DENSITY FUNCTIONAL CALCULATIONS ON SPECTRUM AND ELECTRONIC PROPERTIES OF $W_NCO$ ($N = 1 \sim 6$) CLUSTERS

XIURONG ZHANG*, YANGYANG WANG†, FUXING ZHANG‡ and AIHUA YUAN‡

*School of Mathematics and Physics, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu 212003, P. R. China
†School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu 212003, P. R. China
‡School of Biology and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu 212003, P. R. China
*zh4403701@126.com

Received 11 January 2013
Revised 23 February 2013
Accepted 4 March 2013
Published 1 July 2013

The spectrum and electronic properties of $W_nCO$ ($n = 1 \sim 6$) clusters have been studied by using density functional theory (DFT) at the B3LYP/LANL2DZ level. It is found that the vibrational frequencies of the strongest infrared intensity are in a range of 1674.3–1846.4 cm$^{-1}$. For each cluster, the vibration modes at the strongest peak are both IR and Raman active, and be assigned to CO stretching modes. The polarizability analyses indicate that the mean dipole polarizabilities increase monotonically with the increase of cluster size, except $W_6CO$ cluster. In addition, the ionization energies and electronegativities analyses manifest that the $W_2CO$ cluster has well attracted electronic ability; $W_6CO$ cluster is the easiest to lose electrons in all $W_nCO$ clusters.

Keywords: $W_nCO$ ($n = 1 \sim 6$) clusters; spectrum analysis; electronic properties.

PACS numbers: 36.40.Mr, 36.40.Cg, 31.15.E-

1. Introduction

In the past few years, gas molecules adsorbed on transition metal clusters has been widely investigated owing to their unique physical and chemical properties, such as extreme hardness, high melting point, chemical inertness, interesting catalytic behavior, etc. Carbon monoxide is one of the most important gases which participate in catalytic processes in heterogeneous phase. Adsorption of carbon monoxide on metal and metalloid surfaces is important, especially for transition metals have been...
investigated from many aspects. For example, the interaction of one CO molecule with partial transition metal clusters in geometries and electronic properties by density functional theory (DFT) have been systemically studied by Tian et al.\textsuperscript{11–14} Several studies concerning the energetic\textsuperscript{15,16} and infrared (IR) characteristics\textsuperscript{17,18} of CO adsorption on transition metal surfaces have appeared in the articles, even the adsorption of CO on transition metal doped nanotube has been concerned.\textsuperscript{19}

It is well known that tungsten metal is one of the important catalysts for the removal of carbon monoxide from auto exhaust gases. Thus, several experiments and theories\textsuperscript{20} have been done to comprehend the interaction about CO molecule with tungsten clusters. It was found that adsorption of CO, O\textsubscript{2} on W\textsubscript{n} clusters (n < 10) have low reactivity and low dependence on cluster size. By pulsed fast flow reactor techniques, the CO reactivity of W\textsubscript{1}–W\textsubscript{7} was found to exhibit an essentially monotonic increase with cluster size.\textsuperscript{21} Based on the IR spectrum experiments and DFT calculations, Lyon\textsuperscript{18} reported that only for smaller W\textsubscript{n} clusters with n = 5 ∼ 9, 11 attributable to C–O stretch vibrations are detectable. For larger clusters there are no noticeable absorption bands observed. Hence, tungsten apparently shows size dependant nondissociative bonding of carbon monoxide on the clusters. Ishikawa et al.\textsuperscript{22} studied M(CO)\textsubscript{n} (M = Cr, Mo, W; n = 3 ∼ 6) in the gas phase, showed that C and O could well reproduce the absorption frequency and the symmetry characteristic vibrational patterns of CO coordinated in M(CO)\textsubscript{n}. The results suggest that M(CO)\textsubscript{n}−1 keeps its parent skeleton in M(CO)\textsubscript{n}−1–CO dissociation process.

