

Small Carbon Clusters Doped with Vanadium Metal: A Density Functional Study of VC_n ($n = 1-8$)

Pilar Redondo,* Carmen Barrientos, and Antonio Largo

*Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid,
47005 Valladolid, Spain*

Received January 31, 2006

Abstract: A theoretical study of the different isomers of neutral VC_n ($n = 1-8$) clusters has been carried out. Predictions for their electronic energies, rotational constants, dipole moments, and vibrational frequencies have been made using the B3LYP method with different basis sets. For linear and cyclic VC_n clusters, the lowest-lying states correspond to quartet states, with the only exception being VC, which has a $^2\Delta$ ground state. In the fan-type structures, the electronic ground state is found to be a quartet state for even n values, whereas for odd n values, the ground state is a doublet for VC_3 and VC_5 and a quartet for VC_7 . From the incremental binding energies, we can deduce an even–odd parity effect, with n -even clusters being more stable than n -odd ones in the linear and fan clusters. It was also found that neutral VC_n clusters with $n \leq 6$ prefer fan structures over linear and cyclic isomers, whereas cyclic ground states are predicted for the clusters with $n > 6$.

Introduction

The inclusion of metal atoms in pure carbon clusters provides a way to modify their properties and generate new materials. A wide variety of materials can be formed from the interaction of carbon with transition metals. *Networked* metallofullerenes¹ can be originated when transition metals are incorporated into carbon cages, whereas some rare-earth elements can be trapped inside fullerene cages to form *endohedral* metallofullerenes.² On the other hand, late transition metals have interesting properties as catalysts for carbon nanotube formation.³ Finally, early transition metals have been found to form stable gas-phase metal–carbon clusters, known as metallocarbohedrenes, “*met-car*”,^{4–7} with a M_8C_{12} stoichiometry; observed examples are Ti_8C_{12} ⁸ and V_8C_{12} .⁹

Because of the presence of transition-metal atoms, the interpretation of experimental information is rather difficult. In particular, the prediction of the ground-state structures is complicated because of the large number of local minima on their potential energy surfaces, related to the presence of *nd* shells in the transition-metal atom. However, the deter-

mination of geometry is one of the fundamental problems in clusters research because it may affect chemical properties, and therefore, accurate theoretical information on the structures of transition metal carbides is desirable. In addition, theoretical studies of small carbon clusters containing transition metals provide a way to obtain a detailed description of the metal–carbon interactions and are very useful to understand the growth mechanism of the various metal–carbon nanomaterials. In fact, the type of structure formed depends essentially on the nature of these interactions. Obviously, the study of the structures and reactivity of metal carbides are also important in other areas, such as surface chemistry, combustion chemistry, or astrochemistry.

The competition between different isomers on small first-row transition-metal carbides has recently been the subject of some theoretical studies. In the case of dicarbide compounds (MC_2), linear and cyclic structures have been characterized on ScC_2 ,^{10–12} VC_2 ,¹³ FeC_2 ,^{14,15} and CoC_2 .¹⁶ In all cases, cyclic ground states are predicted. Whereas systematic studies as a function of the size of the clusters on heteroatom-doped carbon clusters containing first- and second-row elements have been extensively carried out by theoretical methods, only a few works are devoted to the study of first-row transition-metal-doped carbon clusters. In

* Corresponding author fax: 34-983-423013; e-mail: predondo@qf.uva.es.

the past few years, different theoretical approaches have been applied to the study of systems such as CrC_n ($n = 1-8$),¹⁷ TiC_n ($n = 2-4$),^{18,19} FeC_n ($n = 1-4$),²⁰ NiC_n ,²¹⁻²³ and ScC_n ($n = 1-8$).^{24,25} In all cases, it is shown that different geometrical configurations can be reached for this type of system.

Vanadium is one of the transition metals that has been shown to form stable “met-car”.⁹ However, to the best of our knowledge, theoretical studies of vanadium carbide compounds have only been performed, at different levels of theory, for VC ,²⁶⁻²⁹ VC_2 ,^{13,30} and V_2C_2 ³⁰ systems. In addition, there are some experimental studies reporting the photoelectron spectra of first-row transition-metal carbides (MC_2 and MC_3).^{31,32} In the present work, we have carried out a theoretical study of the VC_n (with n ranging from 1 to 8) systems taking into account different geometrical conformations. We analyze the relative stability of the different structures as a function of n , and for the most stable isomers, we report their equilibrium structures and some spectroscopic data that could be helpful for their eventual experimental detection. In addition, the knowledge about the behavior of vanadium-doped carbon clusters as a function of the size of the cluster will allow the identification of possible systematic trends, which could help to understand the structure of these systems and could be useful to make extrapolation for some properties and, therefore, predictions for larger clusters.

Computational Methods

We have employed the same theoretical approach as that in our previous studies on ScC_n systems.^{24,25} Therefore, all of our calculations have been made using density functional theory (DFT), in particular, employing the B3LYP exchange-correlation functional.^{33,34} This consists of the Lee–Yang–Parr³⁵ correlation functional in conjunction with a hybrid exchange functional first proposed by Becke.³⁶ The latter is a linear combination of local density approximation, Becke’s gradient correction,³⁷ and the Hartree–Fock exchange energy based on Kohn–Sham orbitals.³⁸ As is known, The DFT/B3LYP method has been widely applied to the study of many medium-sized heteroatom-doped carbon clusters, providing structures in good agreement with the experimental results. In addition, previous studies on vanadium carbide systems, such as the works on VC ^{26,29} and VC_2 ,¹³ have shown that the B3LYP method is in reasonable agreement with multi-configurational approaches predicting similar ground states and lowest-lying excited states. These facts suggest that the B3LYP method can be applied in the study of these compounds.

Computations have been performed using the 6-311+G-(d) basis set that includes diffuse functions and is constructed employing the triple split-valence 6-311G³⁹ for carbon atoms and the Wachters⁴⁰ and Hay⁴¹ basis set with the scaling factor of Ragavachari and Trucks⁴² for vanadium atoms. The use of effective core potential methods for the description of clusters reduces significantly the computational time. In particular, we have also employed a mixed basis set formed by Los Alamos ECP plus DZ, LanL2DZ,⁴³⁻⁴⁵ for vanadium atoms in conjunction with the 6-311+G(d) basis set for carbon atoms, denoted as LAN-6+(d). In our previous study

on the ScC_n system,²⁴ we analyzed the behavior of different basis sets, showing that the 6-311+G(d) and LAN-6+(d) basis sets give the most reliable results.

