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A theoretical study on the excited states of MC_3 ($M = Sc$, V, and Cr)

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Abstract. The ground state structures of MC_3 ($M = Sc$, V, and Cr) and their anions have been investigated, employing the first-principles DFT at the B3LYP level. The calculations predict that the equilibrium geometries of both neutral MC_3 and their anions are cyclic structures with C_{2v} symmetry. The Mulliken charge and spin populations of MC_3 and their anions have also been calculated, and it is found the electron charge changes mainly take place on the M atoms from anions to neutral molecules. The low-lying excited states for the clusters are calculated with time-dependent DFT to assign the features of the photoelectron spectra. Our results agree well with the available experimental and theoretical data.

PACS. 36.40.Mr Spectroscopy and geometrical structure of clusters – 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 71.15.Mb Density functional theory, local density approximation, gradient and other corrections

1 Introduction

Transition metal carbide clusters (met-cars) have been a subject of intense investigation in recent years due to their promising applications in materials sciences, microelectronics, nanotechnology, catalysis, solid state chemistry, and so on [1–3]. $Ti_8C_{12}^+$ was the first discovered metal-carbon cluster [4] and was produced in molecular beams by reacting transition metal vapors with a variety of hydrocarbons. Since then, a lot of experimental and theoretical works on met-cars have been carried out. Small metal-carbon clusters are known as building units of nanomaterials, cluster assembled materials, and met-cars, etc. [1,4–6]. So they provide an ideal medium to obtain a detailed understanding of the metal-carbon interactions, which is important to gain insight into the growth mechanisms of the various metal-carbon nanomaterials. Further more small carbon entities can help us to understand more complex phenomena, such as controlled growth of carbon nanotubes by the late transition metals and various catalytic properties [7–9]. Therefore the experimental and theoretical investigations of small metal-carbon clusters are very important.

Photoelectron spectroscopy (PES) is an effective experimental method to study the electronic structures of free clusters, especially for their low-lying excited states. Li et al. have systematically studied the first-row transition metal-carbon clusters MC_n ($n = 2, 3$) ($M = Sc$, V, Cr, Mn, Fe and Co) by means of photoelectron spectroscopy [10,11]. Theoretically, a lot of efforts on MC_2 [12–20] have been done to investigate their geometric and electronic structures. On the other hand, Wang and Li [11] have found cyclic C_{2v} structures to be the ground state geometries for all first-row transition metal MC_3 and MC_3^- ($M = Sc$, Ti, V, Cr, Mn, Fe) at the B3LYP level. Roszak et al. [21] have studied ScC_3 and ScC_3^- at different levels of computation and also found the cyclic C_{2v} structure is the ground state geometry for them. Then Cao et al. [22] and Hendrickx et al. [13,16] performed a theoretical study on FeC_3, ScC_3 and their anions clusters at the CASSCF level of theory and they got the similar result, i.e. these clusters have the cyclic C_{2v} structure except for FeC_3^- which has a linear Fe–C–C–C conformation. Last year, Ryzhkov et al. [23] investigated the electronic structure and geometry of Fe_mC_n ($m, n \leq 3$), and they also found that FeC_3 possesses a triangle C_{2v} structure. However, most of these theoretical calculations only focused on geometric or electronic structures of the ground state of these clusters, so a theoretical effort to find the excitation energy of MC_3 and to assign their photoelectron spectra is desired.

It's well-known that CI-Singles method can be used to compute the excitation energies, but it is time consuming and the results of computation don't, as a whole, agree well with those of the experiment. Fortunately,

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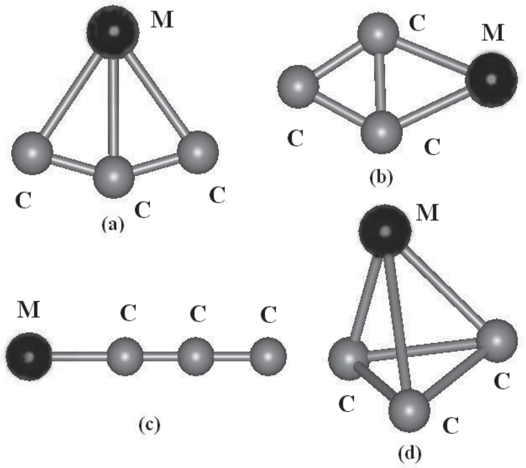

Fig. 1. The optimized structures of MC_3 (M = Sc, V, and Cr). (a) C_{2v} ring; (b) C_{2v} top; (c) $C_{\infty v}$ linear; (d) C_{3v} pyramidal.

time-dependent density functional theory (TDDFT) methodology [24–26] has proved to be a reliable method for calculating excitation energies for many organic and inorganic molecules [27–30], even for some open shell transition metal oxides [31,32] recently. So in the present paper, we will perform a theoretical study on the electron affinities (EA) and excited states of MC_3 (M = Sc, V, and Cr) using the density functional theory (DFT) and TDDFT methods so as to assign the observed anion detachment spectra of these species.