However, there has been no theoretical study on IR vibration spectrum and static polarizability of the W\textsubscript{n}CO (n = 1 ∼ 6) clusters till now. Recently, the structural, adsorption and electronic properties of one single CO molecule adsorbed on W\textsubscript{n} (n = 1 ∼ 6) clusters have been studied by our group.\textsuperscript{23} As an extension work, we perform a comprehensive study on the IR vibration spectrum, static polarizability and thermodynamical property of the W\textsubscript{n}CO (n = 1 ∼ 6) clusters, which could furnish a better understanding in the interaction between CO molecule and tungsten atoms, and could find new functional materials.

2. Computational Methods

In this paper, all calculations for W\textsubscript{n}CO (n = 1 ∼ 6) clusters were performed with the Becke’s three parameters hybrid functional (B3LYP) method and the basis set LANL2DZ in the GAUSSIAN 03 program. In order to test the quality of computational methods which we used, we calculated some properties of W\textsubscript{n} clusters, CO molecule and WCO cluster. For W\textsubscript{n} clusters, the most stable isomers and their optimized geometrical parameter, EA, and dissociation energy (adiabatic and vertical dissociation energies) by using B3LYP/LANL2DZ functional have been reported in our previous works,\textsuperscript{24,25} and all in good agreement with available experimental values.\textsuperscript{26,27} For a free CO molecule, the bond length 0.116 nm and bond energy 10.98 eV are in accordance with the corresponding experimental values (0.1128 nm and 11.24 eV)\textsuperscript{28} and 0.113 nm, 11.02 eV with the 6-311+G(3df)
Density Functional Calculations on Spectrum and Electronic Properties

basis set method. As for WCO cluster, through comparing the B3LYP/LANL2DZ/6-311+G(3df) method (LANL2DZ basis set for W atom, 6-311+G(3df) for CO atoms) and the B3LYP/LANL2DZ method, we could find that they have the same calculated results (bond length about 0.191 nm and spin multiplicity about 5). This test indicates that the B3LYP/LANL2DZ method is reliable and sufficient to the system. Furthermore, we also use Multwif and Gaussian-View softwares to show the graphics of vibration spectrums and static polarizabilities for $W_n CO$ ($n = 1 \sim 6$) clusters.

3. Results and Discussion

3.1. Geometrical structure

One of the most important things in studying clusters is to determine the geometry of the ground states. In order to locate the global minimum and avoiding trapping in the local minima, the initial configurations are obtained by optimizing independent geometries and referring to previous results. During choosing initial configurations of CO–$W_n$ complexes, the low-lying isomers of bare W clusters were considered as the reactants of CO at various possible adsorption sites, including the atop, bridge and hollow sites. Then the adsorption structures are optimized without any symmetry constraints. Finally, the configuration with the lowest energy is taken as the ground-state structure. The ground-state structures of $W_n CO$ ($n = 1 \sim 6$) clusters are shown in Fig. 1. The blue ball is considered as tungsten atom; the red one represents oxygen atom and the gray ball represents carbon atom. The ground state structures of $W_n CO$ ($n = 4 \sim 6$) clusters are trigonal bipyramid structure, quadrangle and triangular prism structure. With the increase of cluster size, the structural growth model of the $W_n CO$ ($n = 1 \sim 6$) clusters transforms from double-dimensional (2D) to three-dimensional (3D). We also find that most of molecular adsorption states about CO on $W_n$ clusters are end-on type geometries; the bridge site adsorption type geometry plays a supplementary role. The interaction of CO on $W_n$ clusters is a nondissociative adsorption; this is in accordance with the previous experimental values.

3.2. Vibrational frequencies and spectrum analysis

The vibrational frequency information about small molecule absorbed on the clusters can usually be used to evaluate the catalytic ability. The vibrational frequency of the strongest IR intensity ($^b$Freq) and the lowest-vibrational frequency ($^a$Freq) about $W_n CO$ ($n = 1 \sim 6$) clusters are listed in Table 1, the vibrational modes are
Fig. 1. Ground state structures of $W_n$ ($n = 2 - 6$) and $W_nCO$ ($n = 1 - 6$) clusters (obtained in Ref. 23).

