A theoretical study of potential energy curves and spectroscopic constants of VC

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Potential energy curves for the various low-lying electronic states of VC have been studied using complete active space multi-configuration self-consistent field (CASMSCF) followed by first-order and multireference singles and doubles configuration interaction (FOCI, MRSDCI) calculations. The MRSDCI calculations included up to 6 million configurations. Two very low-lying electronic states are found as candidates for the ground state of VC, namely a high spin state \( ^2\Delta \) and a low-spin \( ^4\Delta \) state, which is favoured at higher levels.

1. Introduction

The advent of laser-based molecular beam techniques and supersonic jet expansion methods has rejuvenated interest in the spectroscopy of small transition metal carbides in recent times [1–5]. There is also a compelling fundamental need to rationalize the metal–carbon interactions, especially in the context of the rapidly growing field of metal carbide clusters, commonly called ‘met-cars’ [6, 7]. Detailed studies on small metal monocarbides and dicarbides can contribute to our understanding of the building blocks of such clusters.

The electronic structure and bonding characteristics of the first- and second-row transition metal fluorides, oxides and, to a lesser extent, nitrides, are relatively well studied [8, 9]. This is particularly true for the group III–VI metal compounds in which the transition metal has its d shell less than half-filled. In these systems, the ionization potentials (IP) of the atoms that form the molecules are sufficiently different to make the 2p atomic orbitals (AOs) of the ligand atom lie at much lower energies than the ns and \((n-1)d\) AOs \((n = 4, 5)\) of the metal atom. As a result, the highest occupied and the lowest unoccupied orbitals (HOMO and LUMO) in these compounds are metal-based orbitals. Thus, in most of the cases, the symmetries of the ground- and the lowest-excited states are predictable with a high degree of accuracy.

The situation is quite different in transition metal carbides. The IP of carbon \((11.26 \text{eV})\) in these molecular systems is much less than the IPs of fluorine \((17.42 \text{eV})\), oxygen \((13.62 \text{eV})\) and nitrogen \((14.53 \text{eV})\), and consequently closer to the IP of the transition metal atom. Thus the 2p AOs of carbon are closer in energy to the ns and \((n-1)d\) AOs \((n = 4, 5)\) of the metal atom and the energy ordering of the molecular orbitals would be almost impossible to predict a priori. As a result, the visible spectra of these species are often very complex due to the overlapping of metal-based and charge-transfer transitions.

There are remarkably few calculations on monocarbides of transition metals. They include ScC [10], TiC [11], VC [12], CrC [13, 14], NiC [15, 16], NbC [17], TaC [18] and their positive ions ScC\(^+\) [9], CrC\(^+\) [19] and TaC\(^+\) [18]. Although multireference energy calculations are available on ScC, TiC, CrC, NiC and TaC, the calculations on VC and NbC are available only at the density functional (DFT) level. The present paper reports the results of energy calculations on the different electronic states of VC at the CASMCSCF followed by multireference singles and doubles configuration interaction (MRSDCI) level. It is shown that the energy spectrum of this simple molecular system is much more
complex than that predicted at the DFT level, due to the multi-reference characters of the low-lying electronic states.

Gupta and Gingerich [20] first identified VC in a mass spectrometric study of the Knudsen effusate from the vanadium–niobium–molybdenum–graphite systems at high temperature. They have measured the thermodynamic properties of this species. The electron spin resonance (ESR) spectra of VC trapped in solid rare gases (Ne, Ar, Kr) showed that orbital angular moment of this molecule in their ground state is partially quenched [21]. The ground state of VC was proposed to be a \(^2\Delta\) state and based on the nature of the isoelectronic molecule ScO, the ground state of VC was proposed to be highly ionic [21]. The local density functional linear combination of atomic orbital (LDF-LCAO) calculations by Mattar [12] also proposed the ground state of VC as \(^2\Delta\). The calculation of Mattar was mostly restricted to the doublet states. Our present MRSDCI calculations reveal that there are two nearly degenerate electronic states for VC, namely a quartet state (\(^4\Delta\)) and a \(^2\Delta\) state, the latter being slightly favoured over the former at higher levels. The complex energy spectrum of this molecule also shows that there are five other low-lying electronic states within a 1 eV energy separation. Castleman and co-workers have communicated to the current authors [22] about their femtosecond pump–probe study of the VC cluster along with other small vanadium carbide hydride clusters. The interpretation of the femtosecond pump–probe spectra requires sound knowledge of the excited electronic states of these species. Thus the current study on the ground and the excited states of VC would prove to be valuable in aiding interpretation of various spectra of VC.

