

The electronic structure of vanadium carbide, VC

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Within an energy range of 2.4 eV, we have explored 29 of the 36 states of the diatomic molecule VC that arise from the atoms in their ground state, $V(4s^23d^3; ^4F) + C(2s^22p^2; ^3P)$. We use multireference methods with large atomic natural orbital basis sets. The ground state is of $^2\Delta$ symmetry with the first two excited states, $^4\Delta$ and $^2\Sigma^+$, located 4.2 and 7.0 kcal/mol above the X state. All the states examined in this work are relatively strongly bound and show significant charge transfer from V to C. The binding energy of the X $^2\Delta$ state is estimated to be 95.3 kcal/mol in good agreement with the experimental value. © 2005 American Institute of Physics. [DOI: 10.1063/1.1926228]

I. INTRODUCTION

Diatomic first row transition metal (M) carbides constitute the “simplest” chemical species of the enormously complex general carbide family of molecules, yet they are both experimentally and computationally challenging.¹ Motivated by the essential lack of experimental and quantitative *ab initio* results on VC and in line with our previous work on the MC systems neutral (and cations) where, $M = \text{Sc}$ [Ref. 2(a)] (Sc^+) [Refs. 2(b) and 2(c)], Ti [Ref. 2(d)] (Ti^+) [Refs. 2(b) and 2(c)], (V⁺) [Refs. 2(c) and 2(e)], Cr [Ref. 2(f)] (Cr^+) [Refs. 2(c) and 2(e)], and Fe [Ref. 2(g)] (Fe^+) [Refs. 2(h) and 2(i)], we report *ab initio* calculations on 29 of the 36 states of the neutral vanadium carbide (VC), that arise from the atoms in their ground states, $V(4s^23d^3; ^4F) + C(2s^22p^2; ^3P)$.

The first experimental estimate for the dissociation energy D of gaseous VC reported 35 years ago by Gingerich³ was based on a thermochemical dimensionless parameter $\alpha = 1.44$ (Ref. 4) of uranium carbide, UC; he estimated that $D = 111 \pm 15$ kcal/mol. In a subsequent paper Gupta and Gingerich⁵ using Knudsen effusion mass spectrometry to identify the gaseous carbides of VC_n , NbC_n , and MoC_n ($n = 1, 2$), reported a thermochemically obtained value of $D = 100.1 \pm 5.7$ kcal/mol. In 1986, van Zee *et al.*,⁶ employing gas phase electron spin resonance (ESR) spectroscopy, suggested that the ground state of VC is of $^2\Sigma$ symmetry. The authors state, however, that this symmetry was incompatible with the observed Δg_{\perp} and Δg_{\parallel} values. The large negative $\Delta g_{\parallel} \equiv g_{\parallel} - g_e$ found in a more recent ESR experiment, results from the quenching of the X state's orbital angular momentum.⁷ Based on the behavior of the isoelectronic diatomics ScO and TiN, the authors proposed a X $^2\Delta_{3/2}$ as the most likely ground state of VC, and it was this state which was considered as quenched and observed in the ESR spectra.⁷

On the theoretical side, the first computational investiga-

tion of the electronic structure of VC seems to be that of Mattar in 1993,⁸ who studied the $^2\Delta$, $^2\Sigma^+$, and $^2\Pi$ states by the local density functional method. He predicted, correctly, that the $^2\Delta$ is the ground state. However, density functional theory (DFT) calculations strongly overestimated and underestimated the binding energy ($D_e = 156$ kcal/mol) and bond distance ($r_e = 1.577$ Å), respectively (*vide infra*). In 1996, Maclagan and Scuseria⁹ using a variety of DFT, coupled cluster [RCCSD(T)], and multireference methods (MRCI) combined with a $[10s8p3d/4s2p1d]$ basis, studied the X $^2\Delta$ and $^2\Sigma^+$ states of VC. Their results for D_e range from 67.3 [RCCSD(T)] to 150.4(LSDA) kcal/mol.

The most recent work on VC is that of Majumdar and Balasubramanian¹⁰ and of Gutsev *et al.*¹¹ In the first account, potential energy curves (PEC) for 19 molecular states were constructed using first-order configuration interaction and MRCI point calculations combined with relativistic effective core potentials for both atoms. The ground state was found to be of $^4\Delta$ symmetry with the $^2\Delta$ state lying 0.21 eV (4.84 kcal/mol) higher. Including a set of $4f$ functions the $^2\Delta \leftarrow X$ $^4\Delta$ gap decreases to 0.16 eV, while by adding the Davidson correction, the $^2\Delta$ becomes the ground state by 0.13 eV. In Ref. 11 DFT methods were employed for the ground state study of $\text{MC}^{0,\pm 1}$, $M = \text{Sc-Zn}$.

In this paper, we present high level MRCI calculations on 29 states of VC combined with quantitative basis sets. For all states, we have constructed full potential energy curves, reporting energetics, dipole moments, and the usual spectroscopic constants.

II. TECHNICAL DETAILS AND METHODS

For the V atom the atomic natural orbital basis set $20s15p10d6f4g$ of Bauschlicher,¹² and for the C atom the correlation consistent basis set $12s6p3d2f1g$ (cc-pVQZ) by

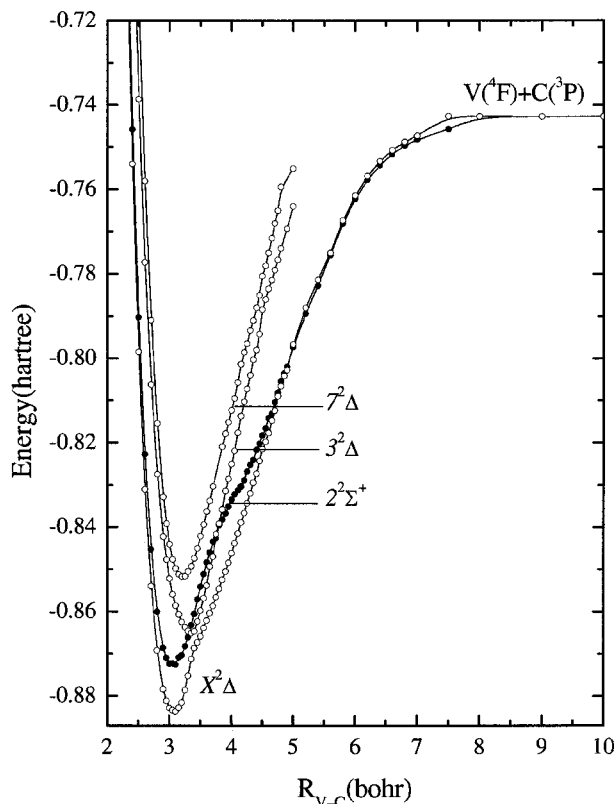


FIG. 1. MRCI potential energy curves of the ${}^2A_1({}^2\Delta, {}^2\Sigma^+)$ symmetry states of VC. Energies have been shifted by $+980.0 E_h$.

