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Ab-initio study on low-lying states of the TiSi molecule

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Abstract. The electronic structure of the TiSi molecule was examined using two types of multireference single and double excitation configuration interactions with highly extended basis sets, one including valence correlation and the other including valence and core–valence correlation. A multireference coupled-pair approximation (MRCPA) was further applied to the latter. The calculations suggest a $^5\Delta$ ground state, and the lowest excited state is $^3\Pi$ and is only slightly (0.12 eV as estimated by MRCPA) above the ground state. The spectroscopic constants of the low-lying $^1\Delta$, $^3\Delta$, $^1\Pi$, $^5\Pi$, and $^7\Sigma^+$ states as well as the $^5\Delta$ ground state and the $^3\Pi$ excited states were evaluated, and we found that the molecule has only a weak σ bond and that six of the eight valence electrons essentially do not contribute to the bonding. The bonding nature of TiSi in these states is discussed in comparison with the TiC molecule.

Key words: Multireference single and double excitation configuration interaction – Multireference coupled-pair approximation – Spectroscopic constants – Dissociation energy

1 Introduction

The nature of the bonding between silicon and transition metal atoms is of great interest [1–10] because of the technological importance of these interfaces and silicides in electronic devices. Of the various transition metals, titanium, in the form of titanium silicide ($TiSi_2$), is used as the contact barrier in the contact holes [2] for making Si ultra-large-scale integration circuits. In this process, the $TiSi_2$ layer is obtained by chemical vapor deposition (CVD) [2, 3], in which deposited Ti reacts with the Si substrate to form $TiSi_2$ on the surface. The Ti–Si interaction and its bonding are thus very important for understanding the surface reactions and crystal growth of the Ti–Si systems. The bulk $TiSi_2$ [4–7] and the CVD mechanism [8] have been well studied experimentally and theoretically, but no experimental or theoretical studies of Ti–Si interaction or bonding have yet been reported. As a first step to understanding Ti–Si bonding, it is necessary to study the TiSi diatomic molecule. The molecule itself, however, has yet to be studied well and its ground state has yet to be identified.

The electronic ground state of the Si atom is ^{3}P ($3s^23p^2$), while that of the Ti atom is ^{3}F ($3d^24s^2$). In Ti, and in atoms on the left-hand side of the transition metal series [11, 12], different $3d$ occupations can occur in various molecular species because the $3d$ and $4s$ orbitals are similar in energy distribution. For instance, the first excited state, ^{5}F ($3d^34s^1$), of a Ti atom is only 0.81 eV [13] above the ground state, and the ^{5}F state is responsible for the bonding in many molecules containing Ti, such as TiO, TiS and TiN [14–16]. The ground state, $^3\Delta_g$, of Ti_2 arises from the $^5F + {}^5F$ asymptote [12], while the bonding of TiH arises from either the Ti $3d^34s^1$ or $3d^24s^2$ occupations [11]. In contrast, large silicon clusters containing a Ti atom as an impurity, like $TiSi_{30}H_{40}$, usually have a Ti excited $3d^4$ configuration in their ground state [9]. Consequently, several electronic states of various spin multiplicities and spatial symmetries may result for the TiSi molecule in the very low energy region. For bulk $TiSi_2$, theoretical [4] and experimental, i.e., photoemission [5] and X-ray photoelectron spectroscopy [6], studies point out that the interaction between Ti d and Si p contributes to chemical bonding [4–7] in the crystal [6] and the silicide–silicon interface [7]. Therefore the solid-state studies also suggest that the Ti $3d$ electrons as well as the Ti $4s$ and Si $3s$ and $3p$ electrons must be treated as valence electrons. Furthermore, the large difference in the correlation energies among different $3d$ occupations [11] requires taking the correlation effect into account at high levels. Additionally, it might be significant to include the inner-shell correlation [17, 18] in calculating energy differences among electronic states, since inner-shell ($3s$ and $3p$) correlation substantially affects the ^{3}F–^{5}F separation in the Ti atom [11] and is

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essential to determine the ground state of the Ti_2 molecule [12].