2 Theoretical methods and computational details

All calculations were performed using the Gaussian 03 [33] program package. The DFT is used in the ground state and the time-dependent DFT (TDDFT) in excited state calculations. Both the ground states of MC_3 and MC_3^-, and the excited states of MC_3 (M = Sc, V and Cr) are calculated within unrestricted Kohn-Sham formalism with a three parameter exchange and correlation functional (B3LYP) [34]. The standard LANL2DZ in Gaussian 03 is employed as the basis set, which has been proved to be suitable for the transition metal systems [35, 36]. Geometry optimizations are carried out until the gradient forces vanished with respect to a threshold value of 0.00045. Vibrational frequencies of these neutral and negative clusters were calculated at the DFT level to characterize stationary points as minima.

3 Results and discussions

One of the most important things in studying a cluster is to determine its equilibrium geometry. So we firstly performed DFT calculations on a wide range of structures of MC_3 (M = Sc, V, and Cr) and their anion clusters. They included C_{2v} ring, C_{2v} top, $C_{\infty v}$ linear, and nonplanar C_{3v} structures as shown in Figure 1. In the view of energy, we found only the C_{2v} ring isomer is the viable candidate for the ground states of neutral MC_3 as well as their anions MC_3^- (M = Sc, V, and Cr), confirming the previous theoretic predictions [11,21].

Table 1. The electron affinities (in eV) of MC_3 (M = Sc, V, and Cr).

	Cal.(AEA)	Cal.(VEA)	Cal. [11]	Exp. [11]
ScC_3	1.63	1.68	1.99	1.64 ± 0.02
VC_3	1.58	1.66	1.40	1.47 ± 0.02
CrC_3	1.31	1.43	1.26	1.50 ± 0.02

Table 2. The Mulliken charge and spin populations of MC_3 (M = Sc, V, and Cr) and MC_3^-.

		M	C	C	C
ScC_3	Charge	0.73	–0.26	–0.24	–0.24
	Net spin	0.35	–0.18	0.41	0.41
ScC_3^-	Charge	–0.06	–0.33	–0.31	–0.31
	Net spin	1.28	–0.18	0.45	0.45
VC_3	Charge	0.53	–0.12	–0.20	–0.20
	Net spin	1.69	0.16	–0.42	–0.42
VC_3^-	Charge	–0.14	–0.22	–0.32	–0.32
	Net spin	3.04	0.23	–0.63	–0.63
CrC_3	Charge	0.48	–0.25	–0.11	–0.11
	Net spin	4.53	0.10	–0.31	–0.31
CrC_3^-	Charge	–0.04	–0.24	–0.36	–0.36
	Net spin	4.42	0.25	–0.84	–0.84

Table 1 summarizes the adiabatic EAs (AEAs) and vertical EAs (VEAs). In order to get the adiabatic electron affinity of the MC_3 clusters, we optimized the geometries of neutral clusters and the negatively charged MC_3^- clusters. The VEAs are calculated at the optimized anionic geometries, and they are corresponding to the available experimental EA obtained by the PES study [11]. All the data we calculated agree well with the experimental and the previous calculated values [11].

Table 2 presents the Mulliken charge and spin populations of MC_3 (M = Sc, V, and Cr) and their anions. From the table, one can find that the additive electron of MC_3^- mainly distributes to the M (M = Sc, V, and Cr) atom, and the charges on the carbon atoms are almost the same, compared with the neutral clusters.

Wang et al. [11] have reported the anion photoelectron spectra of MC_3^- (M = Sc, V, Cr, Mn, Fe, Co, and Ni) clusters using laser wavelength 355 nm and 532 nm. They found there are several prominent peaks located subsequent to the detachment of the electron. To assign the measured PES [11], we first assume that with the detachment of an electron, the transitions from MC_3^- (M = Sc, V, and Cr) to MC_3 are vertical because the detachment is instantaneous in experiments. This assumption is reasonable for the short relaxation time in the experiment, and it means that MC_3 cluster we will use to calculate the transitions keeps the same geometry as MC_3^-. Then we assume that almost all the detachment features are corresponding to the electronic transitions from the ground state of the anion to the ground or excited states of the neutral cluster. That means we will not consider the possible transitions

Table 3. States, configuration and detachment energies of MC_3 (M = Sc, V and Cr).