Harmonic vibrational frequencies were computed from analytical gradient techniques. This allows an estimate of the zero-point vibrational energy (ZPVE) correction for each structure, as well as an assessment of the nature of the stationary points and, therefore, a characterization of whether they are true minima on the respective potential surface.

All calculations reported in this work were carried out with the Gaussian 98 program package.⁴⁶

Results and Discussion

We have carried out a study of the neutral VC_n ($n = 1-8$) system, on the doublet, quartet, and sextuplet potential energy surfaces. In this work, we will only present the three most stable conformations on each potential energy surface: a linear structure with the vanadium atom sited at the end position, a cyclic isomer where the vanadium atom is bonded to the two terminal carbon atoms of the chain, and finally a fan-type structure where the vanadium atom interacts with the whole carbon chain. Other isomers, such as a linear isomer with the vanadium atom in an intermediate position or a cyclic isomer with an exocyclic vanadium atom, have been studied, but they are not presented here because they lie higher in energy.

We will present the results for each type of structure separately in order to analyze systematic trends in their properties with the size of the clusters. After this, the relative stability of the three structures along the series was discussed. It should be pointed out that, for some structures reported in this work, for example, those with $^4\Phi$ or $^6\Phi$ electronic states, the B3LYP method, as well as single-reference-based methods such as HF, MP2, QCISD, and so forth, provides nondegenerate π frequencies. On the other hand, for the states of Σ and Δ symmetry studied in this work, it is possible to obtain degenerate frequencies, and they are denoted in Table S1 (Supporting Information) as (2).

VC_n Linear Clusters. We present in Table 1 some properties, such as absolute and relative electronic energies, $\langle S^2 \rangle$ expectation values, dipole moments, or binding energies, at the B3LYP/6-311+G(d) and B3LYP/LAN-6+(d) levels of theory, for the lowest-lying open-chain VC_n species on the doublet, quartet, and sextuplet potential surfaces. Their corresponding harmonic vibrational frequencies and rotational constants are given as Supporting Information in Table S1. For n -even clusters, we have included results for two quartet states ($^4\Sigma$ and $^4\Phi$) because they are very close in energy and, in all cases, are more stable than the corresponding lowest-lying doublet and sextuplet states. These molecular properties might be helpful in an experimental search for these species. In addition, the optimized geometries at the B3LYP/6-311+G(d) and B3LYP/LAN-6+(d) levels of theory for the most stable structures are shown in Figure 1.

In general, it can be seen that the two basis sets considered here lead to very close results for equilibrium geometries and other properties such as dipole moments, vibrational frequencies, or relative energies. Therefore, it can be

isomer	state	$-E$ (au)	$\langle S^2 \rangle$	BE (eV)	μ (D)	ΔE (kcal mol $^{-1}$)
VC	$^2\Delta$	981.893063	1.1532	3.84	6.02	0.00
		109.224179	1.2432	3.84	6.04	0.00
	$^4\Delta$	981.885398	3.8785		2.84	4.73
		109.215534	3.9237		2.86	5.35
	$^6\Sigma$	981.861752	8.7990		3.93	19.28
VC ₂	$^2\Delta$	109.191867	8.8047		3.93	19.95
		1019.960382	0.9400		6.46	30.33
	$^4\Sigma$	147.289287	0.9520		6.55	31.43
		1020.008738	3.9190	10.78	8.72	0.00
	$^4\Phi$	147.339374	3.9339	10.76	8.79	0.00
		1020.002094	3.9137		9.42	4.31
	$^6\Delta$	147.333478	3.9328		9.55	3.77
		1019.983546	8.7947		4.51	16.19
VC ₃	$^2\Delta$	147.316392	8.7972		4.76	14.82
		1058.052393	1.5419		13.65	19.16
	$^4\Phi$	185.385069	1.5021		13.42	18.22
		1058.081416	4.4493		8.99	0.64
	$^6\Sigma$	185.414436	4.4665		9.10	-0.40
VC ₄	$^2\Delta$	1058.082820	8.7844	16.54	8.63	0.00
		185.414098	8.7853	16.54	8.79	0.00
	$^4\Sigma$	1096.141157	1.3277		8.02	28.68
		223.471035	1.3233		8.15	29.57
	$^4\Phi$	1096.186952	4.0768	23.11	12.22	0.00
		223.518281	4.0900	23.10	12.38	0.00
	$^6\Phi$	1096.183059	4.3260		12.00	2.20
		223.515642	4.3793		11.96	1.44
VC ₅	$^2\Delta$	1096.167774	8.7654		10.03	11.54
		223.501194	8.7659		10.35	10.31
	$^4\Phi$	1134.233757	1.7721		18.03	21.39
		261.566333	1.7326		18.13	21.64
	$^6\Sigma$	1134.267174	4.5837	29.06	11.70	0.00
		261.600513	4.5971	29.11	11.87	0.00
VC ₆	$^2\Delta$	1134.264878	8.8132		11.53	1.82
		261.596343	8.8145		11.76	2.92
	$^4\Sigma$	1172.318571	1.5493		9.30	28.75
		299.648651	1.5519		9.37	30.57
	$^4\Phi$	1172.363472	4.1751		15.13	0.55
		299.694901	4.1870		15.36	1.48
	$^6\Phi$	1172.363720	4.5184	35.40	14.02	0.00
		299.696815	4.5544	35.45	14.07	0.00
VC ₇	$^2\Delta$	1172.353181	8.7709		12.43	6.48
		299.686707	8.7714		12.78	6.22
	$^4\Phi$	1210.413532	1.9346		22.49	22.94
		337.745953	1.8984		22.64	22.39
	$^6\Sigma$	1210.449339	4.6735	41.48	14.14	0.00
		337.782777	4.6856	41.54	14.35	0.00
	$^6\Phi$	1210.444147	8.8435		14.35	3.69
VC ₈	$^2\Delta$	337.775620	8.8452		14.65	4.54
		1248.496004	1.7095		10.	