2. Computational details

Computations of the different electronic states of VC were carried out in the \(C_{2v}\) point group using the relativistic effective core potentials (RECPs) for vanadium and carbon. The valence space for the vanadium RECPs included \(3s^23p^63d^14s^2\) shells [23], while the RECPs of the carbons included \(2s^22p^2\) valence shells [24]. The most diffuse exponents in the original basis sets have been left uncontracted. This led to [6s5p4d] and [3s3p] valence basis sets for V and C, respectively. The V basis was the supplemented with one s and one set of \(p\) functions. The basis set of 10-component 4f functions on V was tested previously by us on the VC\(_2\) cluster by augmenting the V basis set with one set of ten-component 4f functions with \(\xi = 0.40\), but the effect was found to be rather small [25]. In the present calculations, we have included the 4f function in the basis set to gauge its effect on the geometry and energy separations for the \(^2\Delta\) and \(^4\Delta\) states. At the complete active space multi-configuration self-consistent field (CASMCSF) level, the V–C bond lengths with and without the f function are 1.737 and 1.731 Å for the \(^2\Delta\) state, respectively. The energy difference between the \(^4\Delta\) and the \(^2\Delta\) states at the CASMCSF level is 0.28 eV with the vanadium f function (without the f function: 0.30 eV). Thus the 4f function was included in the V basis set primarily to ascertain its effect on the properties of the \(^4\Delta\) and the \(^2\Delta\) states from the CASMCSF to MRSDCI levels. The C basis also included the 3d polarization functions and an additional set of s and p diffuse functions.

The calculations outlined here were carried out at the CASMCSF, first-order configuration interaction (FOCI), and MRSDCI levels in the \(C_{2v}\) symmetry (\(z\) axis is the \(C_2\) axis). In this symmetry group the active space of VC consisted of seven \(a_1\), three \(b_2\), three \(b_1\) and one \(a_2\) orbitals. The semi-core \(3s\) and \(3p\) orbitals of vanadium (two \(a_1\), one \(b_2\) and one \(b_1\)) were not included in the active space, as they play no role in bonding. However, they were allowed to relax. Five \(a_1\), two \(b_2\), two \(b_1\) and one \(a_2\) orbitals constituted the active space and the CASMCSF computations included excitations of 9 active electrons in all possible ways among the active orbitals.

Following the CASMCSF calculations, the FOCI calculations were carried out to include the higher-order correlation effects. The FOCI method included all configurations in the CASMCSF, plus configurations obtained by the distribution of 9 electrons in the internal (active) and the orthogonal external space in all possible ways. The V–C distance was varied to generate the potential energy surfaces at the FOCI level of all the electronic states considered here. The full second-order configuration interaction (SOCl) calculation was not possible because of the large number of configuration spin functions (CSFs). Instead, a MRSDCI technique was adopted to ascertain the minimum of each electronic state. All of the configurations of the CASMCSF with coefficients \(\geq 0.05\) were included in the MRSDCI calculations. In order to compute the dissociation energy and to ascertain the relative order of the \(^4\Delta\) and the \(^2\Delta\) states, this cut-off limit was relaxed to \(\geq 0.01\) for these computations. The above choice of the active space leads to a maximum of 7000 CSFs in the CASMCSF calculations. The FOCI calculations included up to 440 864, while the MRSDCI calculations included up to 6 million CSFs. The effect of unlinked quadruple clusters for the MRSDCI was estimated through a multireference Davidson correction (MRSDCI + Q) technique [26]. All the CASMCSF, FOCI, and MRSDCI calculations were carried out using a modified version of ALCHEMY II [27] package to include RECPs [28].
3. Results and discussion

3.1. Potential energy surfaces of the various electronic states of VC

The computed energy separations of the different electronic states of VC at the dissociation limit are presented in Table 1. The low-lying electronic states (Table 1) of VC considered here dissociate into $V(4F) + C(3P)$ in accordance with rules governing the dissociation of diatomic molecules having atomic configurations $^4F$ and $^3P$ [29]. The $J$ averaged energy separations of the vanadium atom for different electronic states, as obtained from Moore's atomic data table [30], are included for comparison with theory. As seen in Table 1, the computed energy separations are in good agreement with the experimental values at both the FOCI and MRSDCI levels. Thus the computed results should have comparable accuracy in the various regions of the potential energy curves.