State	Configuration	Detachment energy (eV)	
		Present work	Exp.
The ground and excited states of ScC_3			
$^2A_2$	$7a_1^2 2b_1^2 5b_2^2 1a_2\uparrow$	1.64	1.64 ± 0.02
$^2B_1$	$7a_1^2 2b_1^2 4b_2^2 1a_2^2 5b_2\uparrow$	2.08	
$^2B_2$	$7a_1^2 2b_1^2 4b_2^2 8a_1\downarrow 1a_2\uparrow 5b_2\uparrow$	2.34	2.28 ± 0.02
$^2A_2$	$7a_1^2 2b_1^2 5b_2^2 8a_1\uparrow$	2.37	2.28 ± 0.02
The ground and excited states of VC_3			
$^2A_1$	$7a_1^2 1a_2^2 2b_1^2 5b_2^2 8a_1\uparrow$	1.47	1.47 ± 0.02
$^4B_2$	$7a_1^2 2b_1^2 5b_2^2 1a_2\uparrow 8a_1\uparrow\ 3b_1\uparrow$	1.57	
$^2B_1$	$7a_1^2 1a_2^2 2b_1^2 5b_2^2 3b_1\uparrow$	1.84	1.79 ± 0.02
$^4A_1$	$7a_1^2 2b_1^2 5b_2^2 1a_2\uparrow 8a_1\uparrow\ 3b_1\uparrow$	2.62	
$^2A_2$	$8a_1^2 2b_1^2 4b_2^2 1a_2\uparrow 3b_1\uparrow 5b_2\downarrow$	2.76	
$^4B_2$	$8a_1^2 2b_1^2 4b_2^2 1a_2\uparrow 9a_1\uparrow\ 3b_1\uparrow$	2.80	
$^4A_2$	$7a_1^2 2b_1^2 5b_2^2 8a_1\uparrow 9a_1\uparrow\ 3b_1\uparrow$	2.94	2.98 ± 0.02
$^2A_2$	$8a_1^2 2b_1^2 5b_2^2 1a_2\uparrow$	3.01	2.98 ± 0.02
The ground and excited states of CrC_3			
$^5B_2$	$7a_1^2 2b_1^2 5b_2^2 1a_2\uparrow 8a_1\uparrow 3b_1\uparrow 9a_1\uparrow$	1.50	1.50 ± 0.02
$^5B_1$	$7a_1^2 1a_2^2 2b_1^2 4b_2^2 8a_1\uparrow 3b_1\uparrow 5b_2\uparrow 9a_1\uparrow$	1.90	1.81 ± 0.03
$^3B_1$	$7a_1^2 1a_2^2 2b_1^2 5b_2^2 8a_1\uparrow 3b_1\uparrow$	2.11	1.95 ± 0.02
$^3B_2$	$8a_1^2 1a_2^2 2b_1^2 3b_2^2 4b_2\downarrow 9a_1\uparrow 3b_1\uparrow 10a_1\uparrow$	2.48	2.46 ± 0.03
$^3B_1$	$7a_1^2 1a_2^2 2b_1^2 5b_2^2 8a_1\uparrow 9a_1\uparrow$	2.82	2.82 ± 0.04
$^3A_2$	$8a_1^2 2b_1^2 5b_2^2 9a_1\uparrow 3b_1\uparrow$	3.05	
$^3A_1$	$7a_1^2 1a_2^2 2b_1^2 5b_2^2 8a_1\uparrow 3b_1\uparrow$	3.08	

from the excited states of the anion to the ground or excited states of the neutral molecule unless there is apparent experimental evidence.

The excitation energies are defined to be the energy differences between the excited states and the ground state of the neutral molecule keeping the same geometry as its parent anion. The excitation energy and configuration of each low-lying excited state can be calculated through TDDFT directly. In addition, during the calculations, the neutral MC_3 and the detached electron can be viewed as a system whose total spin must be equal to that of precursor MC_3^-. Assume the spin multiplicity of the anion is n, so removing an electron from the anion can only result in two kinds of multiplicities for the neutral molecule, one is $n+1$, and the other is $n-1$.