Table 1. Vibration frequencies of $W_nCO$ ($n = 1 - 6$) clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$W_1CO$ ($C_S$)</th>
<th>$W_2CO$ ($C_S$)</th>
<th>$W_3CO$ ($C_S$)</th>
<th>$W_4CO$ ($C_S$)</th>
<th>$W_5CO$ ($C_S$)</th>
<th>$W_6CO$ ($C_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aFreq/(cm$^{-1}$)</td>
<td>374.1</td>
<td>75.1</td>
<td>74.2</td>
<td>56.3</td>
<td>36.9</td>
<td>23.8</td>
</tr>
<tr>
<td>($a'$)</td>
<td>($a'$)</td>
<td>($a'$)</td>
<td>($a'$)</td>
<td>($a''$)</td>
<td>($a$)</td>
<td></td>
</tr>
<tr>
<td>bFreq/(cm$^{-1}$)</td>
<td>1785.3</td>
<td>1841.6</td>
<td>1674.3</td>
<td>1846.4</td>
<td>1841.9</td>
<td>1772.4</td>
</tr>
</tbody>
</table>

listed in the brackets. The results of vibrational frequency suggest that redshifts of adsorption band occur under the interaction of W atoms. The lowest-vibration frequencies are in a range of 23.8–374.1 cm$^{-1}$, and all datas are positive numbers. In other words, all the ground state structures of $W_nCO$ ($n = 1 - 6$) clusters are stable and have no transition points. While the vibrational frequencies of the strongest IR intensity varies from 1674.3 to 1846.4 cm$^{-1}$, and they can show position of the strongest absorption peak in IR spectrum. Whether a mode is IR active or Raman active can be determined by the symmetry. For clusters with $C_S$ symmetry, $a'$ and
Density Functional Calculations on Spectrum and Electronic Properties

$a''$ modes are both IR and Raman active; for clusters with $C_1$ symmetry, $(a)$ mode is both IR and Raman active. Generally speaking, our values of frequencies presented here are capable for the following vibrational spectroscopy.

In order to determine the structure of a cluster, no matter by diffraction, electronic or vibrational spectroscopy, comparison of the experimentally obtained spectra with simulated spectra is necessary. In this work, we use B3LYP/LANL2DZ method, calculated the IR spectra and Raman spectra for $W_nCO$ ($n = 1 \sim 6$) clusters. And, the results are shown in Fig. 2.

![IR and Raman spectra of $W_nCO$ clusters](image)

Fig. 2. Calculated IR spectra and Raman spectra of $W_nCO$ ($n = 1 \sim 6$) clusters.
X. Zhang et al.

For $W_1CO$ cluster, the strong peak at 1785.3 cm$^{-1}$ is assigned to the symmetric CO stretching mode with $C_S$ symmetry. The intensity of IR spectrum is 690.1 km.mol$^{-1}$ and 53.8 A$^4 \cdot$amu$^{-1}$ in the activity of Raman spectrum in this peak, respectively. The other peak observed at 524.7 cm$^{-1}$ in the Raman spectrum having no IR spectrum is assigned to the symmetric W–CO stretching mode. Besides, the $W_1CO$ cluster has the lowest intensity and activity; we have proved it according to the adsorption energy of $W_1CO$ cluster.\(^{23}\)

For $W_2CO$ cluster, the strong peak at 1841.6 cm$^{-1}$ is assigned to the symmetric CO stretching mode in $C_S$ symmetry. And the intensity of IR spectrum is 995.3 km$\cdot$mol$^{-1}$ and 95.3 A$^4 \cdot$amu$^{-1}$ in the activity of Raman spectrum in this peak. The intensities of IR spectrum in other peaks are almost 0 km$\cdot$mol$^{-1}$. Furthermore, the vibrational frequency at 492.8 cm$^{-1}$ in the Raman spectrum is assigned to a $W_2$ out-of-plane wagging coupled with CO bend vibration modes with lesser contribution, this result indicates that W–C bonds are very important for the vibration of $W_2CO$ cluster.