Dunning¹³ were employed, both generally contracted to $[7s6p4d3f2g1v5s4p3d2f1g/c]$, creating a 139-dimensional one electron Gaussian space.

The complete active space self-consistent field (CASSCF) wave functions were formed by allotting the nine valence electrons, five on V and four on C, among 13 valence orbital functions (those correlating with the $4s+4p+3d$ orbitals on V, and the $2s+2p$ orbitals on C). Under C_{2v} symmetry restrictions the reference expansions contain about 107 000, 89 000, and 29 000 configuration state functions (CSFs) for the doublets, quartets and sextets, respectively. All our reference wave functions obey axial $|\Lambda|$ symmetry. Additional correlation was accounted for by single and double excitations out of the reference space (MRCI = CASSCF + 1 + 2). The ensuing MRCI expansions consist of $\sim 200({}^6|\Lambda|)$ and $\sim 500({}^{2,4}|\Lambda|) \times 10^6$ CSFs. By using the internal contraction approximation as implemented in the MOLPRO 2002.6 package,¹⁴ the above numbers were reduced to $\sim 4({}^6|\Lambda|)$ and $\sim 10({}^{2,4}|\Lambda|) \times 10^6$ CSFs.

III. RESULTS AND DISCUSSION

The ground states of V and C atoms are ${}^4F(4s^23d^3)$ and ${}^3P(2s^22p^2)$, respectively. The following molecular states of ${}^{2S+1}|\Lambda|$ symmetry can be formed according to the well known Wigner and Witmer rules: $V({}^4F)+C({}^3P) \rightarrow VC^{2,4,6}[\Sigma^+(2), \Sigma^-, \Pi(3), \Delta(3), \Phi(2), \Gamma]$, namely, 36 states. With the exception of seven states (${}^2\Sigma^+, {}^{2,4,6}\Sigma^-, {}^{2,4}\Gamma, {}^6\Delta$), the PECs of the remaining 29 states have been calculated; see Figs. 1–6. Corresponding numerical results are presented in Table I, limited to total energies (E), bond distances (r_e),

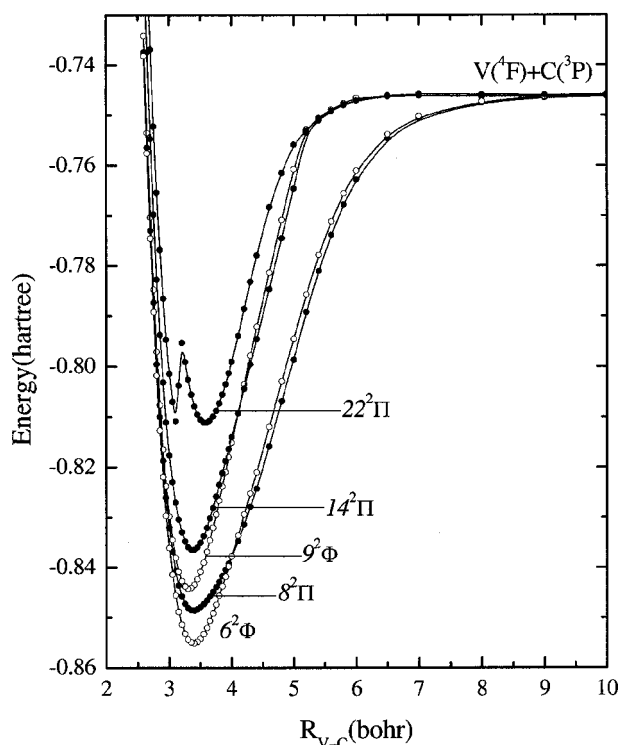


FIG. 2. MRCI potential energy curves of the ${}^2B_1({}^2\Pi, {}^2\Phi)$ symmetry states of VC.

dissociation energies (D_e), vibrational energy levels [$G(0)$], dipole moments (μ), and energy separations (T_e). Note that the 29 states span an energy range of less than 60 kcal/mol, or on the average, one state per 1.7 kcal/mol more or less equally spaced; see Fig. 7.

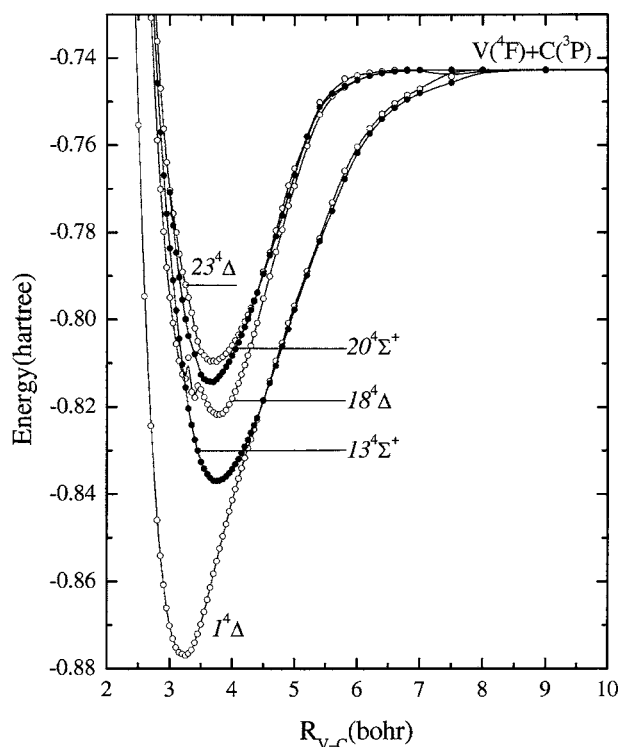


FIG. 3. MRCI potential energy curves of the ${}^4A_1({}^4\Delta, {}^4\Sigma^+)$ symmetry states of VC.

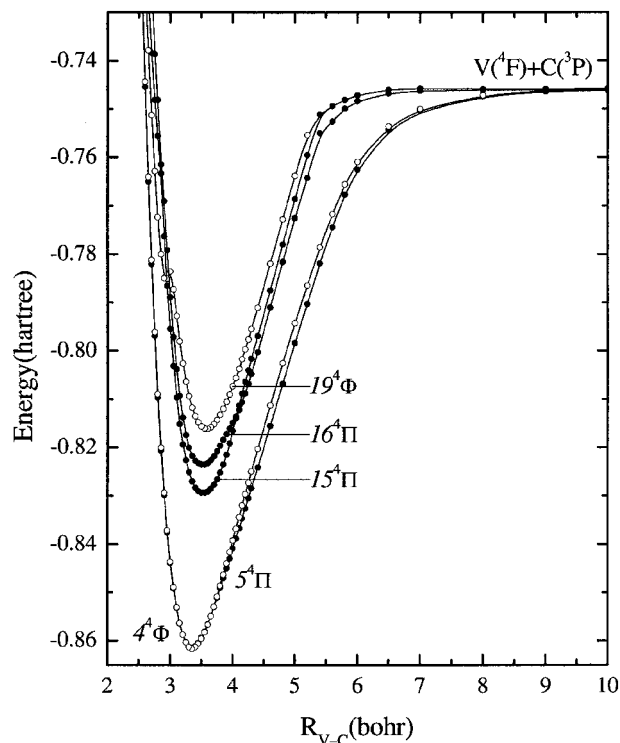


FIG. 4. MRCI potential energy curves of the ${}^4B_1({}^4\Pi, {}^4\Phi)$ symmetry states of VC.