Before discussing our results, we are going to compare them with the previous results that have been reported for VC and VC₂ isomers. The first member of the series, vanadium carbide VC, has been studied both theoretically^{26–29} and experimentally,^{47–49} and it is well-established that the lowest-lying state corresponds to a $^2\Delta$ symmetry. The most complete study of this species was carried out recently by Kalemios et al.,²⁹ where they explored 29 states of VC using MRCI methods with large atomic natural orbital basis sets. From this study, they concluded that the ground state is of $^2\Delta$ symmetry, with the first two excited states, $^4\Delta$ and $^2\Sigma$, located 4.16 and 6.95 kcal/mol, respectively, above the fundamental state. The MRCI(+Q) binding energy of $^2\Delta$ is estimated to be 88.5 (89.3) kcal/mol, and after some corrections (BSSE, ZPVE, relativistic effects, and $3s^23p^6$ semicore), they obtained a value of 95.3 kcal/mol, in good agreement with the experimental one of 100.1 ± 5.7 kcal/mol.⁴⁸ As can be seen in Table 1, we also found $^2\Delta$ and $^4\Delta$ as the ground and first excited states, respectively, and the relative energy (4.73 and 5.35 kcal/mol, obtained with 6-311+G(d) and LAN-6+(d), respectively) is very similar to that obtained at the MRCI(+Q) level. We have also characterized a $^2\Sigma$ state lying 15.57 kcal/mol above the ground state. As in the study of Kalemios et al., this state is more stable than the lowest-lying sextuplet state, $^6\Sigma$. In

addition, our results for the binding energy of ${}^2\Delta$ are very close to those obtained at the MRCI(+Q) level by Kalemios et al.

Theoretical information for the VC_2 system has been reported by Majumdar et al.¹³ using DFT and MRSDCI levels with relativistic effective core potentials (RECPs) for vanadium and carbon atoms. In contrast with our results shown in Table 1, they report ${}^6\Sigma$ and ${}^4\Sigma$ (lying about 4.61 kcal/mol above the ${}^6\Sigma$ state at the MRSDCI+Q level) states as the most stable linear isomers. We have found a ${}^4\Sigma$ state as the lowest-lying state. This isomer has two imaginary π -type frequencies (as can be seen in Table S1) and corresponds to the transition state for the rearrangement of the cyclic isomer (4A_1). In addition, we have located another ${}^4\Sigma$ state that corresponds to a true minimum and is located above the ${}^6\Sigma$ isomer. However, we have characterized ${}^4\Phi$ and ${}^6\Delta$ states (included in Table 1), both lower in energy than the ${}^6\Sigma$ isomer (about 23.92 and 12.03 kcal/mol below the ${}^6\Sigma$ isomer, respectively), reported by Majumdar et al. as the lowest-lying linear one.

It is readily seen in Table 1 that all linear VC_n clusters present quartet ground states, with the only exception being VC, where the scheme is different because the carbon is only bonded to vanadium and presents a ${}^2\Delta$ ground state. Linear clusters with n -odd values have a ${}^4\Phi$ ground state, and the first excited state corresponds to a ${}^6\Sigma$ symmetry. In the case of VC_3 , the B3LYP results show that both states are virtually isoenergetic (ΔE is less than 1.00 kcal/mol). The quartet–sextuplet energy differences slightly increase along the series for n -odd clusters, being 3.69 kcal/mol for the VC_7 isomer, so both states are interesting from an experimental point of view. The stability of the different states can be explained in terms of their electronic configurations. Vanadium-doped carbon clusters, VC_n , present $4n + 5$ valence electrons, and the corresponding electronic configuration for the ${}^4\Phi$ state is

$$\{\text{core}\} 1\sigma^2 \dots 1\pi^4 \dots (n+2)\sigma^1 \left(\frac{n+1}{2}\right)\pi^3 1\delta^1 \quad n\text{-odd clusters}$$

The lowest-lying sextuplet state is obtained upon a $[(n+1)/2]\pi^3 \rightarrow 1\delta$ promotion. Both orbitals are mainly located at the vanadium atom, and the energy difference between the $\sigma^1\pi^3\delta^1$ and $\sigma^1\pi^2\delta^2$ configurations is very small. The lowest-lying doublet state corresponds to a $\pi^4\delta^1$ configuration and is located higher in energy (about 20.00 kcal/mol).

On the other hand, n -even linear VC_n clusters present two quartet states that are very close in energy, ${}^4\Sigma$ and ${}^4\Phi$, corresponding to the following electronic configurations:

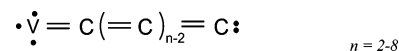
$$\{\text{core}\} 1\sigma^2 \dots 1\pi^4 \dots (n+2)\sigma^1 \left(\frac{n}{2}\right)\pi^4 1\delta^2 \quad {}^4\Sigma \text{ } n\text{-even clusters}$$

$$\{\text{core}\} 1\sigma^2 \dots 1\pi^4 \dots (n+2)\sigma^1 \left(\frac{n+2}{2}\right)\pi^1 1\delta^1 \quad {}^4\Phi \text{ } n\text{-even clusters}$$

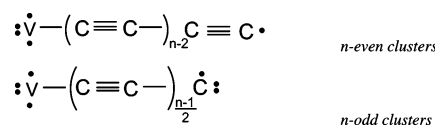
For the smaller members of the series ($n = 2, 4$), the ground state is found to be ${}^4\Sigma$, whereas for clusters with $n = 6$ and 8, the ${}^4\Phi$ state is more favorable. The similar energy of the two quartet states can be related to the fact that the

$[(n+2)/2]\pi$ and the 1δ molecular orbitals are mainly located at the vanadium atom. The lowest-lying sextuplet state, ${}^6\Phi$, is obtained from the ${}^4\Phi$ state upon $(n/2)\pi \rightarrow [(n+2)/2]\pi$ promotion. As can be seen in Table 1, the quartet–sextuplet energy difference decreases as n increases for n -even linear clusters. As in the case of n -odd isomers, the lowest-lying doublet state, ${}^2\Delta$, corresponding to a $\dots(n+2)\sigma^2(n/2)\pi^4 1\delta^1$ electronic configuration, is located higher in energy than quartet and sextuplet ones.