The IR spectrum of $W_3CO$ cluster also has one obvious strong peak, which at 1674.3 cm$^{-1}$ with the intensity of IR spectrum is 800.3 km$\cdot$mol$^{-1}$, which vibration mode is CO stretching mode, the depolarization ratio (D-P) is 0.343, so it has low symmetry. The Raman spectrum of cluster has three obvious peaks, the strongest peak at 1674.3 cm$^{-1}$ is also assigned to CO stretching mode with the activity at 135.4 A$^4 \cdot$amu$^{-1}$. Both peaks observed at 317.0 cm$^{-1}$ and 426.8 cm$^{-1}$ are assigned to the mixture CO torsion and puckering of $W_3$ atom modes.

For $W_4CO$ cluster, the peak at 1846.4 cm$^{-1}$ is assigned to $W_4$ atoms deformation coupled with a CO stretching mode, the corresponding theoretical values are 1604.4 km$\cdot$mol$^{-1}$ in the intensity of IR spectrum and 199.5 A$^4 \cdot$amu$^{-1}$ in the activity of Raman spectrum. And the peak in the IR spectrum is the strongest one in all $W_nCO$ clusters, so the $W_4CO$ cluster has the largest vibrational mode with $C_S$ symmetry. The two weak peaks in the Raman spectrum were observed at 297.2 cm$^{-1}$ and 424.8 cm$^{-1}$. The former one’s vibration mode is assigned to the asymmetric W atom stretching coupled with CO bend mode, the depolarization ratio is 0.015 with high symmetric vibration mode; the later one’s vibration mode is assigned to CO out-of-plane wagging.

For $W_5CO$ cluster, the strongest peak at 1841.9 cm$^{-1}$ is assigned to CO stretching mode with the $C_S$ symmetry, the intensity of IR spectrum is 1598.9 km$\cdot$mol$^{-1}$ and 193.2 A$^4 \cdot$amu$^{-1}$ in the activity of Raman spectrum at this peak. Lyon et al.$^{18}$ have reported that broad bands appear in the spectrum in the 1700–1950 cm$^{-1}$ range by IR vibrational spectra. There are lots of peaks in the Raman spectrum at 0–400 cm$^{-1}$ assigned to mixed $W_5$ atoms sym stretching and CO asymmetric stretching modes, and the activity at 192 ~ 20 A$^4 \cdot$amu$^{-1}$. As shown in Fig. 2, the $W_5CO$ cluster in the Raman spectrum has the most strong peaks, because most of the depolarization ratio is 0.750 with high asymmetric vibration mode; on the other hand, $W_5CO$ cluster is the most stable cluster and the length of W–C bond is the shortest among the $W_nCO$ ($n = 1–6$) clusters.\(^{23}\)
For $W_6CO$ cluster, the peak at 1772.4 cm$^{-1}$ is assigned to CO stretching mode with the $C_1$ symmetry, the intensity of IR spectrum is 1470.6 km·mol$^{-1}$ and 300.6 A$^4$·amu$^{-1}$ in the activity of Raman spectrum at this peak. In fact, the $W_6CO$ cluster has the largest activity of the Raman spectrum in $W_nCO$ ($n = 1 – 6$) clusters. However, the weak peak in the Raman spectrum at 288.9 cm$^{-1}$ is assigned to a symmetric stretching of $W_6$ atoms, and the activity is 57.9 A$^4$·amu$^{-1}$, it’s much lower than the strong peak.

From the vibrational frequencies of $W_nCO$ ($n = 1 ∼ 6$) clusters, the vibrational frequencies of the strongest IR intensity are in a range of 1674.3–1846.4 cm$^{-1}$, similar to those of Ru–CO, Au–CO clusters.\(^{14}\) For each cluster, the vibration modes at the strongest peak are both IR and Raman active, and be assigned to CO stretching modes. This is mainly caused by two aspects: on the one hand, the strong interaction between W and C atom; on the other hand, CO atoms are the major carriers of negative electron. When the vibrational frequencies wavenumber are low, the vibration mode of cluster is assigned to the W atom stretching coupled with CO stretching.