To gain some insight into the nature of the lowest states of VC, we consider the ground state of the VC⁺ cation. According to Kerkinis and Mavridis [Refs. 2(c) and 2(e)] two states are strongly competing for the ground state of VC⁺, the ${}^3\Delta$ and ${}^1\Sigma^+$, separated by about 2 kcal/mol. The valence-bond–Lewis (vbL) diagrams of these two VC⁺ states are

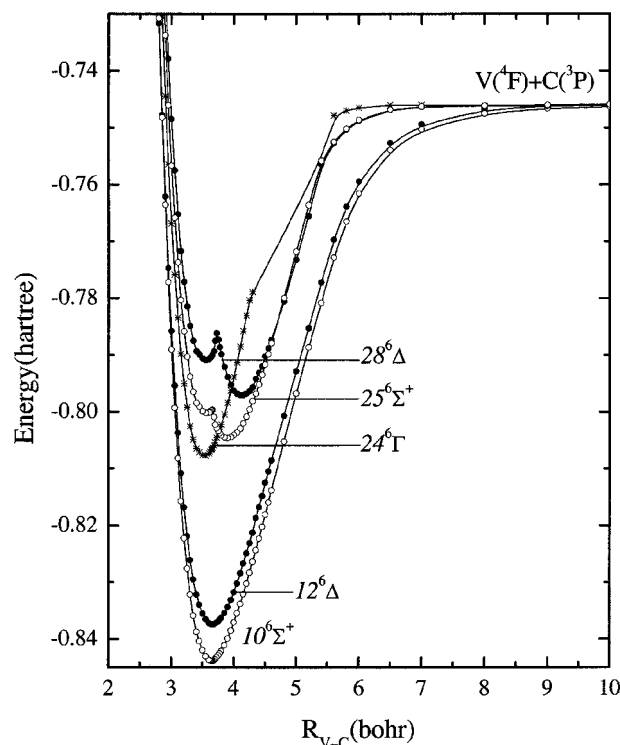


FIG. 5. MRCI potential energy curves of the ${}^6A_1({}^6\Sigma^+, {}^6\Delta, {}^6\Gamma)$ symmetry states of VC.

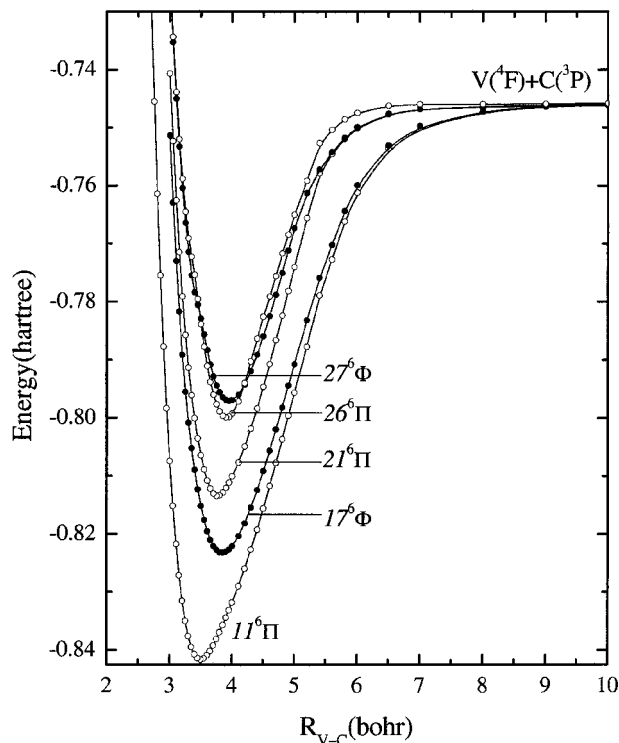
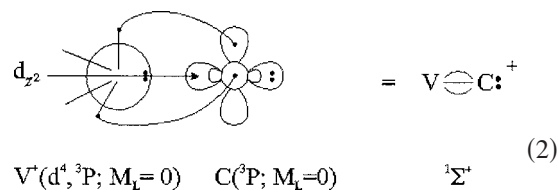
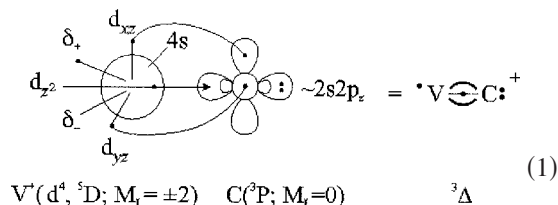


FIG. 6. MRCI potential energy curves of the ${}^6B_1({}^6\Pi, {}^6\Phi)$ symmetry states of VC.



featuring $2\frac{1}{2}$ and 3 bonds, respectively. Note that in the ${}^1\Sigma^+$ state the *in situ* V⁺ cation is in its third excited state, 1.452 eV above the 5D term.¹⁵ By grafting one electron to the ${}^3\Delta$ state of VC⁺ coupled into a doublet or quartet, the resulting states are ${}^2\Delta(\sigma^2\pi^4\delta_{\pm}^1)$, ${}^2,4\Delta(\sigma^1\sigma'^1\pi^4\delta_{\pm}^1)$, ${}^2,4\Sigma^-(\sigma^1\pi^4\delta_{\pm}^1\delta_{\pm}^1)$, and ${}^2\Gamma(\sigma^1\pi^4\delta_{\pm}^2)$. Analogously, two states are obtained from the ${}^1\Sigma^+$ triple bonded configuration, i.e., ${}^2\Sigma^+(\sigma^2\sigma'^1\pi^4)$ or ${}^2\Delta(\sigma^2\pi^4\delta_{\pm}^1)$. By intuition and/or experience, ground state candidates should be sought among the ${}^2\Delta(\sigma^2\pi^4\delta_{\pm}^1)$, ${}^4\Delta$, ${}^4\Sigma^-$, and ${}^2\Sigma^+$ states, and indeed, our calculations corroborate these reflections (*vide infra*).

In what follows we discuss the most interesting of the states starting from the ground state and grouping them according to their “similarity.” Table II collects the leading equilibrium CASSCF configurations and Mulliken distributions of all states studied. Note that the orbital numbering corresponds to the valence electrons only.

TABLE I. Total MRCI equilibrium energies E (hartree), bond distances r_e (Å), dissociation energies D_e (kcal/mol), zero point energies $G(0)$ (cm⁻¹), dipole moments $\mu(D)$, and energy gaps T_e (kcal/mol) of the VC states studied in the present work, in ascending energy order. Values in parenthesis refer to MRCI+Davidson correction.

