Theoretical Investigation of Titanium Carbide, TiC: \(X^3\Sigma^+, a^1\Sigma^+, A^3\Delta, \) and \(b^1\Lambda\) States

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Four states, \(1^1\Sigma^+, 1^3\Sigma^+, 1^3\Delta,\) and \(1^3\Lambda,\) have been investigated by ab initio multireference methods coupled with quantitative basis sets. The ground state is, formally, of \(\Sigma^+\) symmetry with \(D_e = 82.34 \text{ kcal/mol}, r_e = 1.712 \text{ Å},\) and with the \(1^1\Sigma^+\) state just 1.55 kcal/mol above the X-state.

Introduction

The present work reports accurate multireference variational calculations on the ground and three excited states of the TiC carbide. As in all first-row transition metal carbides \(M-C, M = Sc (Z = 21)\) to \(Cu (Z = 29),\) the literature, either experimental or theoretical, is rather limited.\(^1\) Recently, we have investigated the ScC\(^2\) and FeC\(^2\) systems, as well as the series of the cationic carbides ScC\(^+\), TiC\(^+\), and VC\(^+\), CrC\(^+\).\(^5\) For the TiC diatomic Bauschlicher and Siegbahn in 1984\(^6\) reported close to equilibrium multireference (MRCI) calculations on four states \(1^1\Sigma^+, 1^3\Sigma^+, 1^3\Delta,\) and \(1^3\Pi\).

From Table 1 we observe that at the MRCI level\(^6,7\) the ground state is predicted to be of \(1^3\Sigma^+\) symmetry (which is rather correct but see below), with the first excited \(1^1\Sigma^+\) state 3.0306 or 3.5807 kcal/mol higher. We also observe that while \(D_e\) values at the MRCI and CCSD(T) levels are more or less similar, DFT (LSDA, B3LYP, and BPW91) predictions are in striking disagreement among themselves and with ab initio findings. As a matter of fact the LSDA and BPW91 functionals predict the wrong ordering, i.e., the \(1^3\Sigma^+\) as the ground state of TiC. The Monte Carlo approach gives a 12 kcal/mol larger \(D_e\) value than the \(D_e\) values of the MRCI methods, and a rather too large (12.5 kcal/mol) \(1^3\Sigma^+-1^1\Sigma^+\) energy separation.\(^8\)

With the purpose of obtaining quantitative binding energies, to confirm that the \(3^3\Sigma^+\) is indeed the ground state, to accurately locate the first excited state, and to comprehend the Ti–C bonding, we have constructed potential energy curves (PEC) for the \(3^3\Sigma^+, 1^3\Sigma^+, 1^3\Delta,\) and \(1^3\Lambda\) states, employing large basis sets and CASSCF + single + double replacements (=MRCI) methods. In particular, for the Ti atom we have used the ANO basis set of Bauschlicher,\(^10\) 21s16p9d6f4g, and for the C atom the cc-pVQZ correlation consistent basis set of Dunning,\(^11\) both generally contracted to \(7s6p4d3f2g1\sigma_5s4p3d2f1g/c\). Our CASSCF space is composed of the \(4s + 4p + 3d + (3d^2) = 8\) orbitals on Ti, and the \(2s + 2p = 4\) orbitals on the C atom, a total of 12 functions. Considering the \(1s^2(C)\) and \(1s^22s^22p^63s^23p^6\) (Ti) as core electrons, our zeroth-order space was constructed by distributing the \(4+4\) valence electrons to 12 orbitals, enforcing at the same time symmetry and equivalence conditions. Valence “dynamical” correlation was obtained by single+double excitations out of the reference space (CASSCF + 1 + 2 = MRCI) at the internally contracted MRCI level. The size of the MRCI expansions ranges from \(2 \times 10^6\) \((a^1\Sigma^+, b^1\Delta)\) to \(3 \times 10^6\) \((X^3\Sigma^+, A^3\Delta)\) configurations, and the size extensivity error is 1.4(0.5) mhartree at the MRCI(+Davidson correction) level.

For the four states examined we report full potential energy curves (PEC), dissociation energies \((D_e)\), spectroscopic parameters \((r_e, \omega_e)\), and dipole moments \((\mu_e)\).

All our calculations were performed with the MOLPRO 2000.1 suite.\(^12\)

Results and Discussion

At the MRCI level, the atomic energy separations Ti\((a^3\Pi-\)\(a^3\Sigma, b^1\Pi-\)\(a^1\Sigma\)) are 0.958 and 1.556 eV, respectively, in acceptable agreement with the experimental values of 0.806 and 1.420 eV.\(^13\) These separations are of interest to the present work due to their implicit participation in the bonding process (vide infra).