By looking at Figure 1, it can be seen that the C–C bond distances are all in the range 1.24–1.32 Å and, therefore, can be assimilated to moderately strong and typical double bonds, characteristic of cumulenic structures:



On the other hand, a clear alternation in the C–C bond distances can be observed, $C_{\text{odd}}-C_{\text{even}}$ being shorter than $C_{\text{even}}-C_{\text{odd}}$. This fact suggests that there is some polyacetylenic character with alternate triple C–C bonds starting in the C_1-C_2 bond:



It can also be observed that ${}^4\Phi$ states present bigger V–C bond distances (ranging from 1.859 Å for VC_2 to 1.953 Å for VC_8) than those of ${}^4\Sigma$ states (1.842 Å for VC_2 to 1.883 Å for VC_8). Consequently, the contribution of polyacetylenic-type structures is higher for ${}^4\Phi$ states than for the ${}^4\Sigma$ ones, where the cumulenic-type structure is dominant.

Dipole moments are, in all cases, quite high, reflecting a significant charge transfer from the vanadium atom to the C_n unit. Furthermore, the dipole moment increases regularly with the number of carbon atoms for both n -odd and n -even clusters, being higher for n -even members.

As in our previous studies on carbon-doped clusters,^{24,25} the relative stability of linear VC_n compounds will be discussed following the suggestion by Pascoli and Lavendy,⁵⁰ in terms of the incremental binding energies.⁵¹ The incremental binding energy can be defined as the change in energy accompanying the process



and can be computed as the consecutive binding energy differences between adjacent VC_n and VC_{n-1} clusters.

The incremental binding energy for the different linear VC_n clusters as a function of the number of carbon atoms is shown in Figure 2. From this figure, it can be observed that a clear even–odd alternation in stability exists for linear clusters, with their n -even members being more stable than the corresponding $n-1$ and $n+1$ ones. The difference in stability between n -odd and n -even clusters is attenuated for the last members of the series. This parity effect can be attributed to the electron number in π -type and δ -type highest occupied molecular orbitals. In the case of the smaller clusters of the series, a ground state corresponding to a δ^2 electronic configuration (n -even) is energetically more favor-

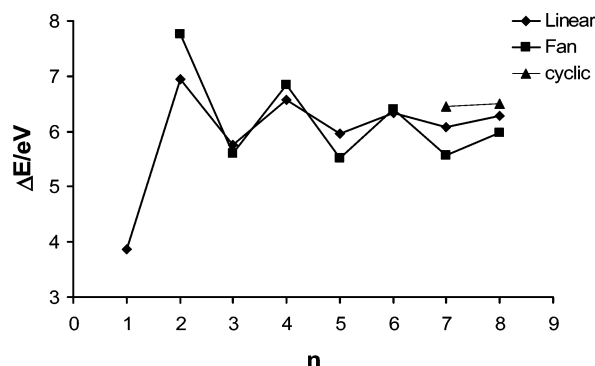


Figure 2. Incremental binding energies (eV) for the VC_n linear, fan, and cyclic clusters vs the number of carbon atoms at the B3LYP/6-311+G(d) level.

able than a $\pi^3\delta^1$ one (n -odd). On the other hand, linear VC_n clusters with $n = 6$ and 8 have ground states resulting from an electronic configuration of $\pi^1\delta^1$, which is only slightly more stable than the corresponding $\pi^3\delta^1$ for n -odd clusters.

VC_n “Fan” Clusters. The molecular properties (absolute and relative energies, S^2 expectation values, and dipole moments) for the lowest-lying doublet, quartet, and sextuplet states for fan-type VC_n clusters are given in Table 2, whereas the corresponding vibrational frequencies and rotational constants are included as Supporting Information in Table S2. In addition, in Figure 3, the geometrical parameters for the ground states are shown. In general, all of the structures reported in Figure 3 are true minima on their respective potential energy surfaces, with the only exception being the 4B_2 state of VC_7 at the B3LYP/LAN-6+(d) level. The doublet state of VC_6 also presented an imaginary frequency when the LAN-6+(d) basis set was employed (as can be seen in Table S2). In both cases, all of our attempts to find a true minimum failed. For the 4B state of VC_8 , we only reached the fan structure with the 6-311+G(d) basis set; all of our attempts to obtain this structure with the LAN-6+(d) basis set led to the cyclic conformation, which is lower in energy. As in the case of linear isomers, the inclusion of effective core potentials in the basis set of the vanadium atom does not seem relevant for the description of fan VC_n isomers, because not only are the geometrical parameters obtained with both basis sets, 6-311+G(d) and LAN-6+(d), very coincident (see Figure 3) but also all other properties are very close (see Tables 2 and S2).

There are only available theoretical results for the first member of the series, VC_2 .^{13,30} Majumdar et al.¹³ have studied the different states of the VC_2 system in C_{2v} symmetry. As in the case of linear structures, they employed MRSDCI and DFT/B3LYP methods with a RECPs basis set for vanadium and carbon atoms. They found that, in general, the geometries and the energy separations of the reported electronic states at the DFT level are similar to the MRSDCI data for most of the states. An 2A_2 symmetry and an 6A_1 state are reported as the lowest-lying doublet and sextuplet states, which are located about 27.90 and 28.59 kcal/mol, respectively, above the 4B_1 ground state at the MRCISD+Q level. We also found $^2A''$ (corresponding to an 2A_2) and 6A_1 states with energy differences relative to the 4B_1 state very similar to that