State	$-E$	r_e	D_e	$G(0)$	μ^a	T_e
$X^2\Delta$	980.883 66 (980.894 5)	1.636 (1.636)	88.5 (89.3)	587.3 (472.8)	7.36	0.0 (0.0)
$1^4\Delta$	980.877 02 (980.887 3)	1.719 (1.712)	84.3 (84.8)	395.2 (419.3)	2.42	4.16 (4.50)
$2^2\Sigma^+$	980.872 58 (980.881 5)	1.636 (1.636)	81.6 (81.2)	411.0 (440.8)	2.88	6.95 (8.11)
$3^2\Delta$	980.865 13 (980.875 2)	1.782 (1.786)	76.9 (77.3)	496.6 (555.7)		11.6 (12.1)
$4^4\Phi$	980.863 20 (980.872 3)	1.756 (1.790)	73.8 (75.0)	395.6 (368.1)	2.84	12.8 (13.9)
$5^4\Pi$	980.863 13 (980.872 3)	1.751 (1.788)	73.4 (74.7)	382.5 (357.7)	2.81	12.9 (13.9)
$6^2\Phi$	980.855 12 (980.864 6)	1.794 (1.795)	68.7 (70.1)	340.0 (339.8)	2.41	17.9 (18.8)
$7^2\Delta$	980.851 72 (980.862 2)	1.703 (1.704)	68.5 (69.1)		2.96	20.0 (20.2)
$8^2\Pi$	980.848 57 (980.858 1)	1.789 (1.794)	64.3 (65.8)	283.0 (283.2)	2.11	22.0 (22.8)
$9^2\Phi$	980.844 26 (980.853 8)	1.752 (1.753)	61.9 (63.4)	393.5 (391.6)	2.21	24.7 (25.5)
$10^6\Sigma^+$	980.843 83 (980.855 2)	1.928 (1.923)	61.4 (64.0)	330.8 (339.5)	2.93	25.0 (24.6)
$11^6\Pi$	980.841 58 (980.852 4)	1.853 (1.845)	59.9 (62.2)	320.7 (335.1)	2.10	26.4 (26.4)
$12^6\Delta$	980.837 45 (980.847 1)	1.935 (1.931)	57.5 (59.1)	305.6 (309.4)	2.81	29.0 (29.7)
$13^4\Sigma^+$	980.836 93 (980.846 8)	1.981 (1.969)	59.1 (59.2)		2.55	29.3 (29.9)
$14^2\Pi$	980.836 53 (980.846 4)	1.785 (1.784)	56.9 (58.6)	372.4 (373.5)	2.31	29.6 (30.2)
$15^4\Pi$	980.829 40 (980.840 4)	1.865 (1.851)	52.4 (54.9)	294.8 (290.0)	1.75	34.0 (33.9)
$16^4\Pi$	980.823 54 (980.835 4)	1.866 (1.847)	48.9 (51.9)	282.5 (276.9)	2.65	37.7 (37.0)
$17^6\Phi$	980.823 32 (980.833 4)	2.033 (2.022)	48.5 (50.4)	263.3 (269.0)	2.21	37.9 (38.3)
$18^4\Delta$	980.821 76 (980.832 1)	1.989 (1.995)	47.7 (49.7)	340.4 (340.6)	2.91	38.8 (39.2)
$19^4\Phi$	980.816 14 (980.827 6)	1.892 (1.882)	44.2 (47.0)	308.4 (315.6)	1.38	42.4 (41.9)
$20^4\Sigma^+$	980.814 31 (980.825 2)	1.952 (1.922)	44.9 (51.7)	306.4	1.83	43.5 (43.4)
$21^6\Pi$	980.813 45 (980.824 8)	1.992 (1.987)	42.4 (45.1)	334.7 (354.1)	2.64	44.1 (43.7)
$22^2\Pi$	980.811 16 (980.822 1)	1.893 (1.886)	41.1 (43.5)	353.5 (352.3)	1.99	45.5 (45.4)
$23^4\Delta$	980.809 62 (980.821 0)	1.981 (1.940)	40.0 (42.6)	272.1 (269.0)	2.45	46.5 (46.1)
$24^6\Gamma$	980.807 72 (980.818 9)	1.864 (1.870)	38.8 (41.4)	339.5 (350.5)	3.03	47.6 (47.4)
$25^6\Sigma^+$	980.804 62 (980.816 4)	2.061 (2.035)	37.0 (39.9)	284.6 (399.2)	1.45	49.6 (49.0)
$26^6\Pi$	980.799 93 (980.810 7)	2.070 (2.077)	34.1 (36.4)	337.4 (329.5)	2.07	52.5 (52.6)
$27^6\Phi$	980.797 43 (980.807 7)	2.092 (2.082)	32.5 (34.4)	272.1 (278.3)	1.73	54.1 (54.5)
$28^6\Delta$	980.797 06 (980.806 8)	2.196 (2.173)	32.2 (33.9)	269.3 (282.5)	3.00	54.3 (55.0)

^aDipole moments obtained as expectation values. The finite field dipole moment of the $X^2\Delta$ state is $\mu_{FF} = 7.30$ D.

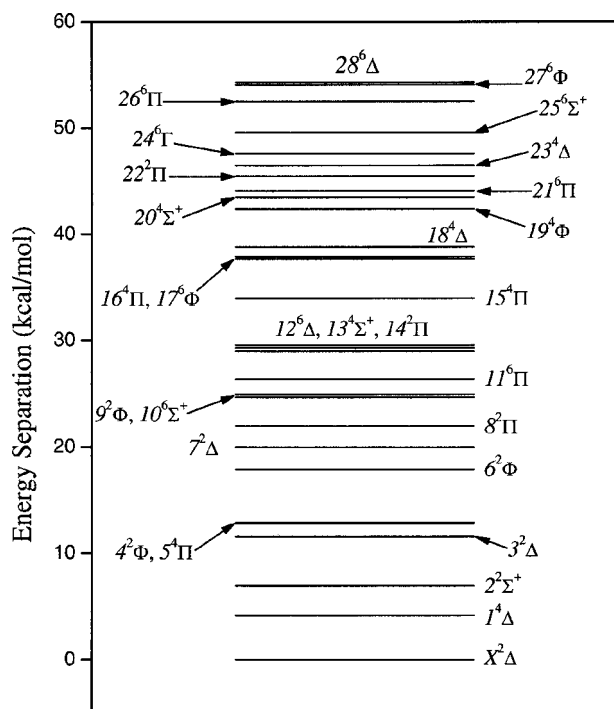
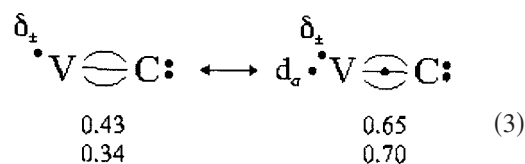


FIG. 7. Energy level diagram of the 29 VC states at the MRCI level of theory.