The potential energy curves for the different low-lying electronic states of VC are presented in Figures 1 and 2 at the FOCI level. The energy calculations were carried out up to sextet states of VC, and three roots were computed for each of the irreducible representations of the $C_{2v}$ group. The states were then reassigned according to the $C_{\infty v}$ group. Figure 1 includes the potential energy curves of the electronic states having energy separations ($T_e$) up to 1.50 eV with respect to the ground state. The potential energy curves of the electronic states having $T_e > 1.50$ eV are included in Figure 2. The results of the energy calculations at the FOCI and MRSDCI levels are included in Tables 2 and 3.

The results of our energy calculations show that the ground state of VC is $^4\Delta$. This is supported both at the FOCI and MRSDCI levels. In fact, apart from a few excited states, the ordering of the electronic states at both levels is similar. The energy separations of the different excited electronic states at the MRSDCI level are slightly higher relative to the FOCI level. Since our MRSDCI calculations are more reliable, the calculated electronic properties of various electronic states will be discussed using these results.

Table 1. Energy separations between the atomic states of V
(experimental values are also included for comparison).

<table>
<thead>
<tr>
<th>Atomic state</th>
<th>FOCI</th>
<th>MRSDCI</th>
<th>Experiment $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4F\ (3d^24s^2)$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$^2D\ (3d^24s^2)$</td>
<td>1.56</td>
<td>1.47</td>
<td>1.66</td>
</tr>
<tr>
<td>$^4G\ (3d^44s^1)$</td>
<td>2.02</td>
<td>1.97</td>
<td>2.08</td>
</tr>
</tbody>
</table>

$^a$From [28].
Table 2. Equilibrium bond distances ($r_e$), energy separations ($T_e$), vibrational frequencies ($\omega_0$) and dipole moments ($\mu_d$) of the different electronic states of VC at the FOCI level.

<table>
<thead>
<tr>
<th>State</th>
<th>$r_e$ (V–C)/Å</th>
<th>$T_e$/eV</th>
<th>$\omega_0$/cm$^{-1}$</th>
<th>$\mu_d$/Debye</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4\Delta$</td>
<td>1.719</td>
<td>0.00</td>
<td>824</td>
<td>2.68</td>
</tr>
<tr>
<td>$^2\Delta$</td>
<td>1.640</td>
<td>0.16</td>
<td>824</td>
<td>3.59</td>
</tr>
<tr>
<td>$^4\Phi$</td>
<td>1.787</td>
<td>0.29</td>
<td>754</td>
<td>2.71</td>
</tr>
<tr>
<td>$^2\Delta$(II)</td>
<td>1.732</td>
<td>0.46</td>
<td>674</td>
<td>3.12</td>
</tr>
<tr>
<td>$^2\Phi$</td>
<td>1.849</td>
<td>0.60</td>
<td>519</td>
<td>2.18</td>
</tr>
<tr>
<td>$^2\Delta$(III)</td>
<td>1.717</td>
<td>0.77</td>
<td>890</td>
<td>3.13</td>
</tr>
<tr>
<td>$^6\Phi$</td>
<td>1.941</td>
<td>1.03</td>
<td>812</td>
<td>2.28</td>
</tr>
<tr>
<td>$^2\Pi$</td>
<td>1.856</td>
<td>1.04</td>
<td>521</td>
<td>2.19</td>
</tr>
<tr>
<td>$^6\Delta$</td>
<td>1.957</td>
<td>1.11</td>
<td>579</td>
<td>2.59</td>
</tr>
<tr>
<td>$^4\Delta$(II)</td>
<td>1.993</td>
<td>1.45</td>
<td>671</td>
<td>2.96</td>
</tr>
<tr>
<td>$^4\Pi$</td>
<td>1.986</td>
<td>1.64</td>
<td>523</td>
<td>1.52</td>
</tr>
<tr>
<td>$^2\Sigma^+$</td>
<td>1.627</td>
<td>1.85</td>
<td>824</td>
<td>3.59</td>
</tr>
<tr>
<td>$^6\Pi$</td>
<td>1.958</td>
<td>1.85</td>
<td>1107</td>
<td>1.80</td>
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<tr>
<td>$^6\Pi$(II)</td>
<td>1.792</td>
<td>1.95</td>
<td>821</td>
<td>2.59</td>
</tr>
<tr>
<td>$^4\Delta$(III)</td>
<td>1.953</td>
<td>2.06</td>
<td>658</td>
<td>2.83</td>
</tr>
<tr>
<td>$^6\Delta$(II)</td>
<td>2.234</td>
<td>2.15</td>
<td>477</td>
<td>2.53</td>
</tr>
<tr>
<td>$^2\Pi$(II)</td>
<td>1.905</td>
<td>2.18</td>
<td>760</td>
<td>1.39</td>
</tr>
<tr>
<td>$^6\Pi$(II)</td>
<td>1.909</td>
<td>2.36</td>
<td>794</td>
<td>2.12</td>
</tr>
<tr>
<td>$^4\Delta$(III)</td>
<td>1.999</td>
<td>2.51</td>
<td>1265</td>
<td>2.55</td>
</tr>
</tbody>
</table>