Table 2. Electronic Energies, $\langle S^2 \rangle$ Values, Binding Energies (for the Ground States), Dipole Moments, and Relative Energies for Fan VC_n Clusters with the B3LYP/6-311+G(d) (First Line) and B3LYP/LAN-6+(d) (Second Line) Methods

isomer	state	$-E$ (au)	$\langle S^2 \rangle$	BE (eV)	μ (D)	ΔE (kcal mol ⁻¹)
VC_2	$^2A''$	1019.995993	0.7753		6.41	27.08
		147.326054	0.7789		6.48	27.01
	4B_1	1020.039824	3.7897	11.78	6.77	0.00
		147.370027	3.7906	11.75	6.80	0.00
	6A_1	1019.985001	8.7680		4.28	34.14
		147.314893	8.7691		4.66	34.29
VC_3	2A_1	1058.109391	0.8748	17.56	5.34	0.00
		185.436671	0.8909	17.44	5.28	0.00
	4B_2	1058.100062	3.8157		5.32	5.23
		185.427137	3.8256		5.47	5.31
	6A_1	1058.081370	8.7977		5.02	16.57
		185.409567	8.7994		5.24	15.94
VC_4	2B_1	1096.209770	1.6403		3.67	8.35
		223.534658	1.6368		3.68	9.11
	4B_1	1096.223033	3.7891	24.53	3.96	0.00
		223.549048	3.7910	24.39	4.01	0.00
	6B_1	1096.150580	8.7721		3.61	44.25
		223.479310	8.7707		4.07	42.52
VC_5	$^2A'$	1134.287688	1.6061	30.18	2.32	0.00
		261.609891	1.6533	29.92	2.29	0.00
	$^4A'$	1134.281289	3.8096		1.86	3.71
		261.603569	3.8195		1.83	3.31
	6B_2	1134.250284	8.8448		1.98	22.78
		261.575483	8.8449		2.14	20.81
VC_6	$^2A'$	1172.361429	0.8137		3.77	14.81
		299.681196	0.8324		3.82	16.23
	4A_2	1172.385474	3.7883	36.72	0.84	0.00
		299.708020	3.7892	36.48	0.74	0.00
	6B_1	1172.316781	8.7860		0.58	41.62
		299.642708	8.7864		0.23	39.66
VC_7	2A	1210.445070	1.6656		3.12	5.29
	2A_1	337.764383	1.7390		3.21	5.16
	4B_2	1210.453569	3.8122	42.46	3.28	0.00
		337.772336	3.8278	42.11	3.35	0.00
	$^6A'$	1210.438130	8.8444		1.43	9.52
		337.763581	8.8460		1.34	5.61
VC_8	$^2A''$	1248.531749	1.7721		3.30	2.53
		375.841624	1.7449		3.42	
	4B	1248.535327	3.7743	48.57	4.24	0.00
	6B_1	1248.496690	8.8059		1.38	23.70
		375.824748	8.8095		1.26	

estimated by Majumdar et al. (27.08 and 34.14 kcal/mol, respectively; see Table 2).

As can be seen in Table 2, all n -even fan VC_n clusters have quartet ground states, and the quartet–doublet energy difference has a tendency to decrease as the number of carbon atoms increases, obtaining an energy difference of only 2.53 kcal/mol for $n = 8$. For n -odd clusters, doublet and quartet states are close in energy, and we have found that for VC_3 and VC_5 isomers the ground state corresponds to 2A_1 ($^2A'$), whereas in the case of VC_7 , a 4B_2 state is predicted to lie lower in energy than the corresponding doublet one. Along all of the series, the sextuplet states are the most unstable

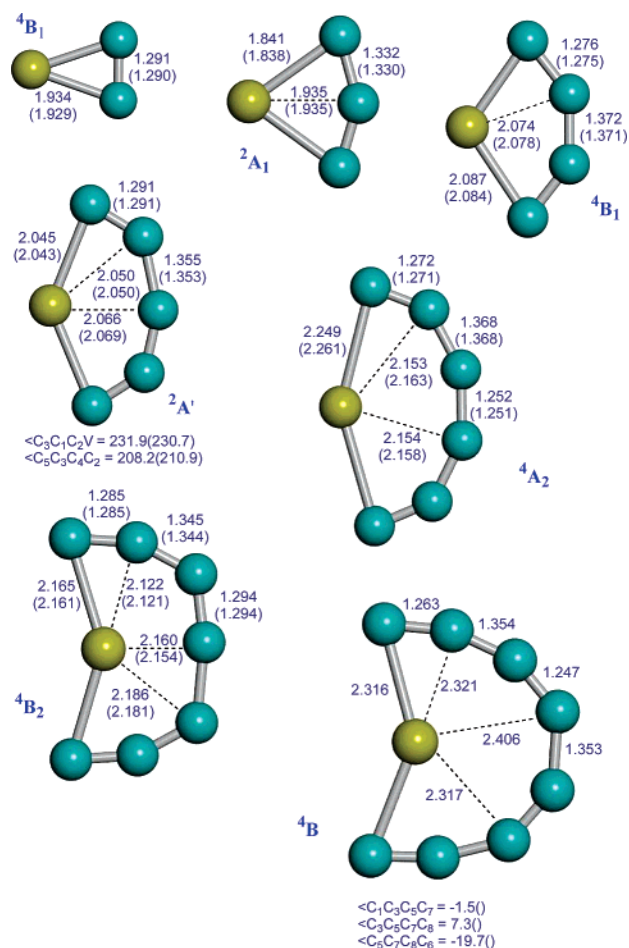


Figure 3. Equilibrium geometries of VC_n fan clusters at the B3LYP/6-311+G(d) and B3LYP/LAN-6+(d) (in parentheses) levels of theory. Distances are given in angstroms.

ones, with an energy difference respective to the quartet states that is lower for n -odd clusters. In general, we can see that in fan type structures there is a stabilization of doublet states with respect to the linear ones, whereas sextuplet states increase their energy relative to quartet ones.