A. $X^2\Delta$, $3^2\Delta$, $7^2\Delta$ states

In the ground $^2\Delta$ state the leading configuration ($C_0 = 0.80$) in conjunction with the populations at equilibrium and infinity, support the bonding Scheme (1) with an additional electron coupled into a singlet in the σ frame, thus forming a whole σ bond. The *in situ* $M_L=0$ component of the C atom is the cause of about $0.4 e^-$ transfer from the $(4s4p_z)^{1.0}$ V hybrid to the empty $2p_z$ C orbital. The MRCI(+ Q) binding energy is 88.5(89.3) kcal/mol at $r_e = 1.636(1.636)$ Å (Table I). Assuming that the $3s^23p^6$ semi-core+scalar relativistic effects+basis set superposition error (BSSE) contribute the same to the D_e value of $X^2\Delta$ of VC as in the $X^3\Delta$ state of $VC^{+,2(e)}$ i.e., $4.0+3.81-0.16 = 7.65$ kcal/mol, and including the zero point energy correction [$G(0)$] of 1.68 kcal/mol, we obtain $D_0 = 88.5+5.97 = 94.5$ or 95.3 kcal/mol including the Davidson (+ Q) correction with a corresponding value of $r_e = 1.614$ Å. This value of D_0 compares favorably with the experimental one of 100.1 ± 5.7 kcal/mol.⁵ It is rather evident that a strong interaction between the $X^2\Delta$ and $3^2\Delta$ states is developing around 3.5 bohr (see Fig. 1).

The next two states of the same symmetry, $3^2\Delta$ and $7^2\Delta$, are located 11.6(12.1) and 20.0(20.2) kcal/mol above the $X^2\Delta$ state at the MRCI(+ Q) level. Although the $3^2\Delta$ state correlates to $|M_L = \pm 3\rangle_V \otimes |M_L = \mp 1\rangle_C$, its *in situ* atoms show a $|M_L = \pm 2\rangle_V \otimes |M_L = 0\rangle_C$ character. Judging from the most important configurations given in Table II along with the Mulliken distributions, the bonding of both $3^2\Delta$ and $7^2\Delta$ states can be described by the following “resonating” vBL structures [see also Scheme (1)]:



The pair of numbers (0.43, 0.65) and (0.34, 0.70), being the most important coefficients in the CASSCF expansions (Table II), if squared represent the weighted contributions to the $3^2\Delta$ and $7^2\Delta$ states, respectively.

Concluding, we note that Majumdar and Balasubramanian,¹⁰ suggested that the ground state of VC is of $^4\Delta$ symmetry with $D_e = 71.0(77.9)$ kcal/mol at the MRCI (+ Q) level; their T_e values for the $3^2\Delta \leftarrow X^4\Delta$, and $7^2\Delta \leftarrow X^4\Delta$ transitions are 18.9 and 33.9 kcal/mol, respectively, as contrasted to our values of 11.6($3^2\Delta \leftarrow X^2\Delta$) and 20.0($7^2\Delta \leftarrow X^2\Delta$) kcal/mol.

B. $1^4\Delta$, $18^4\Delta$, $23^4\Delta$ states

According to our calculations, the $1^4\Delta$ is the first excited state of VC 4.16(4.50) kcal/mol higher at the MRCI (+ Q) level of theory. The bonding structure is that of Scheme (1) of $VC^{+(3)\Delta}$ by attaching a single electron coupled into a quartet to a d_{σ} orbital, in conformity with the Mulliken populations (Table II). Clearly, we have two π bonds and a half σ (one electron) bond, while $0.2 e^-$ move through the σ frame from V to C ($M_L=0$).

The intense multireference character of the next two $^4\Delta$ states 38.8(39.2) and 46.5(46.1) kcal/mol above the X state prohibits any bonding interpretation; PECs of the $^4\Delta$ states are given in Fig. 3. Similar T_e values with respect to the ground state ($^4\Delta$) are given in Ref. 10.

C. $2^2\Sigma^+$ state

The addition of an electron to the σ frame of the $^1\Sigma^+$ state of VC^+ , Scheme (2), gives rise to the second excited state of VC lying 6.95(8.11) kcal/mol above the $X^2\Delta$ at the MRCI(+ Q) level. The bonding structure is identical to that of the $X^2\Delta$ state, the difference being the movement of the symmetry defining electron from a $\delta_{\pm}(^2\Delta)$ to a σ orbital ($^2\Sigma^+$), leaving the triple bond practically undisturbed. This is nicely reflected in the nearly identical bond distances, $r_e = 1.636$ Å computed for both the $X^2\Delta$ and $2^2\Sigma^+$ states. What is striking, however, is the completely different dipole moment values between the two states 7.36($X^2\Delta$) vs 2.88($2^2\Sigma^+$) D, the reason being the centroid of the electronic σ distribution at the back of the metal in the $2^2\Sigma^+$ state.

A state of $^2\Sigma^+$ symmetry is also reported in Ref. 10 with $r_e = 1.770$ Å and $T_e = 49.4$ kcal/mol, obviously a different one than the one just discussed.

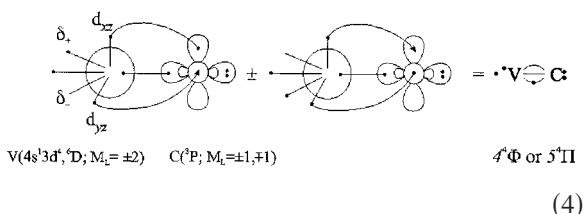
D. $4^4\Phi$, $5^4\Pi$ states

The leading configurations and equilibrium Mulliken populations of the essentially degenerate $4^4\Phi$, $5^4\Pi$ states with nearly identical PECs (Fig. 4), point clearly to the bonding Scheme (4), suggesting a σ and $3/2 \pi$ bonds

TABLE II. Leading equilibrium CASSCF CFs and Mulliken atomic populations of 29 VC states.

