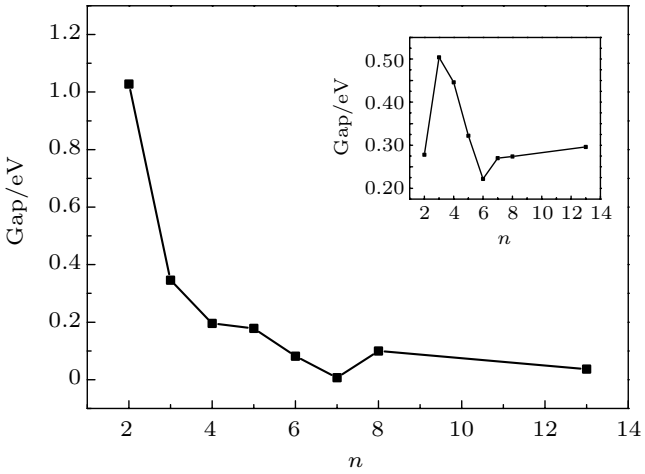



**Fig. 4.** HOMO–LUMO gaps of $Sc_n$ (small figure) and $COSc_n$ ($n = 2$–8, 13) clusters.

First, the change trends of the HOMO–LUMO gaps of $Sc_n$ ($n = 2$–8, 13) calculated here are in consistence with the outcomes presented in Ref. [8]. It is found that within the calculated range, the HOMO–LUMO gaps for $Sc_n$ maintain the values in a range of about 0.28 eV–0.4 eV in most sizes, with a sharp drop from $n = 3$ (0.50 eV) to $n = 6$ (0.21 eV). However, dramatic changes occur due to the adsorbing CO molecule. One can see that the energy gap has a relatively large value (about 1.0276 eV) at $n = 2$, then it rapidly decreases as the size increases from $n = 3$. Also, all of the values are less than 0.1 eV in a range of $n = 6$, 7, 8, and 13, in which a value of local minimum (about 0.0073 eV) is found at $n = 7$. Smaller energy gap usually means high chemical activity for corresponding cluster, so it is possible for $COSc_n$ clusters to interact with more CO molecules in the relatively larger size.

For exploring the essence of interaction between CO and $Sc_n$ cluster, the partial densities of states (PDOSs) for different size clusters are calculated. Here, the PDOS for $COSc_n$ ($n = 3$, 5, and 7) are selectedas displayed in Figs. 5–7, respectively.