From the spectrum of $W_nCO$ ($n = 1 ∼ 6$) clusters, the IR spectrum graphics of clusters which we studied are similar to each other, this may be caused by the adsorption of the CO molecule. The intensity of IR spectrum is about between 0 km·mol$^{-1}$ and 1605 km·mol$^{-1}$, and the intensity IR spectrum of $W_4CO$ cluster is the strongest than any other $W_nCO$ ($n = 1 ∼ 6, n ≠ 4$) clusters. On the other hand, the Raman spectrum graphics of the $W_nCO$ ($n = 1 ∼ 6$) clusters are different to each other. We can see the activity is in range of 0–300.6 A$^4$·amu$^{-1}$. In general, the $W_6CO$ cluster has the largest activity (300.6 A$^4$·amu$^{-1}$) of the Raman spectrum in $W_nCO$ ($n = 1 – 6$) clusters, which indicates that the polarizability changed heavily, we will discuss it at below.

### 3.3. Polarizability

In the development of photonic materials, it is important to understand the optical response properties of the materials, specifically the static polarizabilities at the molecular levels.\(^{24}\) However, there did not present any assignments of the polarizabilities for $W_nCO$ clusters. Here, the polarizability the mean dipole polarizability ($\langle \alpha \rangle$), the mean polarizability per atom ($\langle \bar{\alpha} \rangle$) and the polarizability anisotropy ($\Delta \alpha$) are calculated by using the B3LYP/LANL2DZ method and displayed in Table 2. Furthermore, the mean dipole polarizability ($\langle \alpha \rangle$) and the polarizability anisotropy ($\Delta \alpha$) are defined as in the following formulas:\(^{30}\):

$$\langle \alpha \rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \quad (1)$$

$$\Delta \alpha = \left[\frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2)}{2}\right]^{\frac{1}{2}}. \quad (2)$$
As Table 2 shows, we find that the $\alpha_{XX}$, $\alpha_{YY}$ and $\alpha_{ZZ}$ are the major components for the values of polarizabilities in each cluster. However, in other Cartesian components, the values of polarizability are very small. For $W_6CO$ cluster has large value of polarizability, so the Raman spectrum activity is strong. The value of $\langle \hat{\alpha} \rangle$ increases monotonically going from $W_1CO$ to $W_5CO$; however, for $W_6CO$, the value of $\langle \hat{\alpha} \rangle$ abruptly descend. Because the geometrical configuration has an effect on the mean dipole polarizability for $W_nCO$ ($n = 1 \sim 6$) clusters. According to the Fig. 1, for $W_1CO$-$W_5CO$ clusters, the $C_S$ symmetry can be found in their ground state structures, however, the $W_6CO$ is $C_1$ symmetry. For example, the $W_5CO$ cluster in $C_S$ symmetry has larger $\langle \hat{\alpha} \rangle$ value than any other clusters, so the W–CO bonding interaction of $W_5CO$ cluster is the strongest in all $W_nCO$ ($n = 1 \sim 6$) clusters.

We also find that the values of mean polarizability per atom present the same trend as mean dipole polarizabilities, $W_1CO$ has the lowest mean polarizability per atom value in $W_nCO$ ($n = 1 \sim 6$) clusters, which result in a weaker electron delocalization and more compact electronic structure. All the values of $\Delta \alpha$ show the odd–even oscillation behavior, the $\Delta \alpha$ values of the cluster with even $W$ atoms are much larger than those of the clusters with odd $W$ atoms. This result indicates that the response of anisotropy under the external static electric field for the even-size clusters is stronger than the odd-size clusters. Interestingly, this behavior is contrary to $Cu_nCO$ ($n = 1 \sim 9$) clusters. Because the LUMO–HOMO gap for the $W_nCO$ ($n = 1 \sim 6$) clusters is contrary to $Cu_nCO$ ($n = 1 \sim 9$) clusters, showing an opposite electron delocalization between W–CO atoms and Cu–CO atoms.

3.4. Ionization energies and electronegativities

The ionization of a molecule by photoionization or by electron impact is governed by the Franck–Condon principles, which suggest that with the increase of ionization energies, the ability to attract electron for a molecule apparently strengthens. Accordingly we calculated the vertical ionization potentials (VIP) and the vertical electron affinities (VEA). These energies are listed in Figs. 3 and 4, respectively.
Density Functional Calculations on Spectrum and Electronic Properties

Fig. 3. Values of VIP for $W_n\text{CO}$ ($n = 1 \sim 6$) and $W_{n+1}\text{Ref}$ clusters.