There are some interesting features of the geometrical parameters for fan VC_n clusters. It can be seen, in Figure 3, that the V–C distances for fan structures are, in general, longer than in the case of linear isomers. An analysis of the V–C bond distances shows that there is a π -type interaction between the vanadium atom and the entire carbon unit, and consequently, all of the V–C distances are very close. As an example, V–C₁, V–C₂, V–C₃, and V–C₄ are respectively 2.165, 2.122, 2.186, and 2.160 Å for VC_7 , suggesting that, in fact, there is a similar interaction between the vanadium and each of the carbon atoms. On the other hand, V–C bond lengths are higher for n -even clusters, and in both cases (n -even and n -odd), these distances are systematically longer as n increases, showing a lower degree of participation of the vanadium atom in each bonding when the number of carbon atoms in the C_n unit is higher. The C–C bond distances are within the range 1.25–1.37 Å, following a pattern that resembles the behavior found for linear isomers, with a clear alternation of C–C distances ($C_{\text{odd}}-C_{\text{even}}$ distances shorter than $C_{\text{even}}-C_{\text{odd}}$ ones).

Table 3. Electronic Energies, $\langle S^2 \rangle$ Values, Binding Energies (for the Ground States), Dipole Moments, and Relative Energies for Cyclic VC_n Clusters with the B3LYP/6-311+G(d) (First Line) and B3LYP/LAN-6+(d) (Second Line) Methods

isomer	state	$-E$ (au)	$\langle S^2 \rangle$	BE (eV)	μ (D)	ΔE (kcal mol ⁻¹)
VC_6	2A_2	1172.333646	1.7228		3.99	21.11
		299.661755	1.7121		4.69	20.49
	$^4A''$	1172.365666	3.8083	36.18	5.14	0.00
		299.694943	3.8144	36.12	5.21	0.00
	6A_1	1172.332800	8.7985		3.07	20.28
		299.655621	8.8017		3.29	24.26
VC_7	2B_1	1210.465646	1.1611		4.48	0.24
		337.793869	1.2476		4.27	-0.34
	2A_1	1210.463828	1.1736		4.44	1.32
		337.792043	1.2732		4.19	0.76
	4B_2	1210.465486	3.8578	42.78	3.44	0.00
		337.792814	3.8880	42.67	3.29	0.00
VC_8	6A_1	1210.448359	8.8787		0.20	9.68
		337.776627	8.8811		0.47	9.12
	2B_1	1248.543512	1.5622		0.26	14.51
		375.870105	1.6257		0.24	15.26
	$^4A''$	1248.566679	3.7820	49.42	0.12	0.00
	4B_1	375.894644	3.7880	49.33	0.05	0.00
	6A_2	1248.510595	8.8032		0.25	34.25
		375.838716	8.8108		0.42	34.10

It is also worth mentioning that the dipole moment decreases when n increases for small fan clusters, but an inversion in the trend is observed from $n = 6$. This change can be related with the fact that the vanadium atom tends to be included into the C_n unit for larger fan structures. As expected, the dipole moments of fan clusters are lower than the corresponding ones of linear species.

In Figure 2, the incremental binding energies for the fan VC_n clusters are also represented. It can be readily seen that incremental binding energies for fan clusters follow the same general pattern as their linear analogues. Again, n -even clusters are more stable than n -odd ones, and the difference in stability between n -odd and n -even clusters is attenuated when n increases. But now, the incremental binding energies vary more drastically for consecutive members in the series than for linear clusters.

VC_n “Cyclic” Clusters. Cyclic structure where the vanadium atom is bonded to the two terminal carbon atoms of the C_n unit are only reached for $n = 6, 7$, and 8 (in the case of $n = 5$, a cyclic structure was located, but we have not included it because it is lying very high in energy). All of our attempts to obtain this rearrangement for $n < 5$ collapsed to the fan-type structure with the two basis sets employed in this work. The main properties for the lowest-lying doublet, quartet, and sextuplet states of cyclic VC_n clusters are given in Table 3, whereas geometries for the ground states are shown in Figure 4. As in previous sections, the vibrational frequencies and rotational constants for the lowest-lying doublet, quartet, and sextuplet states of cyclic clusters are given as Supporting Information in Table S3. As in the case of linear and fan clusters, the effect of employing effective core potentials to describe the vanadium

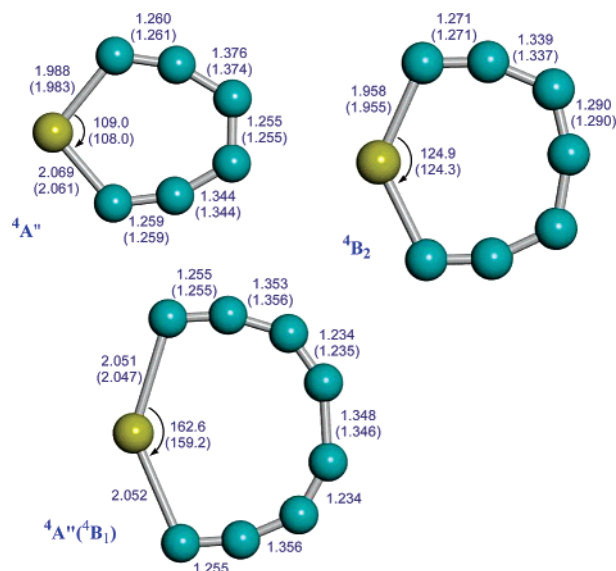


Figure 4. Equilibrium geometries of VC_n cyclic clusters at the B3LYP/6-311+G(d) and B3LYP/LAN-6+(d) (in parentheses) levels of theory. Distances are given in angstroms.

atom on the geometrical parameters, harmonic frequencies, dipole moments, and energies is not particularly important. All of the isomers included in Table 3 are true minima on their respective potential energy surfaces, except the 2A_2 state of VC_6 , which has an imaginary frequency at the B3LYP/LAN-6+(d) level. All of our attempts to find a true minimum at this level in C_s symmetry failed.

From Table 3, it is readily seen that cyclic clusters have quartet ground states. However, in the case of the VC_7 cluster, there are two doublet states, 2B_2 and 2A_1 , that are very close in energy to the 4B_2 ground state (energy differences between the three states are about 1.00 kcal/mol), and therefore, the three states could be accessible to experimental detection. The lowest-lying sextuplet state of VC_7 , 6A_1 , is only located about 9.68 kcal/mol above the ground state. The doublet–quartet, and sextuplet–quartet energy differences are larger for n -even clusters than for VC_7 . In the case of n -even, it seems that the doublet states tend to be more stable when n increases, whereas the energy differences for sextuplet ones increase when going from VC_6 to VC_8 clusters.