The MRSDCI level is composed of the following leading configurations:

$$76\% | 1\sigma^2 2\sigma^2 ... 4\sigma^2 5\sigma^1 1\pi^4 2\pi^4 1\delta^1 \rangle$$
$$+ 5\% | 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\pi^4 1\pi^2 2\pi^2 1\delta^1 \rangle$$
$$+ 3\% | 1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 5\sigma^1 1\pi^4 2\pi^4 1\delta^1 \rangle + \cdots$$

Thus the single reference calculations cannot fully account for the proper geometry and the energy separation of this electronic state. Our present calculation also differs from the previously calculated energy separation [12] of the $^2\Pi$ state relative to the $^2\Delta$ state at the LDF-LCAO level (17326 cm$^{-1}$) [12]. Although $^2\Pi$ is a high-energy state, its energy separation from the $^2\Delta$ state is much less (0.96 eV, 7680 cm$^{-1}$).

Because the energy separation between the $^2\Delta$ and the $^4\Delta$ states is very small, we have further investigated the energy separation between the two states at the MRSDCI level by including the 4f function in the vanadium basis set. The energy difference between the $^4\Delta$ and $^2\Delta$ states at the MRSDCI (4f) level of calculation is 0.16 eV. This is similar to our MRSDCI calculation without the 4f function ($T_e = 0.21$ eV). But at the MRSDCI + Q (4f) level, the $^2\Delta$ state is 0.13 eV more stable than the $^4\Delta$ state. Thus at the lower level of calculations, the $^4\Delta$ state is stabilized through the spin exchange effect, while at the higher level the $^2\Delta$ state is more stable over the $^4\Delta$ state via the correlation effect. Thus the relative placing of the $^2\Delta$ and $^4\Delta$ states is equivocal due to the near-degeneracy of the two states.

The calculated vibrational frequencies of the various electronic states of VC are listed in tables 1 and 2 at the FOCI and MRSDCI levels. The results at both levels show good agreement. These calculated values are lower than those predicted at the LDF-LCAO level [12]. There is no direct experimental data to verify our results. The V–C symmetric stretching modes were experimentally determined for a few low-lying electronic states of the VC$_2$ molecule by Li and Wang [31]. Their measured value is around 590 cm$^{-1}$ for the ground state of VC$_2$. Our calculated values seem reasonable with respect to this measured frequency.

In a very interesting rare gas-isolated ESR study, Hamrick and Welttnr [21] have observed quenching of the angular momentum in the ground state of VC. This is based on large negative values of $\Delta B_1$, which suggest that the angular momentum of the ground state is quenched. These authors consider this effect as unprecedented and attribute it to a strong unsymmetrical interaction of the ionic VC with the matrix. On the basis of the hyperfine structure, the ground state of VC was proposed as $^2\Delta_{3/2}$. It should be noted that the low-lying $^4\Delta$ state also yields $\Omega = 3/2$ state and the two $\Omega$ states will couple in the presence of spin–orbit coupling, and

(FOCI: 1.719 Å) and the $^2\Delta$ state is 1.690 Å (FOCI: 1.640 Å). The calculated V–C distance by Mattar [12] at the LDF-LCAO level is shorter (1.577 Å) than our calculated results. In actuality, the $^2\Delta$ state is multireference in nature and the wave function of this state at
thus an intermediately coupled Ω = 3/2 state is consistent with the observed ESR hyperfine structure. Thus our computations support these findings. As seen in Table 2, the 2Π state of VC is considerably higher in energy than the 4Δ state and thus we believe that spin-orbit mixing with 4Δ would be larger than the 2Π state suggested by Hamrick and Welter [21].