Table 2 reports all our numerical results and Figure 1 shows the four potential energy curves at the MRCI level.

Now, the ground state of the TiC\(^+\) cation is of \(2^3\Sigma^+\)\((\sim 1\sigma\text{g}^2 2\sigma\text{g}^2 1\pi\text{g}^2 1\xi\text{g}^2)\) symmetry, portrayed in the following valence-bond-Lewis (vBL) picture,

![Ti(C)\(^+\) \(X^3\Sigma^+\)](image)

suggesting two \(\pi\) and \(\perp\sigma\) bonds, with \(D_e = 86.4(88) \text{ kcal/mol}\) and \(r_e = 1.696(1.70) \text{ Å}\) at the MRCI(+Q) level (ref 4). Given the above scheme, one could surmise on the low-lying states of the neutral TiC species, and the TiC\(^+\) cation to be of \(1^3\Delta\) or \(1^3\Sigma^+\) symmetry, respectively. In addition, due to the passive character of the \(3d\) or \(3d\) added electron, it is anticipated that the bonding features of TiC will be very similar to those of TiC\(^+\).

Indeed, our numerical findings are in keeping with the above discussion: the states \(3^3\Sigma^+\) and \(1^3\Sigma^+\) are essentially degenerate within the accuracy of our methods, with the \(3^3\Sigma^+\)
TABLE 1: Previous Theoretical Results on TiC

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Reference 6

Produced by Knudsen effusion mass spectrometric methods; o_e of unknown origin.

**Note:** E (hartree), dissocation energies D_e (kcal/mol), bond lengths r_e (Å), harmonic frequencies o_e (cm⁻¹), dipole moments μ (debye), and energy separations T_c (kcal/mol). Complete active space SCF of 8 active electrons in 10 orbitals. [5s4p3d1f]_Ti [3s3p1d]_C basis.

Figure 1. Potential energy curves of the TiC XΣ⁺, a¹Σ⁺, AΔ, and b¹Δ TiC states at the MRCl level. Energies have been shifted by +886.0 hartree.

is obvious, while a half σ bond is created due to a transfer of ~0.4 e⁻ from the Ti 3s¹ 3p⁻ electrons to the almost empty 2p C orbital. Notice the complete removal of the 3d_e⁻ 3d_g⁻, 3d_f⁻, and 3d_h⁻ upon bonding, clearly described by the following icon with

![Ti(4s^2 3d^0 2p^1 1p^0)](image)
Titanium Carbide

shorter by 0.04 Å, and our dipole moment µ larger by 1.1 D than those of ref 6. We attribute these significant numerical differences to the smaller basis sets, and, perhaps, to the truncated zeroth order space of these workers. As was expected the D_C = 86.4(88.0) kcal/mol, r_e = 1.696(1.70) Å, and o_w = 859(847) cm^{-1} values of the TiC(1Σ^\text{+}) at the MRCI(+) level,^3 are very similar to the corresponding values of TiC(1Σ^\text{+}) at the same level of theory, namely, D_C = 82.3(83.2) kcal/mol, r_e = 1.712(1.716) Å, and o_w = 896(861) cm^{-1}, Table 2. Experimentally, an upper limit D_C = 105 ± 6 kcal/mol value is reported in the literature obtained by Knudsen effusion mass spectrometry. By using the results of TiC^+ (ref 4) the ionization energy (IE) of TiC is obtained, IE = 6.49 eV.

\( \text{a}^1Σ^+ \) and \( \text{a}^1Σ^+ \) states are almost degenerate within our methods, the \( \text{a}^1Σ^+ \) – \( \text{X}^1Σ^+ \) difference being 1.55(1.71) kcal/mol at the MRCI(+) level. By extracting more valence correlation and/or by adding core-correlation effects it is understandable that the ordering of the two states could even be inverted on the nonrelativistic level of theory. The corresponding energy gap obtained by Bauschlicher and Siegbahn\(^6\) is twice as large, indicating again the effect of the oneelectron set.