Concerning the geometrical parameters, it can be seen in Figure 4 that V–C bond distances in cyclic systems are between those found for linear and fan isomers, according to the fact that the vanadium atom is bonded to the two terminal carbon atoms. On the other hand, the C–C bond distances exhibit a behavior quite similar to that found in the linear and fan isomers, with an alternation of C–C bond distances ($C_{\text{odd}}-C_{\text{even}}$ distances being shorter than $C_{\text{even}}-C_{\text{odd}}$ ones). In cyclic isomers, the dipole moments are relatively high but decrease significantly for VC_8 .

Incremental binding energies for cyclic VC_n clusters can only be calculated for $n = 7$ and 8. As can be seen in Figure 2, the incremental binding energies for cyclic VC_7 and VC_8 are very similar, the VC_8 cluster being only slightly more stable. Therefore, the parity effect for cyclic systems seems to be lower than that in linear and fan structures.

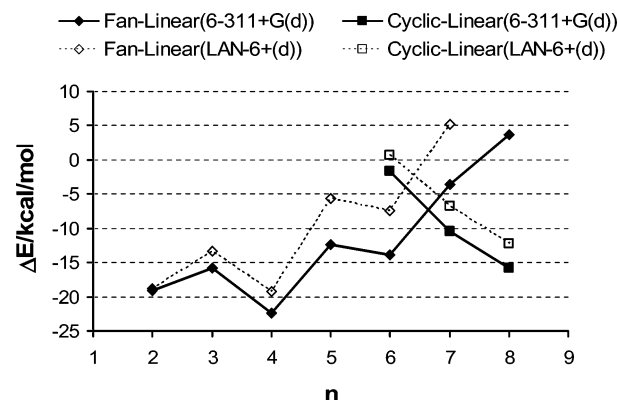


Figure 5. Relative energies (kcal/mol) of linear, fan, and cyclic VC_n clusters vs the number of carbon atoms.

Linear–Fan–Cyclic Stability. The energy differences between linear, fan, and cyclic structures for VC_n clusters are shown in Figure 5 as a function of the number of carbon atoms. We have represented the relative energies of fan and cyclic structures with respect to the linear ones, and a negative value means that the fan or the cyclic structure is more stable than the corresponding linear one. In general, we can see that the results obtained with the LAN-6+(d) basis set show similar trends to those obtained with the 6-311+G(d) basis set. Nevertheless, it can be seen that the LAN-6+(d) basis set slightly favors the linear isomer compared to the 6-311+G(d) basis set. This effect is larger for the last members of the series.

From Figure 5, we can see that for $n \leq 6$, VC_n clusters are predicted to prefer fan structures, and it seems that fan isomers could be the most favorable to be characterized in experimental studies. There is also a clear even–odd alternation, n -even fan clusters being comparatively more stable than n -odd ones. This alternation can be related to the fact that fan structures have higher incremental binding energies for n -even clusters than do linear ones, whereas for n -odd the incremental binding energy is smaller than that of the corresponding linear isomers. On the other hand, when $n > 6$, the trend is to favor linear structures, and for $n = 8$, the linear isomer is even more stable than the fan structure. However, the behavior of the cyclic–linear energy differences is the opposite. For $n = 6$, linear and cyclic isomers are nearly isoenergetic, and the differences decrease almost linearly when going from VC_6 to VC_8 . This fact results in the prediction that cyclic structures are the most stable VC_n isomers with $n > 6$.

Finally, as it can be seen in Figure 5, although the LAN-6+(d) basis set favors linear structures over fan and cyclic ones, both basis sets predict that, for $n \leq 6$, the most stable isomer is the fan structure and, for $n > 6$, the cyclic one is.

Conclusions

A theoretical study using the B3LYP method with the 6-311+G(d) and LAN-6+(d) basis sets has been carried out for the most stable isomers (linear, fan, and cyclic) of VC_n ($n = 1-8$) neutral clusters. Predictions for their geometrical parameters and other properties that could be useful for an eventual experimental characterization have been provided.

According to our calculations, linear VC_n clusters have quartet lowest-lying states, with the only exception being VC, which has a $^2\Delta$ ground state. n -odd clusters have a $^4\Phi$ ground state, and the lowest-lying sextuplet, $^6\Sigma$, is very close in energy, whereas for n -even, the $^4\Sigma$ and $^4\Phi$ states are very close in energy. The $^4\Sigma$ state is the most stable for clusters with $n = 2$ and 4, whereas VC_6 and VC_8 have a $^4\Phi$ ground state. In the case of fan VC_n clusters, n -even species have quartet ground states. For n -odd clusters, doublet states are favored for the first members of the series ($n = 3, 5$), whereas quartet ground states are found for the VC_7 isomer. The three cyclic VC_n clusters characterized have quartet lowest-lying states.

The stability of linear and fan clusters as a function of the size has been discussed in terms of the incremental binding energies. For both linear and fan structures, a clear even–odd alternation in stability is found, n -even clusters being more stable than n -odd ones. It is also found that this parity effect decreases along the series.

Concerning a possible experimental work on this system, one of the most interesting results of the present work refers to the competition between linear, fan, and cyclic structures. Our results suggest that for $n \leq 6$ there is a preference for fan structures over linear ones, especially for low n values. A parity effect is also observed, fan isomers being more stable for n -even clusters. For larger clusters ($n = 7$ and 8), the cyclic structure is the most stable. The linear structure is the least stable structure considered in this work for neutral VC_n clusters, only for VC_8 , the linear structure is slightly more stable than the fan isomer.

Finally, the results obtained with both basis sets for the descriptions of geometrical parameters, energies, and other properties are very close. Therefore, the employ of effective core potentials for the description of the vanadium atom can be useful in the study of large vanadium–carbon clusters.

Acknowledgment. This research has been supported by the Ministerio de Ciencia y Tecnología of Spain (Grant BQU2004-07405-C02-01) and by the Junta de Castilla y León (Grant VA 085/03).