State	Configurations	V										C			
		4s	4p _z	3d _z 2	4p _x	3d _{yz}	4p _y	3d _{yz}	3d _{xy}	3d _{xy}	2s	2p _z	2p _x	2p _y	
X ² Δ	0.80 1σ ² 2σ ² 1δ _x ¹ π _x ² π _y ² +0.32 1σ ² 2σ ² 3σ ¹ 1δ _x ¹ π _x ² 1π _y ²) 0.85 1σ ² 2σ ² 3σ ¹ 1π _x ² 1π _y ² 1δ _x ¹)	0.29	0.22	1.05	0.06	0.97	0.06	0.97	1.0	0.0	1.60	0.82	0.94	0.94	
1 ⁴ Δ	-0.15 1σ ² 2σ ² 3σ ¹ (2π _x ² 1π _y ² +1π _x ² 2π _y ²)1δ _x ¹) +0.15 1σ ² 2σ ² 3σ ¹ (1π _x ² 2π _x ¹ 1π _y ² +1π _x ² 1π _y ² 2π _y ¹)1δ _x ¹)	0.85	0.26	0.66	0.05	0.96	0.05	0.96	1.0	0.0	1.64	0.60	0.96	0.96	
2 ² Σ ⁺	0.81 1σ ² 2σ ² 3σ ¹ 1π _x ² 1π _y ²) - 0.20 1σ ² 2σ ² 3σ ¹ 2π _x ² 1π _y ²)	0.90	0.35	1.22	0.04	1.09	0.04	1.09	0.05	1.64	0.86	0.83	0.83		
3 ² Δ	0.65 1σ ² 2σ ² 3σ ¹ 1δ _x ¹ 1π _x ² 1π _y ²) + 0.43 1σ ² 2σ ² 1δ _x ¹ 1π _x ² 1π _y ²) + 0.22 1σ ² 2σ ² 3σ ¹ 1δ _x ¹ 1π _x ² 1π _y ²)	0.66	0.20	0.73	0.05	0.99	0.05	0.99	1.0	0.0	1.62	0.79	0.93	0.93	
4 ⁴ Φ	0.57 1σ ² 2σ ² 3σ ¹ (1π _x ² 1π _x ¹ 1δ _x ¹ +1π _x ¹ 1π _x ² 1δ _x ¹)	0.83	0.32	1.05	0.04	0.71	0.04	0.71	0.50	1.74	1.02	0.74	0.74		
5 ⁴ Π	0.57 1σ ² 2σ ² 3σ ¹ (1π _x ² 1π _x ¹ 1δ _x ¹ -1π _x ¹ 1π _x ² 1δ _x ¹)	0.82	0.32	1.01	0.04	0.73	0.04	0.73	0.50	1.74	1.02	0.74	0.74		
6 ² Φ	0.58 1σ ² 2σ ² 3σ ¹ (1π _x ² 1π _x ¹ 1δ _x ¹ +1π _x ¹ 1π _x ² 1δ _x ¹)	0.84	0.36	1.06	0.04	0.67	0.04	0.67	0.50	1.73	0.98	0.77	0.77		
7 ² Δ	0.70 1σ ² 2σ ² 3σ ¹ 1δ _x ¹ 1π _x ² 1π _y ²) -0.37 1σ ² 2σ ² 3σ ¹ 1δ _x ¹ 1π _x ² 1π _y ²) -0.34 1σ ² 2σ ² 1δ _x ¹ 1π _x ² 1π _y ²)	0.72	0.23	0.76	0.05	0.98	0.05	0.98	1.0	0.0	1.61	0.67	0.95	0.95	
8 ² Π	0.58 1σ ² 2σ ² 3σ ¹ (1π _x ² 1π _x ¹ 1δ _x ¹ -1π _x ¹ 1π _x ² 1δ _x ¹)	0.83	0.36	0.96	0.04	0.73	0.04	0.73	0.50	1.73	0.97	0.77	0.77		
9 ² Φ	0.59 1σ ² 2σ ² 3σ ¹ (1π _x ² 1π _x ¹ 1δ _x ¹ +1π _x ¹ 1π _x ² 1δ _x ¹)	0.88	0.33	1.08	0.04	0.69	0.04	0.69	0.50	1.72	0.95	0.77	0.77		
10 ⁶ Σ ⁺	1σ ² [(0.62)2σ ² 3σ ¹ + (0.53)2σ ² 3σ ²]1π _x ¹ 1π _y ¹ 1δ _x ¹)	0.87	0.26	0.98	0.06	0.26	0.06	0.26	0.95	1.78	1.07	0.72	0.72		
11 ⁶ Π	0.78 1σ ² 2σ ² 3σ ¹ 1π _x ² 1π _y ¹ 1δ _x ¹)	0.84	0.27	0.54	0.07	0.78	0.05	0.29	0.93	1.73	0.74	1.07	0.72		
12 ⁶ Δ	0.58 1σ ² 2σ ² 3σ ¹ (1π _x ² 2π _x ¹ 1π _y ² +1π _x ² 1π _y ² 2π _y ¹)1δ _x ¹) 1σ ² 2σ ² 3σ ¹ 1δ _x ¹ [(0.48)1π _x ¹ 1π _y ¹ 1δ _x ¹ + (0.34)1π _x ¹ 1π _y ¹ 1δ _x ¹)	0.87	0.23	0.44	0.08	0.99	0.08	0.99	1.0	1.69	0.76	0.92	0.92		
13 ⁴ Σ ⁺	-0.25 1σ ² 2σ ² 3σ ¹ 1δ _x ¹ 1π _x ¹ 1π _y ¹ 1δ _x ¹)	0.87	0.33	1.02	0.04	0.29	0.04	0.29	0.87	1.76	0.98	0.80	0.80		
14 ² Π	0.55 1σ ² 2σ ² 3σ ¹ (1π _x ² 1π _x ¹ 1δ _x ¹ -1π _x ¹ 1π _x ² 1δ _x ¹)	0.87	0.32	1.07	0.04	0.69	0.04	0.69	0.50	1.72	0.96	0.76	0.76		
15 ⁴ Π	0.48 1σ ² 2σ ² 1δ _x ¹ 1π _x ² 1π _y ¹ 1δ _x ¹ +0.32 1σ ² 2σ ² 3σ ¹ 1δ _x ¹ 1π _x ² 1π _y ¹ 1δ _x ¹)	0.83	0.33	0.52	0.06	0.81	0.05	0.41	0.84	1.73	0.88	0.95	0.71		
16 ⁴ Π	0.43 1σ ² 2σ ² 3σ ¹ 1δ _x ¹ 1π _x ² 1π _y ¹ 1δ _x ¹) +0.38 1σ ² 2σ ² 3σ ¹ 1δ _x ¹ 1π _x ² 1π _y ¹ 1δ _x ¹)	0.88	0.27	0.58	0.06	0.83	0.05	0.32	0.84	1.70	0.83	0.96	0.78		
17 ⁶ Φ	0.38 1σ ² 2σ ² 3σ ¹ (1δ _x ¹ 1π _x ¹ 1π _y ² 1π _x ¹ +1π _x ² 2π _x ¹ 1π _y ¹ 1δ _x ¹) -0.28 1σ ² 2σ ² 3σ ¹ 4σ ¹ (1δ _x ¹ 1π _x ¹ 1π _y ² +1π _x ² 1π _x ¹ 1δ _x ¹) +0.22 1σ ² 2σ ² 3σ ¹ (1δ _x ¹ 1π _x ¹ 2π _x ¹ +1π _x ² 2π _x ¹ 1π _y ¹ 1δ _x ¹) +0.17 1σ ² 2σ ² 4σ ¹ (1δ _x ¹ 1π _x ¹ 2π _x ¹ +1π _x ² 2π _x ¹ 1π _y ¹ 1δ _x ¹)	0.91	0.37	1.0	0.05	0.62	0.05	0.62	0.50	1.75	0.94	0.82	0.82		
18 ⁴ Δ	0.41 1σ ² 2σ ² 1δ _x ¹ (1π _x ² 2π _x ¹ 1π _y ² +1π _x ² 1π _y ² 2π _y ¹) +0.16 1σ ² 2σ ² 3σ ¹ 1δ _x ¹ (1π _x ² 2π _x ¹ 1π _y ² +1π _x ² 1π _y ² 2π _y ¹)	0.84	0.30	0.32	0.05	1.02	0.05	1.02	1.0	0.0	1.73	0.80	0.91	0.91	
19 ⁴ Φ	0.42 1σ ² 2σ ² 3σ ¹ (1π _x ² 1π _x ¹ 1δ _x ¹ -1π _x ¹ 1π _x ² 1δ _x ¹)	1.10	0.29	0.98	0.05	0.62	0.05	0.62	0.51	1.72	0.87	0.83	0.83		
20 ⁴ Σ ⁺	1σ ² [(0.46)2σ ² 3σ ¹ - (0.40)2σ ² 3σ ²]1δ _x ¹ 1π _x ¹ 1π _y ¹ 1δ _x ¹) - 1σ ² [(0.29)2σ ² 3σ ² + (0.21)2σ ² 3σ ¹]1δ _x ¹ 1π _x ¹ 1π _y ¹ 1δ _x ¹)	0.92	0.31	1.01	0.04	0.29	0.04	0.29	0.89	1.74	0.98	0.78	0.78		
21 ⁶ Π	0.50 1σ ² 2σ ² 3σ ¹ 1δ _x ¹ 1π _x ² 1π _y ¹ 1δ _x ¹) +0.36 1σ ² 2σ ² 1δ _x ¹ 1π _x ² 2π _x ¹ 1π _y ¹ 1δ _x ¹) +0.33 1σ ² 2σ ² 3σ ¹ (1δ _x ¹ 1π _x ¹ 1π _y ² 1π _x ¹ -1π _x ² 2π _x ¹ 1π _y ¹ 1δ _x ¹)	0.89	0.29	0.68	0.07	0.70	0.05	0.44	0.76	1.75	0.82	1.0	0.75		
22 ² Π	0.41 1σ ² 2σ ² 3σ ¹ 1δ _x ¹ 1π _x ² 1π _y ¹ 1δ _x ¹) +0.31 1σ ² 2σ ² 1δ _x ¹ 1π _x ² 1π _y ¹ 1δ _x ¹) +0.27 1σ ² 2σ ² 3σ ¹ (1π _x ² 1π _y ¹ 1δ _x ¹ -1δ _x ¹ 1π _x ² 1π _y ¹)	0.82	0.35	0.49	0.04	0.89	0.03	0.36	0.84	1.70	0.92	0.91	0.76		
23 ⁴ Δ ^a	0.46 1σ ² 2σ ² 3σ ¹ (1π _x ² 2π _x ¹ 1π _y ¹ -1π _x ¹ 1π _x ² 2π _y ¹)1δ _x ¹) +0.46 1σ ² 2σ ² 3σ ¹ (1π _x ² 2π _x ¹ 1π _y ¹ -1π _x ¹ 1π _x ² 2π _y ¹)1δ _x ¹)	0.84	0.20	0.61	0.10	0.89	0.10	0.89	0.50	1.70	0.63	0.98	0.98		
24 ⁶ Γ	1σ ² [(0.48)2σ ² 3σ ² - (0.34)2σ ² 4σ ¹]1π _x ¹ 1π _y ¹ 1δ _x ¹)	1.07	0.28	1.02	0.06	0.19	0.06	0.19	0.91	1.72	0.88	0.84	0.84		
25 ⁶ Σ ⁺	+ 1σ ² [(0.34)2σ ² 3σ ¹ 4σ ¹ 1δ _x ¹ - (0.29)2σ ² 3σ ¹ 1δ _x ¹]1π _x ¹ 1π _y ¹ 1δ _x ¹)	0.88	0.32	0.73	0.06	0.67	0.05	0.48	0.72	1.74	0.84	0.99	0.75		
26 ⁴ Π ^a		1.09	0.32	0.97	0.05	0.58	0.05	0.58	0.50	1.73	0.32	0.86	0.86		
27 ⁶ Φ ^a															
28 ⁶ Δ	0.70 1σ ² 2σ ² 1δ _x ¹ 1π _x ² 2π _x ¹ 1π _y ² 1π _y ¹) +0.35 1σ ² 2σ ² 3σ ¹ 1δ _x ¹ 1π _x ² 2π _x ¹ 1π _y ² 1π _y ¹) +0.33 1σ ² 3σ ¹ 1δ _x ¹ 1π _x ² 2π _x ¹ 1π _y ² 1π _y ¹)	0.96	0.28	0.17	0.06	1.02	0.06	1.02	1.0	0.0	1.74	0.82	0.91	0.91	