The \( \text{a}^1Σ^+ \) state traces its lineage to Ti(a\(^5\)F;M(=±2)+C(3P;M(=0)) described at equilibrium by two leading CASSCF configurations,

\[ |\text{a}^1Σ^+\rangle \approx 0.78|1σ^22σ^21τ_z^21τ_y^2⟩ - 0.44|1σ^33σ^11τ_z^1τ_y^2⟩ \]

The CASSCF atomic Mulliken populations (Ti,C),

\[ 4s^{0.63}3d_{z^2}^{0.36}4p_x^{0.41}4p_y^{0.04}4p_z^{0.04}3d_{x^2}^{0.02}3d_{y^2}^{0.02}4f^{0.03}\]

\[ 2s^{1.72}2p_x^{0.85}2p_y^{0.91}2p_z^{0.91}3d^{0.06} \]

in conjunction with the atomic populations at infinity (see state \( \text{X}^1Σ^+ \)), indicate the formation of two \( \sigma \) bonds and a \( \pi \) interaction caused by the transfer of about 0.5 e\(^{-}\) from the 4s3d\(_{z^2}\) to the 2p\(_x\) orbitals on Ti to the empty 2p\(_C\) C orbital. However, the presence of the \[|1σ^22σ^21τ_z^21τ_y^2⟩ \] configuration with a relatively large coefficient diminishes the bonding ability of the \( 2\sigma \) orbital. This is also corroborated by the fact that the D\(_C\) value of the present state is practically the same to the bonding energy of the \( \text{X}^1Σ^+ \) state which carries a \( 1/2\) \( \sigma \) bond, that is the “0.44” configuration, somehow, partially cancels the “0.78” one. The D\(_C\) and r\(_e\) values obtained at the MRCI(+) level are 80.8(81.5) kcal/mol and 1.761(1.765) Å, as compared to 66.6(68.8) kcal/mol and 1.80(1.79) Å, respectively, of Bauschlicher and Siegbahn,\(^6\) Tables 1 and 2.

By examining Table 1, it is proper to say at this point that the density functional approach for both states, \( \text{X}^1Σ^+ \) and \( \text{a}^1Σ^+ \) (ref 7), fails. The PEC of Figure 1 displays two minima, a local (L) and a global (G) one at 3.75 and 3.30 bohr, respectively. The leading MRCI configurations and atomic Mulliken distributions at the L and G minima are

\[ |\text{A}^3Δ\rangle \sim \\
|1σ^22σ^23σ^1 \quad (0.62 \quad 1τ_x^1 \quad 1τ_y^1 \quad 1δ_z^1 \quad - \quad 0.44 \quad 1τ_x^1 \quad 1τ_y^1 \quad 1δ_z^1) \quad + \quad 0.36 \quad 1τ_x^1 \quad 1τ_y^1 \quad 1δ_z^1⟩ | \]

\[ 4s^{0.83}3d_{x^2}^{0.97}4p_x^{0.34}4p_y^{0.05}4p_z^{0.05}3d_{x^2}^{0.17}3d_{y^2}^{0.17}3d_{z^2}^{0.10}4f^{0.04} \]

\[ 2s^{1.74}2p_x^{1.05}2p_y^{0.77}2p_z^{0.77}3d^{0.06} \]

and

\[ |\text{A}^3Δ\rangle \sim \\
|1σ^22σ^23σ^1 \quad (0.89 \quad 1τ_x^2 \quad 1τ_y^2 \quad - \quad 0.13 \quad 2τ_x^1 \quad 1τ_y^2) \quad + \quad 0.13 \quad 1τ_x^2 \quad 2τ_y^1) \quad 1δ_z^1⟩ | \]

\[ 4s^{0.14}3d_{x^2}^{0.46}4p_x^{0.13}4p_y^{0.07}4p_z^{0.07}3d_{x^2}^{0.83}3d_{y^2}^{0.84}3d_{z^2}^{0.10}4f^{0.03} \]

\[ 2s^{1.62}2p_x^{1.05}2p_y^{1.05}2p_z^{1.05}3d^{0.06} \]

The \( \text{A}^3Δ \) state correlates to Ti(a\(^5\)F;M(=±2)+C(3P;M(=0)) atomic states. The populations in conjunction with the leading configurations clearly support the following bonding picture implying a σ bond due to the migration of 0.7 e\(^{-}\) from the Ti 4s\(_2\) orbital to the 2p\(_C\) C atom, while through the π frame ~0.4 e\(^{-}\) are moving from the C to the d\(_x^2\) and d\(_y^2\) empty orbitals of the Ti atom, causing a slight π interaction. Overall 0.4 e\(^{-}\) are moving from Ti to the C atom. With respect to the asymptotic products, D\(_L\) = 58.6 kcal/mol at r\(_e\) = 1.993 Å. Moving now toward the G-minimum a complete reorganization of the electronic structure takes place due to a severe avoided crossing with a higher \( 3Δ \) state originating from a Ti a\(^5\)F(4s\(_1\)3d\(_3\)) state, 0.806 eV above the \( a^3\)F state. Despite our efforts it was not possible to avoid the sharp drop of the PEC around the G-minimum.