Supporting Information Available: Vibrational frequencies and rotational constants for linear VC_n , fan VC_n , and cyclic VC_n clusters are given in Tables S1–S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Clemmer, D. E.; Hunter, J. M.; Shelomov, K. B.; Jarrold, M. F. *Nature* **1994**, 372, 248–250.
- (2) Chai, Y.; Guo, T.; Jin, C.; Haufler, R. E.; Chibante, L. P. F.; Fure, J.; Wang, L.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* **1991**, 95, 7564–7568.
- (3) Iijima, S.; Ichihashi, T. *Nature* **1993**, 363, 603–605.
- (4) Wei, S.; Guo, B. C.; Purnell, J.; Buzza, S.; Castleman, A. W. *Science* **1992**, 256, 818–820.
- (5) Wei, S.; Guo, B. C.; Purnell, J.; Buzza, S.; Castleman, A. W. *J. Phys. Chem.* **1992**, 96, 4166–4168.
- (6) Pilgrim, J. S.; Duncan, M. A. *J. Am. Chem. Soc.* **1993**, 115, 6958–6961.
- (7) Rohmer, M. M.; Benard, M.; Poblet, J. M. *Chem. Rev.* **2000**, 100, 495–542.
- (8) Guo, B. C.; Kearns, K. P.; Castleman, A. W. *Science* **1992**, 225, 1411–1413.
- (9) Guo, B. C.; Wei, S.; Purnell, J.; Buzza, S.; Castleman, A. W. *Science* **1992**, 256, 515–516.
- (10) Roszak, S.; Balasubramanian, K. *J. Phys. Chem. A* **1997**, 101, 2666–2669.
- (11) Jackson, P.; Gadd, G. E.; Mackey, D. W.; van der Wall, H.; Willett, G. D. *J. Phys. Chem. A* **1998**, 102, 8941–8945.
- (12) Hendrickx, M.; Clima, S. *Chem. Phys. Lett.* **2004**, 388, 284–289.
- (13) Majumdar, D.; Roszak, S.; Balasubramanian, K. *J. Chem. Phys.* **2003**, 118, 130–141.
- (14) Arbuznikov, A. V.; Hendrickx, M.; Vanquickenborne, L. G. *Chem. Phys. Lett.* **1999**, 310, 515–522.
- (15) Hendrickx, M.; Clima, S. *Chem. Phys. Lett.* **2004**, 388, 290–296.
- (16) Arbuznikov, A. V.; Hendrickx, M. *Chem. Phys. Lett.* **2000**, 320, 575–581.
- (17) Zhai, H. J.; Wang, L. S.; Jena, P.; Gutsev, G. L.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **2004**, 120, 8996–9008.
- (18) Sumathi, R.; Hendrickx, M. *Chem. Phys. Lett.* **1998**, 287, 496–502.
- (19) Sumathi, R.; Hendrickx, M. *J. Phys. Chem. A* **1998**, 102, 4883–4889.
- (20) Noya, E. G.; Longo, R. C.; Gallego, L. J. *J. Chem. Phys.* **2003**, 119, 11130–11134.
- (21) Froudakis, G. E.; Muhlhauser, M.; Andriotis, A. N.; Menon, M. *Phys. Rev. B* **2001**, 64, 241401-1–241401-4.
- (22) Grey, G.; Alemany, M. M. G.; Dieguez, O.; Gallego, L. G. *Phys. Rev. B* **2000**, 62, 12640–12643.
- (23) Longo, R. C.; Alemany, M. M. G.; Fernandez, B.; Gallego, L. J. *Phys. Rev. B* **2003**, 68, 167401-1–167401-3.
- (24) Redondo, P.; Barrientos, C.; Largo, A. *J. Phys. Chem. A* **2005**, 109, 8594–8603.
- (25) Redondo, P.; Barrientos, C.; Largo, A. *J. Phys. Chem. A* **2006**, 110, 4057–4064.
- (26) Maclagan, R. G. A. R.; Scuseria, G. E. *Chem. Phys. Lett.* **1996**, 262, 87–90.
- (27) Gutsev, G. L.; Andrews, L.; Bauschlicher, C. W., Jr. *Theor. Chem. Acc.* **2003**, 109, 298–308.
- (28) Majumdar, D.; Balasubramanian, K. *Mol. Phys.* **2003**, 101, 1369–1376.
- (29) Kalemios, A.; Dunning, T. H.; Mavridis, A. *J. Chem. Phys.* **2005**, 123, 14301–14309.
- (30) Tono, K.; Torasaki, A.; Ohta, T.; Kondow, T. *Chem. Phys. Lett.* **2002**, 351, 135–141.
- (31) Li, X.; Wang, L.-S. *J. Chem. Phys.* **1999**, 111, 8389–8395.
- (32) Wang, L.-S.; Li, X. *J. Chem. Phys.* **2000**, 112, 3602–3608.
- (33) Becke, A. D. *J. Chem. Phys.* **1986**, 84, 4524–4529.
- (34) Becke, A. D. *J. Chem. Phys.* **1988**, 88, 2547–2553.
- (35) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785–789.
- (36) Becke, A. D. *J. Chem. Phys.* **1988**, 88, 1053–1062.

- (37) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (38) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133–1139.
- (39) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654.
- (40) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033–1036.
- (41) Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377–4384.
- (42) Ragavachari, K.; Trucks, G. W. *J. Chem. Phys.* **1989**, *91*, 1062–1065.
- (43) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270–283.
- (44) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284–298.
- (45) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299–310.
- (46) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millan, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelly, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian Inc.: Pittsburgh, PA, 1998.
- (47) Gingerich, K. A. *J. Chem. Phys.* **1969**, *50*, 2255–2256.
- (48) Gupta, S. K.; Gingerich, K. A. *J. Chem. Phys.* **1981**, *74*, 3584–3590.
- (49) Hamrick, Y. M.; Weltner, W., Jr. *J. Chem. Phys.* **1991**, *94*, 3371–3380.
- (50) Pascoli, G.; Lavendy, H. J. *Phys. Chem. A* **1999**, *103*, 3518–3524.
- (51) Raghavachari, K.; Binkley, J. S. *J. Chem. Phys.* **1987**, *87*, 2191–2197.

CT060033Q