Fig. 4. Calculated values of VEA for $W_n\text{CO}$ ($n = 1 \sim 6$) clusters.

They are defined as:

$$E_{\text{VIP}} = E_n^+ - E_n,$$

(3)

($E_n$ and $E_n^+$ both at the geometry of the ground state for $W_n\text{CO}$),

$$E_{\text{VEA}} = E_n - E_n^-,$$

(4)

($E_n$ and $E_n^-$ both at the geometry of the ground state for $W_n\text{CO}^-$),

in which $E_n$ is the energy of $W_n\text{CO}$ ($n = 1 \sim 6$) clusters and $E_n^-$ is the energy of $W_n\text{CO}^-$ cluster.
As shown in Fig. 3, experimental VIP (VIP_{ref}) of W_{n+1} is listed\textsuperscript{32} to compare with our results. Our calculated VIP values are greater than the experimental VIP (VIP_{ref}) of W_{n+1}, which suggests that W\textsubscript{n}CO clusters are easier to be oxidized than W\textsubscript{n+1} clusters, so the redox characteristics of W\textsubscript{n} are enhanced by adsorbed CO molecule. In addition, the values of VIP for W\textsubscript{n}CO clusters decrease as atomic size increases, this means different growth patterns in the geometry structures have different ionizing transition. According to Fig. 4, an oscillation behavior is observed from W\textsubscript{1}CO to W\textsubscript{6}CO. The W\textsubscript{2}CO cluster has the largest value of VEA, while the smallest value of VEA is W\textsubscript{6}CO cluster. Which indicates that W\textsubscript{2}CO cluster has well attracted electronic ability; however, W\textsubscript{6}CO cluster is the easiest to lose electrons in all W\textsubscript{n}CO clusters.

The absolute electronegativity (\chi) is a good method to measure the ability of molecules attracted electrons. The absolute electronegativity\textsuperscript{33} has been defined as:

\[
\chi = -\left(\frac{\partial E}{\partial N}\right)_{\nu},
\]

where E is the energy and N is the number of electrons in the system considered. In a finite difference approximation using integer values for N, the expressions can be rewritten as\textsuperscript{34}:

\[
\chi = \frac{\text{VIP} + \text{VEA}}{2}.
\]

Figure 5 displays the \chi of W\textsubscript{n}CO clusters, the values of \chi decrease significantly with the increase in atomic size, except W\textsubscript{5}CO cluster. It indicates that the ability to attract electrons of W\textsubscript{n}CO (n = 1 \sim 6, n \neq 5) clusters becomes lower as the cluster size increases. This may be due to the following reasons: first, the stability of CO on tungsten clusters increase as atomic size increase; second, hybridized orbital has a heavy influence on \chi, according to the natural bond orbital (NBO) analysis of

Fig. 5. Calculated values of absolute electronegativity (\chi) for W\textsubscript{n}CO (n = 1 \sim 6) clusters.
Density Functional Calculations on Spectrum and Electronic Properties

Table 3. Thermodynamical properties of W$_n$CO ($n = 1 \sim 6$) clusters.

<table>
<thead>
<tr>
<th></th>
<th>W$_1$CO</th>
<th>W$_2$CO</th>
<th>W$_3$CO</th>
<th>W$_4$CO</th>
<th>W$_5$CO</th>
<th>W$_6$CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^\theta$/(eV)</td>
<td>−10.723</td>
<td>−14.443</td>
<td>−18.620</td>
<td>−23.151</td>
<td>−28.242</td>
<td>−33.302</td>
</tr>
<tr>
<td>$C_V$/(Cal·mol$^{-1}$·K$^{-1}$)</td>
<td>8.709</td>
<td>13.756</td>
<td>19.700</td>
<td>24.963</td>
<td>30.767</td>
<td>36.322</td>
</tr>
<tr>
<td>$S^\theta$/(Cal·mol$^{-1}$·K$^{-1}$)</td>
<td>56.668</td>
<td>80.932</td>
<td>91.738</td>
<td>104.329</td>
<td>118.935</td>
<td>126.468</td>
</tr>
</tbody>
</table>

W$_n$CO clusters, the charge transfer among W, C and O atoms are larger than W$_n$ clusters. While the $\chi$ value of W$_5$CO cluster is higher than its neighboring clusters, this is attributed to the ionization energy which is far from the experimental VIP (VIP$_{ref}$) of W$_{n+1}$.