The bonding icon is similar to that of the \( \text{X}^1Σ^+ \) state but with the 2e electron moved to a 3d\(_y^2\) orbital, therefore the two atoms form two \( \sigma \) and a \( 1/2\) \( \pi \) bonds. With respect to Ti(a\(^5\)F)+C(3P) the binding energy is 64.1 + ΔE(3F−F−) = 82.7 kcal/mol at r\(_e\) = 1.75 Å, using the experimental a\(^5\)F−a\(^5\)F gap, practically the same with the corresponding values of the \( \text{X}^1Σ^+ \) state. The diabatic origin of the \( \text{A}^3Δ \) state rationalizes the fact that this state is 18.8 kcal/mol above the \( \text{X}^1Σ^+ \) and not degenerate, or even lower in energy than the \( \text{X}^1Σ^+ \) state.

\[ \text{b}^1Δ \] This is the singlet analogue of the previously discussed \( \text{A}^3Δ \) state; it correlates to Ti(a\(^5\)F;M(=±2)+C(3P;M(=0)) and its PEC presents two minima, a local (L) and a global (G), at the same internuclear distances as in the \( \text{A}^3Δ \) state, Figure 1. Also, the leading configurations and Mulliken densities differ only slightly from those of the \( \text{A}^3Δ \) state, therefore both states share the same bonding description. The L-minimum occurs at 2.030 Å, 0.04 Å larger than the corresponding \( \text{A}^3Δ \) minimum, stems directly from the end products, and lies just 1.38 kcal/mol above the \( \text{A}^3Δ \) state, Figure 1. Moving toward the G-minimum a severe avoided crossing occurs around 1.77 Å creating similar morphological features as in the \( \text{A}^3Δ \) PEC, Figure 1, but correlating to Ti \( \text{b}^5\)F(4s\(_1\)3d\(_3\))+C(3P). With respect to the Ti-(b\(^5\)F) + C(3P) fragments the binding energy (internal bond strength) obtained is, 59.2 + ΔE(b\(^5\)F−a\(^5\)F) = 91.9 kcal/mol using the experimental ΔE gap. Naturally, the bonding features of the \( \text{b}^1Δ \) state are identical to those of the \( \text{A}^3Δ \) with the former state being 4.9 kcal/mol above the latter. Finally, we would like to observe the very large differences between the \( 1^3Δ \) and \( 1^3Δ \) dipole moments, \( Δμ ≈ 4 \) D.

**Final Remarks**

The \( 1^3Σ^+ \) and \( 1^3Δ \) states of the TiC system were examined by CASSCF+1+2 methods and quantitative basis sets. Somehow in line with Hund’s rules the \( 1^3Δ \) states are lower in energy.
than the corresponding $^1\text{A}_\text{g}$ ones, albeit by only 1.55 (a$^2\text{Σ}^+\rightarrow\text{X}^2\text{Σ}^+$) and 1.38 (b$^2\text{Δ}^+\rightarrow\text{A}^2\text{Δ}^+$) kcal/mol. Formally, the X-state is of $^2\text{Σ}^+$ symmetry with $D_\text{e} = 82.34(83.2)$ kcal/mol at the MRCI(+Q) level, contrasted to an upper limit experimental value of 105 ± 6 kcal/mol. Our previous experience with similar systems and the MRCI approach, suggest that the experimental $D_\text{e}$ value is rather overestimated. For the present system, further increase of the basis set, inclusion of core-valence correlation and scalar relativistic effects, does not seem to affect the binding energy significantly. The electronic structure of these four states can be rationalized by grafting a $\sigma$ or $\delta$ “observer” electron to the TiC$^+$ X$^2\text{Σ}^+$ state without perturbing seriously the bonding characteristics of TiC$^+$, as reflected on the $D_\text{e}$ and $r_\text{e}$ values of TiC. In all states the bonding can be attributed to a $^1/2\sigma$, $\pi_x$, $\pi_y$ interaction, with the observer electron defining the symmetry of each state. The formation of two $\pi$ and a half $\sigma$ bonds forces the C atom in a $M^0$ configuration ($2p^32p^3$), with the empty 2p orbital acquiring electron density originating from the Ti 4s$^2$ or 4s$^13d^3$ configurations.

References and Notes

(1) For instance, see: Harrison, J. F. Chem. Rev. 2000, 100, 679 and references therein.