3.2. Dissociation energy of VC

We have computed the dissociation energy (D_c) of VC at the MRSDCI and MRSDCI + Q levels for the following reaction:

$$\text{VC}(4\Delta) = V(4F) + C(3P).$$  \hfill (1)$$

Energy calculations were done for the supermolecular system V--C with an energy separation of 8 Å. Our potential energy surface ensures that at 8 Å separation, the 4Δ state of VC dissociates into the correct atomic states of V and C, as indicated in equation (1). The energy difference of this supermolecular state from the 4Δ equilibrium state gives the dissociation energy of VC. We have used a threshold of 0.01 for the MRSDCI reference selection from the CASMCSF configurations to ensure higher accuracy of the calculated D_c at the MRSDCI level. Our calculated values at the MRSDCI and MRSDCI + Q levels are 3.08 and 3.38 eV, respectively. It is to be noted that the V atom has spin–orbit ground state stabilization of 376 cm⁻¹ (0.046 eV) [30]. Thus the calculated D_c values would decrease by at most 0.046 eV as VC is less affected by spin–orbit coupling in comparison to the V atom.

The experimental dissociation energy (ΔH₀) of VC was deduced by Gupta and Gingerich [20] from the third law using second or third law methods from the measured enthalpies obtained through high temperature mass spectrometry to be 419 ± 24 kJ mol⁻¹ (4.35 ± 0.25 eV). This requires knowledge of the structure and the spectroscopic properties of the gaseous VC molecule. Since no data on the electronic states of VC were available, the ΔH₀ was estimated using empirical rules. The V–C distance was taken to be 1.67 Å and the electronic contribution to the free energy function of VC was estimated from the excited electronic levels and the degeneracy of VO, listed by Huber and Herzberg [32]. Since the equilibrium bond length of VC in its ground state is larger than the assumed value of 1.67 Å, it is expected that the dissociation energy of VC would be less than what was estimated. In the case of VC₂, thermodynamic corrections were also needed to obtain an accurate dissociation energy [25]. We expect our computed D_c to be a lower bound since further improvement to the basis set and level of treatment by including additional electron correlation effects would increase our computed D_c of VC. It is to be mentioned in this connection that the calculated D_c value at the LDF-LCAO level was 6.77 eV [12] which also yielded an unusually short bond distance for VC. In view of the present discussion, this value does not seem reliable.

3.3. The nature of bonding

The leading configurations in the MRSDCI wavefunctions for the low-lying electronic states of VC are presented in Table 4. The 4Δ ground state of VC is predominantly composed of 1σ²2σ²3σ²4σ¹5σ¹1π²2π³4Δ (82%). The first excited state 2Δ is formed from the 4Δ electronic state by excitation of the 5σ electron to the 4σ orbital. This partly explains the very low energy