Table 3 gives the states, electronic configurations and detachment energies of MC_3^- (M = Sc, V and Cr). In order to correlate these excited states to the states in the PES of MC_3^-, we first determine the X state in the experimental PES. The X state in PES is usually believed to correspond to the ground state of the neutral cluster at the anionic geometry, i.e., the vertical electron affinity of the cluster. With the X state, we can transform the excitation energies of the doublets to the binding energies (BEs) in the PES by adding the vertical EA. In order to avoid the effect by the deviation of calculated EA, we use the experimental EA in the above transformations. It shows from Table 3 that the first states of ScC_3^-, VC_3^- and CrC_3^- are $^2A_2$, $^2A_1$ and $^5B_2$ respectively. We assign them to the X peak in PES [11] of MC_3 (M = Sc, V, and Cr).

For ScC_3^-, two bands are located at the binding energies (BE) of 1.64, 2.28 eV, identified with the X, A states [11] in its photoelectron spectrum, respectively. In fact, each of the peaks in PES is a broad one, which corresponds to more than one excited states. So we assign its first state ($^2A_2$) to the X band. The $^2B_2$ and $^2A_2$ states of ScC_3 are two occasional degenerate states with the detachment energies 2.34 eV and 2.37 eV respectively, and we assign them to the A state with detachment energy 2.28 eV in the PES.

Similar to ScC_3, the states of VC_3 can be found corresponding state bands in its PES. Because the detachment energies of the $^4A_2$ (2.94 eV) and $^2A_2$ (3.01 eV) states of VC_3 are almost equal, so we assign them to one peak with detachment energy 2.98 eV in the PES. But we should notice that a few calculated excited states cannot be found in the PES, such as $^4A_1$ state of VC_3 with the detachment energy 2.62 eV. We think there are mainly two reasons result in this discrepancy between theory and experiment. One is that the intensity of transitions from the anions to these excited states is too weak, so they could not be definitively identified by the experimental PES. Because of the complexity of computations, we have not studied the intensity of transitions in this paper. The other is the precision of TDDFT. It is commonly stated that TDDFT is accurate to about 0.3 eV. Though most of our calculated excited states compare well with the measured ones, we cannot exclude the possibility that the calculated energies of some transitions are far from the experimental ones.

For CrC_3^-, the photoelectron spectrum obtained by Wang et al. [11] exhibits a few bands at 1.50, 1.65, 1.81, 1.95, 2.46, 2.82 eV, namely, X, A, B, C, D, E, respectively. We have shown our computed vertical energy separations for the excited states in Table 3. As can be seen from the table, the agreement between our computed vertical energy separations and the experiment is excellent except the band B that we can't give an explicit assignment. We think there are too many peaks to be distinguished with each other in the PES on one hand, and the accurate excited energy for higher excited states could not be easily obtained via the calculation on the other hand.

Compared with the experimental peaks, our results fit best for VC_3^-, and worst for CrC_3^-. The main reason is that all the peaks in PES of VC_3^- are strong enough and are separated each other very clearly, so the interactions between different states are the weakest. The TDDFT methods, like the CI singles, use a configuration interaction type expansion to define a new wavefunction made up of a linear combination of determinants and do not consider the interactions between different electronic states, and this approximation suits best for VC_3^- and worst for CrC_3^-. Anyway, the calculated spectrum do give the good agreement with the experimental data in the location of peaks. Therefore, the TDDFT is a reliable method to calculate the excited states of such clusters.

4 Conclusion

In this study, we have investigated the structural and electronic properties of MC_3 (M = Sc, V and Cr) clusters in their neutral and anionic states, employing the first-principles DFT at the B3LYP level. The geometries and electronic configurations of ground states of the neutral clusters and their anions are obtained. From the calculations one can conclude that the cyclic C_{2v} structure is the geometry of the ground states both for the MC_3 and for MC_3^- (M = Sc, V and Cr). We also have calculated the adiabatic electron affinity and vertical electron affinity of these clusters. All the data we calculated agree well with the experimental ones. The Mulliken charge and spin populations of MC_3 (M = Sc, V and Cr) and their anions are also presented, from which we can find the electron charge changes mainly take place on the metal M (M = Sc, V and Cr) atoms from anions to neutral molecule. The excited states are calculated employing TDDFT at the B3LYP level and are used to assign the photoelectron spectrum. The assignment of the excited state is in good agreement with the experimental excitation energy.

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