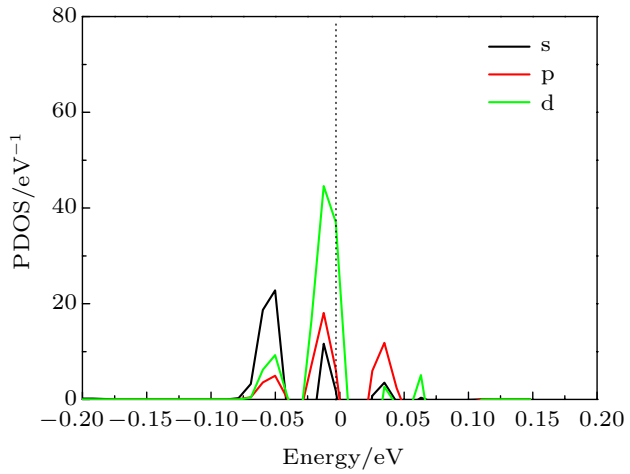



**Fig. 5.** (color online) Partial densities of states (PDOSs) of $COSc_3$ clusters.

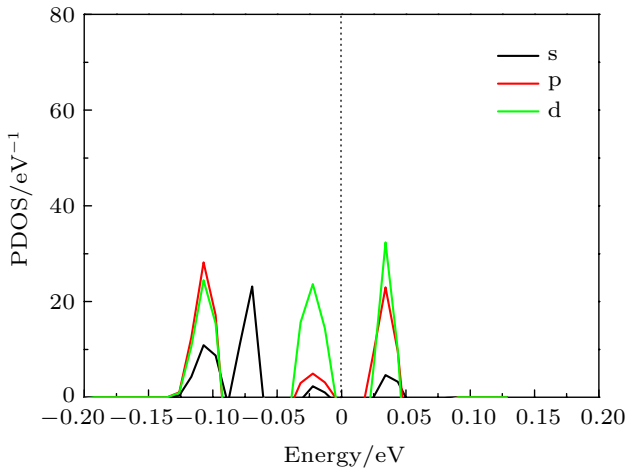



**Fig. 6.** (color online) Partial densities of states (PDOSs) of $COSc_5$ clusters.

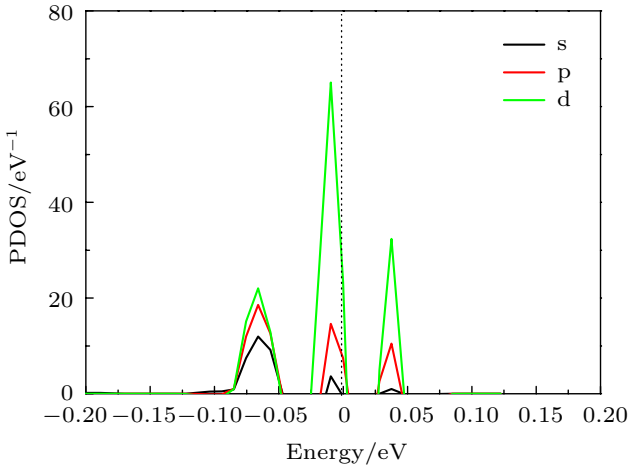



**Fig. 7.** (color online) Partial densities of states (PDOSs) of $COSc_7$ clusters.

It is seen that both $COSc_3$ and $COSc_7$ have similar features at the lower energy states. Namely, two sharp peaks at the Fermi level can be clearly observed which means that the strong s–p–d overlaps. Besides, the contribution from d state seems to be large near the Fermi level (about −0.01 eV), whereas weak s–p–d overlaps, which is the same characteristic at the higher energy level (about 0.03 eV) for both $COSc_3$ and $COSc_7$.

However, distingushing features of three prominent peaks for $COSc_5$ at the energy levels from −0.15 eV to 0 are observed, showing strong localization of bonding electrons. Generally, more peaks of s–p–d overlaps near the Fermi level always mean the intense interactions between CO and $Sc_5$ cluster. This resultaccords well with the description of adsorption energy, as well as the exhibition of C–O bond length and vibrational frequency.

### 3.3. Charge transfer and magnetism

The variation of magnetism of $Sc_n$ cluster, derived from the adsorption of CO molecule, is also the interesting topic to be discussed. As we know, $Sc_n$ ($n = 2$–13) complexes always

possess relatively large magnetic moments in certain cluster sizes as shown in Table 1. However, adsorbing CO results in the dramatic decreases in these sizes, even the quenching for $n = 2$, 4, and 6. This result is adverse to Mn cluster, in which the adsorbed CO molecule enhances the magnetism of pure $Mn_n$ cluster at $n = 4$, 6–8.[12] Even though the magnetism of $Y_n$cluster is weakened due to the adsorption of CO, the $COY_n$ complexes still maitain certain magnetic moments in a few sizes such as $n = 3$, 6.[16]

Given this, the analysis of charge transfer, as well as the magnetic ordering of $COSc_n$ complexes is necessary, which is calculated as displayed in Table 1.

In CO–$X$ ($X$ = Ni, Au, Mn, Pd ) series, much attention has been paid to the variation of C–O bond which provides sufficient information about the electronic properties of corresponding cluster.[12–15] However, the interaction between O and $X$ atom ($X$ = Ni, Au, Mn) is regarded as being weak due to the indirect bond between O and $X$ atoms, so the authors insist that O–$X$ ($X$ = Ni, Au, Mn) bond makes almost no contribution to the stability of corresponding cluster. By contrast, Y–O bond has important effects on the stability, electronic properties and magnetism of $COY_n$ clusters. Nevertheless, no comparison can be found between Y–C and Y–O bond.[16] As is well known, the adsorption behavior of CO on $Sc_n$ cluster is similar to those of $COY_n$ complexes. Then, it is significant to study the interplay between Sc–C and Sc–O, as well as the charge transfer between CO and $Sc_n$ clusters. Here, both the average bond lengths of Sc–C and Sc–O are simultaneously calculated to compare these differences.

**Table 1.** Values of average bond length of Sc–C and Sc–O ($L$), Mulliken charge transfer distribution ($Q$) of the C and O atoms, magnetic moments ($M$) of $Sc_n$, $COSc_n$, C, and O atoms.

| $n$ | $L$/Å | | $Q$/e | | $M/\mu_B$ | | | |
|---|---|---|---|---|---|---|---|---|
| | Sc–C | Sc–O | C | O | $Sc_n$ | $COSc_n$ | C | O |
| 2 | 1.961 | 2.000 | −0.018 | −0.482 | 4 | 0 | 0 | 0 |
| 3 | 2.094 | 2.088 | −0.191 | −0.569 | 1 | 1 | −0.028 | −0.015 |
| 4 | 2.009 | 2.094 | −0.149 | −0.572 | 2 | 0 | 0 | 0 |
| 5 | 2.187 | 2.004 | −0.220 | −0.607 | 1 | 1 | −0.028 | −0.003 |
| 6 | 2.118 | 2.114 | −0.150 | −0.576 | 2 | 0 | 0 | 0 |
| 7 | 2.119 | 2.104 | −0.141 | −0.572 | 1 | 1 | 0 | −0.001 |
| 8 | 2.124 | 2.113 | −0.125 | −0.576 | 4 | 2 | −0.006 | −0.004 |
| 13 | 2.135 | 2.113 | −0.120 | −0.570 | 19 | 5 | −0.026 | −0.006 |