3.5. Thermodynamical properties

We now discuss the thermodynamical properties of W$_n$CO ($n = 1 \sim 6$) clusters. Under the condition of the temperature at 298.15 K and the atmospheric pressure at 1.01 x 10$^5$ Pa, we calculated the heat capacity at constant volume ($C_V$), standard entropy ($S^\theta$) and the standard enthalpy of formations ($\Delta H^\theta$) of the neutral W$_n$CO ($n = 1 \sim 6$) clusters by using B3LYP/LANL2DZ method. The results are listed in Table 3. It is well known that if the calculated value of $\Delta H^\theta$ is negative, the reaction between W atoms and CO molecule is exothermic reaction and the W$_n$CO ($n = 1 \sim 6$) cluster has strong chemical stability; however, if it is positive, the reaction between W atoms and CO molecule is endothermic reaction and the W$_n$CO ($n = 1 \sim 6$) cluster has weak chemical stability. The calculated values of $\Delta H^\theta$ can be obtained from the following formula:

$$\Delta H^\theta = E(W_nCO) - nE(W) - E(C) - E(O),$$

(7)

where the $E(*)$ values represent the energies of the ground state structure for W$_n$CO cluster, free W, O and C atoms, respectively.

As shown in Table 3, the values of $\Delta H^\theta$ for clusters are all negative numbers, this behavior indicates that the chemical reactions between W atoms and CO molecule are exothermic reactions and the chemical stabilities are good. This behavior is similar to the Holmgren L’s results. Furthermore, the results of $C_V$ and $S^\theta$ show that the structures of W$_n$CO cluster increase more stably with an increase in atomic size. The $C_V$ value of per cluster (W$_n$CO ($n = 2 \sim 6$)) increases 5–6 cal·mol$^{-1}$·K$^{-1}$, compared with the former one. However, there is no obvious regularity about the increase of $S^\theta$ value for per cluster (W$_n$CO ($n = 2 \sim 6$)).

4. Conclusion

In this paper, based on the ground state structures of W$_n$CO ($n = 1 \sim 6$) clusters, the spectrum and electronic properties of W$_n$CO ($n = 1 \sim 6$) clusters have been studied by using DFT at the B3LYP/LANL2DZ level. It is found that the structural growth model of W$_n$CO clusters transform from 2D to 3D. The vibrational
frequencies and spectrum analysis show that in each cluster, the vibration modes at the strongest peak are both IR and Raman active, and assigned to CO stretching modes. The IR spectrums graphics of clusters which we studied are similar to each other; the Raman spectrum graphics of the $W_n CO$ ($n = 1 \sim 6$) clusters are different to each other.

The polarizability analyses indicate that the $\alpha_{XX}$, $\alpha_{YY}$ and $\alpha_{ZZ}$ are major components for the values of polarizability in each cluster. The mean dipole polarizabilities increase monotonically with the increase of cluster size, except $W_6 CO$ cluster. All the values of polarizability anisotropy show the odd-even oscillation behavior. Both the ionization energies and electronegativities show that the values of VIP for $W_n CO$ clusters decrease as atomic size increases, $W_2 CO$ cluster has well attracted electronic ability; $W_6 CO$ cluster is the easiest to lose electrons in all $W_n CO$ clusters. According to thermodynamical property analysis, the chemical reactions between W atoms and CO molecule are exothermic reactions and the chemical stabilities are good.

Acknowledgments
This work is partially supported by the National Natural Science Foundation of China (Grant No. 51072072), by the National Natural Science Foundation of Jiangsu Province of China (Grant No. BK2010343).

References
Density Functional Calculations on Spectrum and Electronic Properties

32. Y. Bai, MS. Thesis, Jilin University, Changchun, China (2008).