^aThe sum of the first ten variational coefficients squared, $\sum_0^9 |C_i|^2$, is about 0.5.

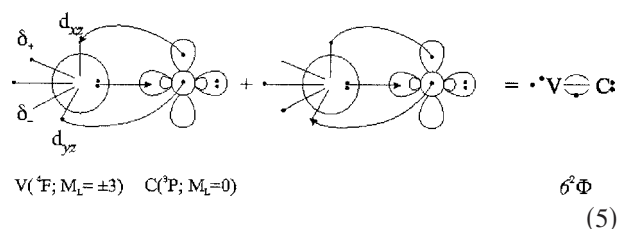


The “+” and “−” signs relate to the $^4\Phi$ and $^4\Pi$ states, respectively. Note that the *in situ* V atom is in the first excited $^6D(4s^1 3d^4)$, experimentally (theoretically) 0.245 (0.299/MRCI+*Q*) eV above the ground 4F term.¹⁵ Because at infinity the V atom is in its ground $4s^2 3d^3$ configuration, the σ bond is created by decoupling the $4s^2 e^-$ pair ($\rightarrow 4s^1 3d^4$) and the simultaneous coupling of the $4s^1 e^-$ with the $2p_z$ on C; see Scheme (4). The MRCI(+*Q*) D_e (kcal/mol) and r_e (Å) values for the $^4\Phi$ and $^4\Pi$ states are 73.8(75.0), 1.756(1.790) and 73.4(74.7), 1.751(1.788), respectively.

E. $6^2\Phi$, $8^2\Pi$, $9^2\Phi$, $14^2\Pi$, $22^2\Pi$ states

The $8^2\Pi$, $14^2\Pi$, and $9^2\Phi$ states could be considered as the doublet analogs of the $5^4\Pi$ and $4^4\Phi$ states, respectively, their difference being a $(\pi_y^1, \pi_x^1) \rightarrow (\bar{\pi}_y^1, \bar{\pi}_x^1)$ spin flip in going from the $5^4\Pi$ to the $8^2\Pi$ state, and similarly a $(\delta_-^1, \delta_+^1) \rightarrow (\bar{\delta}_-^1, \bar{\delta}_+^1)$ spin reversal from the $5^4\Pi$ to $14^2\Pi$ state and $4^4\Phi$ to $9^2\Phi$ state; see Table II. The leading CASSCF configurations and Mulliken densities of the above three doublets are in essence identical to those of the corresponding quartet states, $5^4\Pi$ and $4^4\Phi$. Therefore, their bonding character is adequately described by Scheme (4).

In the $6^2\Phi$ state the spin flip occurs in the (π_y^1, π_x^1) pair, its leading CSFs and Mulliken distributions are the same to those of the three doublets or two quartets, but it correlates to $|M_L = \pm 3\rangle_V \otimes |M_L = 0\rangle_C$ resulting in a purely dative σ and $3/2 \pi$ bonds, Scheme (5).