<table>
<thead>
<tr>
<th>State</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>4Δ</td>
<td>1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (82%), 1σ²2σ²3σ²4σ¹5σ¹1π²2π³3π¹8¹ (2%)</td>
</tr>
<tr>
<td>2Δ</td>
<td>1σ²2σ²3σ²4σ¹1π²2π³18¹ (76%), 1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (5%), 1σ²2σ²3σ²4σ¹1π²2π³3π¹8¹ (3%)</td>
</tr>
<tr>
<td>4Φ</td>
<td>1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (77.6%), 1σ²2σ²3σ²4σ¹5σ¹1π²2π³3π¹18¹ (2.3%), 1σ²2σ²3σ²4σ¹5σ¹1π²2π³3π¹8¹ (1.4%)</td>
</tr>
<tr>
<td>2Φ</td>
<td>1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (75.9%), 1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (3%)</td>
</tr>
<tr>
<td>2Δ(II)</td>
<td>1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (58.1%), 1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (9.7%)</td>
</tr>
<tr>
<td>6Φ</td>
<td>1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (74.8%), 1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (7.3%)</td>
</tr>
<tr>
<td>6Δ</td>
<td>1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (84.2%), 1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (2.0%), 1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (1.4%)</td>
</tr>
<tr>
<td>2Π</td>
<td>1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (72.1%), 1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (2.6%), 1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (2.5%)</td>
</tr>
<tr>
<td>4Δ(II)</td>
<td>1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (75.4%)</td>
</tr>
<tr>
<td>2Δ(III)</td>
<td>1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (40.4%), 1σ²2σ²3σ²4σ¹5σ¹1π²2π³18¹ (13%)</td>
</tr>
<tr>
<td>1σ²2σ²3σ²4σ¹16Δ (4.8%), 1σ²2σ²3σ²5σ¹1π²2π³18¹ (2%)</td>
<td></td>
</tr>
</tbody>
</table>
difference between the $^4\Delta$ and the $^2\Delta$ states. The formation of the next low-lying electronic state $^4\Phi$ state [1$^a_2^2\sigma^2_3\sigma^2_3\sigma^2_5\sigma^1_1\pi^4_2\pi^2_3\pi^1_1\delta^1_1$ (77.6%)] involves the excitation of a single electron from the 2\pi orbital of the $^4\Delta$ state to the 4\sigma orbital. Since such excitation is a low energy process, the $T_e$ of the $^4\Phi$ state is quite low (0.34 eV, table 3). The energy separation between the $^4\Phi$ and its next low-lying state $^2\Phi$ is quite high (0.34 eV, table 3). The $^2\Phi$ and the $^4\Phi$ states have similar leading configurations (table 4). However, since the formation of the $^4\Phi$ state involves more alpha spins in the same orbital compositions, the energy of this state is much lower than the $^2\Phi$ state by Hund’s rule (table 3). The next low-lying state to $^2\Phi$ is $^2\Delta$ (II), and its energy separation with respect to the $^4\Delta$ ground state is quite high (table 3). Both the $^4\Delta$ and $^2\Delta$ (II) states have similar leading electronic configurations, and thus their energy separations could be explained using similar arguments for the $^2\Phi$ and $^4\Phi$ states. The formation of the other low-lying states, namely $^6\Phi$, $^6\Delta$, $^4\Delta$ (II) and $^2\Delta$ (III), could similarly be explained from their leading electronic configurations considering the nature of the electronic excitations. It is to be noted in this connection that apart from the leading configurations (configurations contributing $\geq 70\%$), the low-lying electronic states have other dominant configurations (table 4). Thus the states are multireference in nature and it justifies the use of the MRSDCI calculations to determine their energy separations.

Figures 3 and 4 show the active space orbitals of VC in its ground state ($^4\Delta$). The composition of the natural orbitals in the MRSDCI wave functions could be qualitatively expressed as follows:

$$
\psi(3\sigma) = V(4s + 4p_z + 3d_{x^2+y^2}-2z^2) - C(2s), \\
\psi(4\sigma) = V(4s + 4p_z - 3d_{x^2+y^2}-2z^2) + C(2s + 2p_z), \\
\psi(5\sigma) = V(3d_{x^2+y^2}-2z^2 - 4s) + C(2s + 2p_z), \\
\psi(2\pi) = \begin{cases} \\
\psi(2p_x) = V(3d_{x^2+y^2}) + C(2p_x), \\
\psi(2p_y) = V(3d_{x^2+y^2}) + C(2p_y). 
\end{cases}
$$

(2)

The 1\delta orbital is a non-bonding V(\delta_{xy}) or V(\delta_{x^2-y^2}) orbital. Thus the compositions show that among the active orbitals, only 1\delta is a pure V orbital. All the other orbitals show considerable mixing of V and C orbitals. For example, in the singly occupied 5\sigma molecular orbital, the 3d_{x^2+y^2} and 4s orbitals of V mix with the 2s and 2p_z orbitals of C. Similar mixing are found in the 3\sigma, 4\sigma and 2\pi molecular orbitals, as expected.

The orbital pictures presented in figures 3 and 4 are consistent with these compositions. These mixings are quite usual in transition metal carbides having metal configurations ns(n-1)d (n = 4, 5). Our previous calculations on VC$_2$ [24] and ScC$_3$ [33] clusters have shown similar orbital mixings. Due to the lower IP of carbon, the 2s and 2p AOs energetically come closer to the V(d) orbital and mix. The outcome of such mixings is that the electron donation and back-donation process facilitate the V–C bond formation.