It could be readily seen that the change of average bond length of Sc–C is closely related to the cluster size, from 1.961 Å at $n = 2$ to 2.135 Å as $n = 13$. By contrast, the Sc–O bond in corresponding size seems to be shorter, indicating that the interaction between Sc and O is stronger than that of Sc–C. Specially, the local minimum (2.003 Å), except for $n = 2$, is observed with $n = 5$, implying comparatively strengthened interplay occurs between CO and $Sc_5$ cluster. This is coincident with the exhibition of stability discussed above. In comparison with $COY_n$ clusters, the values of Sc–O are apparently smaller than those of Y–O bonds (2.147 Å–2.169 Å),[16] which illustrates that the action force between CO and $Sc_n$ clusters is greater than that between the $COY_n$ complexes.

In regard to the charge transfer of $COSc_n$ clusters, we find that both C and O atoms gain electrons in all of the calculated sizes, and the electrons accepted by O atom are more than those by C atom, and the difference between the numbers of accepted electrons is about 0.45e. Obviously, the fact that more electrons are accepted by O atom means the strengthened interaction between O and Sc atoms as comparedwith that between C–Sc bonds. Moreover, the number of electrons accepted by O atom (0.607e) for $COSc_5$ is the biggest in all of the calculated range, which is in accord with the exhibition of the shortest bond length of Sc–O at $n = 5$. Such a result is fundamentally different form those from $COMn_n$, $COAu_n$ series, in which C atom prefers to lose electrons whereas O atom prefers to accept electrons.[12,13] Although similar charge distributions of C and O atoms in $COY_n$ clusters is also observed,[16] the accepted electrons of them are less than those of $COSc_n$ series calculated here.

Besides, we perform a detailed investigation of the magnetism of $COSc_n$ series so as to analyze the influence of adsorbing CO on the $Sc_n$ clusters. First, the magnetic moment of pure $Sc_n$ clusteris calculated as shown in Table 1, and the outcomes accord well with the results reported earlier.[8]

As is well known, the free CO molecule has no magnetic moment. However, adsorbing CO has an effect on the magnetic moments of the $Sc_n$ clusters. One can see that the magnetic moments of bare $Sc_n$ clusters decrease as a whole, along with the exhibition of antidirection magnetic ordering of C and O atoms in certain sizes. For example, the antiferromagnetic moments of C and O atoms (−0.028 $\mu_B$ for C, and −0.003 $\mu_B$ for O) are found in $COSc_5$ cluster. It is clear that adsorbing CO tends to weaken the magnetic moments of pure $Sc_n$ clusters, even the quenching for $n = 2$, 4, and 6.

In general, the magnetic moments of clusters are closely related to the overlap of the orbitals and geometrical symmetry. This is the fact in the $COSc_n$ complexes. One can see that

the adsorption of CO molecule lowers the symmetry of corresponding structure of the host $Sc_n$ cluster. Meanwhile, severe interaction between CO and $Sc_n$ cluster contributes to the improvement in the orbital hybridization between them. All of these make Sc atom of corresponding cluster not keep the 3d state localized, which naturally gives rise to the reduction of the magnetic moment in corresponding cluster size.

## 4. Conclusions

The structures, electronic, and magnetic properties of the $COSc_n$ clusters ($n = 2$–8, 13) are investigated by using density-functional theory (DFT) with spin-polarized generalized gradient approximation. The results show that the basic frameworks of most host $Sc_n$ clusters, except for $n = 5$ and 7, still have the adsorption the same as the that of CO molecule. The C atom prefers to be adsorbed on the face site while the O atom is also inclined to bond with the neighboring Sc atoms. The $Sc_n$ clusters exhibit high adsorption ability based on the analysis of the large adsorption energy, lengthened C–O bond, and weakened vibrational frequency between the C and O atoms. Adsorption of CO contributes to the enhancement of chemical activity of the corresponding $Sc_n$ cluster. The Sc–O bond has a particularly important effect on the interaction between CO and $Sc_n$ clusters. The adsorbing of CO reduces the magnetic moments for certain host $Sc_n$ clusters by providing the antiferromagnetic moments of C and O atoms.

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