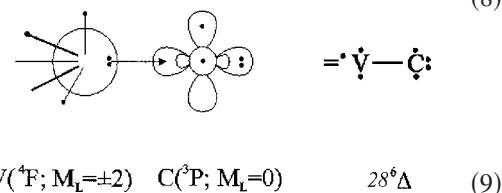
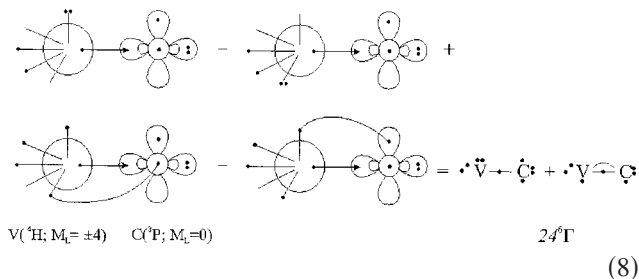
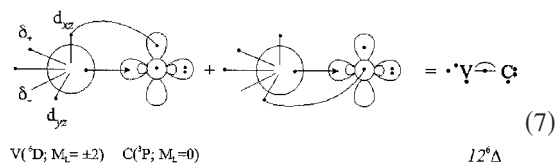
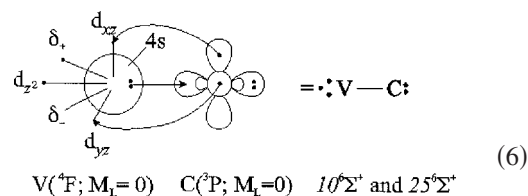


Although the bonding character of the $22^2\Pi$ state is shadowed because of its extreme multireference description, the *in situ* atomic symmetries and atomic populations are indicative of a σ and $3/2 \pi$ bonds.

We now discuss in ascending energy order, the manifold of the ten sextet states grouped in two symmetry blocks A_1 (Fig. 5) and B_1 (Fig. 6).

F. $10^6\Sigma^+$, $12^6\Delta$, $24^6\Gamma$, $25^6\Sigma^+$, $28^6\Delta$ states

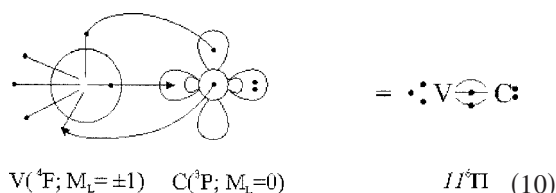
The MRCI(+*Q*) T_e values of the five sextet states above (symmetry A_1) starting from the $10^6\Sigma^+$ state, are 25.0(24.6), 29.0(29.7), 47.6(47.4), 49.6(49.0), and 54.3(55.0) kcal/mol, respectively. Notwithstanding their multireference character (Table II), their bonding features can be summarized in the vbL Schemes (6)–(9)



Note that in all five states the C atom orients itself to its $M_L = 0$ projection, so electrons can flow along the σ frame from the V atom to the empty $2p_z$ C orbital. With respect to ground state atoms, the binding energies range from 61.4($10^6\Sigma^+$) to 32.2($28^6\Delta$) kcal/mol at the MRCI level of theory (Table I). MRCI potential energy curves of the A_1 sextets are given in Fig. 5.

G. $11^6\Pi$, $17^6\Phi$, $21^6\Pi$, $26^6\Pi$, $27^6\Phi$ states

Figure 6 shows the MRCI PECs of the titled sextet states (symmetry B_1). Their binding energies with respect to the ground state fragments range from 59.9($11^6\Pi$) to 32.5($27^6\Phi$) kcal/mol. With the exception of the $11^6\Pi$ state where a leading configuration can be discerned, the extreme multireference character of the other four sextets poses insurmountable interpretational difficulties as to their bonding character. The bonding of the $11^6\Pi$ state can be represented graphically by Scheme (10) featuring $3/2 \pi$ and $1/2 \sigma$ bonds



In all the ten sextets 0.30 – $0.35 e^-$ are transferred from V to C rendering the bonding character “semi-ionic.”

H. $13^4\Sigma^+$, $20^4\Sigma^+$ states

The bonding of these two quartet states is similar to the one of the $6^6\Sigma^+$ states previously discussed, Scheme (6), i.e., a σ bond, the result of significant charge transfer from the metal to the $2p_z$ C orbital. At MRCI equilibrium bond distances of 1.981($13^4\Sigma^+$) and 1.952($20^4\Sigma^+$) Å, the D_e values are 59.0 and 44.9 kcal/mol, respectively; the resulting PECs are displayed in Fig. 3.

I. $15^4\Pi$, $16^4\Pi$, $19^4\Phi$ states

According to Table II all the quartets above show intense multireference character making their interpretation very difficult. From the PECs shown in Fig. 4 bond distances and binding energies are 1.865, 1.866, and 1.892 Å and 52.4, 48.9, and 44.2 kcal/mol, respectively.

IV. SUMMARY

Using high level MRCI/[$7s6p4d3f2g/v5s4p3d2f1g/c$] calculations we have constructed the potential energy curves (Figs. 1–6) of 29 out of a total of 36 states of VC, correlating to the ground state atoms V($4s^23d^3$; 4F) + C($2s^22p^2$; 3P) and spanning an energy range of 2.40 eV. Our main conclusions can be condensed as follows.

- (1) The ground state is of $^2\Delta$ symmetry featuring a genuine triple bond with r_e and D_e values of 1.636(1.636) Å and 88.5(89.3) kcal/mol, respectively, at the MRCI(+ Q) level. Considering core-valence ($\sim 3s^23p^6$), scalar relativistic, and BSSE effects as obtained in the VC+($X^3\Delta$) species,^{2(e)} our recommended D_e value is 94.5 kcal/mol, in fair agreement with a thermochemical value of 100.1 ± 5.7 kcal/mol.⁵
- (2) A level diagram shown in Fig. 7 displays the high density of molecular states found in VC, averaging energy separations of less than 2 kcal/mol per state. Obviously, one cannot be certain about the exact ordering of most of the excited states at this level of theory.
- (3) It is interesting that all the states studied show relatively high binding energies ranging from 88.5($X^2\Delta$) to 32.2($28^6\Delta$) kcal/mol at the MRCI level. In all states, a significant electronic density amounting to $\sim 0.3 e^-$ is transferred from the metal to the empty $2p_z$ C orbital ($M_L=0$). We would also like to underline the intense multireference character of practically all states examined, resulting in severe computational and interpretational problems.

- (4) Finally, a comment on the dipole moment values is in order. With the exception of the $X^2\Delta$ state, the dipole moments (calculated as expectation values) of all other states range from 1.38($19^4\Phi$) to 3.03($24^6\Gamma$)D, or an average of $\bar{\mu}=2.4$ D, a difference of about 5 D from the $X^2\Delta$ state. We believe that this remarkable difference between the X and all the other states, is caused by the absence of a $\sim d_\sigma$ electron distribution on the back of the V atom in the ground state.

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