The V–C bond of the vanadium mono-carbide was proposed to be highly ionic by Hamrick and Weltner [21]. The previous LDF-LCAO calculation by Mattar [12] also proposed a high dipole moment for the doublet states of VC. Our calculated dipole moments at the FOCI and MRSDCI levels (tables 2 and 3) show that the ground and the low-lying electronic states of VC are ionic but less than expected [21]. The $^4\Delta$ ground state and the next low-lying $^2\Delta$ state have dipole moments of 2.26 and 2.94 D, respectively (table 3). Only a few excited states, e.g. $^2\Delta$ (III), $^6\Pi$ and $^2\Sigma^+$, have higher dipole moments. Thus although the V–C bond formation involves electron donation and back-donation,
the overall charge separation between the V and the C atoms is not so high.

Table 5 lists the results of gross Mulliken population analyses on the low-lying electronic states of VC. As seen in table 5, the total Mulliken population of V is less than 13 for all the low-lying electronic states of VC. This suggests transfer of electronic charge from V to C and thus the V–C bond is polar. The extent of the polarity would, of course, depend on the amount of charge transfer and back transfer. The total charges on the atoms of the low-lying electronic states of VC suggest charge separation between the V and C atoms. Thus the bonds are polar, consistent with the calculated dipole moment values. However, the bonds are less ionic than the corresponding oxides, as expected. All the low-lying electronic states of VC have common charge distribution patterns. The $3s^23p^63d^14s^2$ configuration of vanadium and the $2s^22p^2$ configuration of carbon suggest that in the calculated population analyses data (table 5), the d and p orbitals of vanadium and the p orbital of carbon have higher charges while the vanadium s and the carbon s orbitals have lower charges than their normal values. Thus electrons from the carbon s orbitals are donated to the p and d orbitals of vanadium while the vanadium s orbital back-donates charges to the carbon. Thus an electron donation and back-donation process is operative in the V–C bond formation. The density difference plot of VC, shown in figure 5 for the $^4\Delta$ state, is consistent with this observation. The contour map is drawn as the difference of VC charge densities and those of the separated V and C atoms. The map clearly shows the charge depletion around the s orbital regions of V and C, and enhancement of charges around the d and p orbitals of V and the p orbitals of the C atoms.

Figure 5. The electron density difference maps of VC in the ground state ($^4\Delta$). The contours are derived from the CASMCSF natural orbitals and are drawn with respect to the separated V and C atoms. The separation between the contour lines is 0.015 electron bohr$^{-1}$. The contours with no density are labelled with zeros, while solid lines indicate enhancement of the electron density.

4. Conclusions

In this investigation, we have computed the spectroscopic constants ($r_e$, $\omega_e$ and $T_e$) of the low-lying electronic states of VC. The calculations have been carried out at the CASMCSF, FOCI and MRSDCI levels. The results of these calculations are presented at the FOCI, MRSDCI and MRSDC+Q levels. All these calculations suggest the possibility of two competing states as a candidate for the ground state of VC, namely.
$^4\Delta$ and $^2\Delta$ states. The $^2\Delta$ state is stabilized at the MRSDCI + Q(4f) level, while the $^4\Delta$ state is lower at the CASSCF, FOCl and MRSDCI levels. There are five other low-lying excited states ($^4\Phi$, $^2\Phi$, $^2\Delta$(II), $^6\Phi$ and $^6\Delta$) within the 1 eV energy separation with respect to the ground state. The spectroscopic states of the molecule are yet to be observed experimentally, but the calculated bond energy is consistent with the predicted experimental range of Gupta and Gingerich [20] considering that further improvements in the computational treatment would increase the dissociation energy. The calculated dipole moments of the low-lying electronic states suggest that the V–C bond is polar. However the bond polarity is not as high as those for other oxides or carbides. The calculated atom charges through gross Mulliken population analyses support this fact. The Mulliken population analyses of the orbitals of the vanadium and the carbon atom further suggest an electron donation and a back-donation process for the V–C bond formation. Our calculations are consistent with the previous experiment of Hamrick and Weltnr [21] but we suggest the $^4\Delta$ state as a more attractive candidate for the spin–orbit coupling with the $^2\Delta_{3/2}$ state of VC than the $^2\Pi$ state suggested by Hamrick and Weltnr [21].

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References

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