In this work, we investigated the electronic structure of the TiSi molecule by using very accurate *ab-initio* calculations with highly extended basis sets. We used the complete-active-space self-consistent-field (CASSCF) technique and then multireference single and double excitation configuration interaction (MRSDCI) calculations with CASSCF molecular orbitals (MOs) to determine the potential-energy curves and spectroscopic constants, i.e., the bond length (R_e), the dissociation energy (D_e), the vibrational frequency (ω_e), and the dipole moment (μ) of seven low-lying electronic states. We classified the ground state of TiSi and considered the electronic structures and the bonding nature for the ground and low-lying states. We also estimated the effects from a correlation between core and valence electrons for selected low-lying states by performing more extensive MRSDCI calculations and we applied the multireference coupled-pair approximation (MRCPA) [19, 20], which gave us successful results in a previous CuSi study [10], to the ground and the lowest excited states to estimate the effect of higher excitations precisely. As far as we know, the present work is the first quantum chemical study of this molecule. We compared our results with those of a study of the TiC molecule [16, 21] since C and Si are valence isoelectronic atoms and found that the bonding in TiSi is totally different from that in TiC.

2 Calculation methods

We chose the Ti basis set in which functions having significant distributions in the 3s and 3p region are uncontracted in order to describe inner-shell correlation well. The basis sets used were derived from Ahlrichs's valence triple-zeta set [22, 23], i.e., (14s9p5d)/[8s5p3d] for Ti and (12s9p)/[7s5p] for Si. For Ti, we also used Hay's diffuse function [24] and one s and two p diffuse functions, whose exponents were obtained by multiplying the exponent of the outermost primitive function by 1/3 for s ($\zeta_s = 0.01064215$) and by 1/3 and 1/9 for p ($\zeta_p = 0.12744653, 0.04248218$). We further added three f functions: Wachters' polarization functions [23, 25, 26,] in the uncontracted form and a g function ($\zeta_g = 0.64967786$), which was obtained by multiplying 1.3 by the exponent of the f function whose spatial expansion is in the middle of those of the three f functions. The final Ti basis set is of the form (15s10p6d3f1g)/[9s7p4d3f1g]. For Si, we added one s and one p diffuse function, whose exponents were obtained by multiplying the exponent of the outermost s and p primitive functions by 1/3 ($\zeta_s = 0.03083056$, $\zeta_p = 0.0264568$) and three d and two f polarization functions obtained from the aug-cc-pVTZ set proposed by Dunning and coworkers [23, 27]. The final form for Si is (13s10p3d2f)/[8s6p3d2f].

Preliminary CASSCF calculations were carried out to select candidates of the ground state and prepare the orbital sets for the following MRSDCI calculations and to select the reference configuration state functions (CSFs). CASSCF calculations were performed independently on the corresponding lowest Σ^+, Σ^-, Π, and Δ spatial symmetry states with almost all possible spin multiplicities, for example, $^1\Sigma^+$, $^3\Sigma^+$, $^5\Sigma^+$, and $^7\Sigma^+$ states for the Σ^+ symmetry species. In this procedure the active space consisted of ten orbitals originating from the Ti 3*d* and 4*s* and Si 3*s* and 3*p* orbitals. Eight valence electrons were distributed among these orbitals. All calculations were performed in C_{2v} symmetry, but various assumptions were introduced to impose the $C_{\infty v}$ symmetry on the orbitals as much as possible.

The dynamical correlation of valence electrons was taken into account by MRSDCI calculations using corresponding CASSCF natural orbitals. These calculations were performed for the $^7\Sigma^+$ state, the $^5\Pi$, $^3\Pi$, and $^3\Pi$ states, and the $^5\Delta$, $^3\Delta$, and $^1\Delta$ states, because these states were thought to be ground-state candidates according to the results of the CASSCF calculations for a wide range of internuclear distances. The reference configurations were chosen from the CASSCF wave functions, i.e., CSFs whose absolute values of the coefficient are greater than 0.06. The contributions of quadruple excitation to the MRSDCI energy were estimated by using Davidson's scheme [28], and these results are denoted by "+Q" in this study. To study the effect of inner-shell correlation, we also performed MRSDCI + Q calculations, which included the correlation between the valence and Ti 3*p* electrons for some selected states. Furthermore, we applied MRCPA [19, 20] to the two lowest states, $^5\Delta$ and $^3\Pi$, to settle the ground state. Because of the high computational demand, we did not include the correlation of Ti 3*s* electrons, which seems to be less important than that of Ti 3*p* electrons. We also assumed that core–core correlation energies are nearly the same among the electronic states considered.

To evaluate the dissociation energy, we carried out similar calculations on the high-spin (quintet) state of a supermolecule with a nuclear distance of 100 au corresponding to the Ti ^{3}F ($3d^24s^2$) + Si ^{3}P asymptote. In this calculation, only the SCF configuration could be used as the reference CSF in the MRSDCI calculations. All calculations except for MRCPA were done using the program system ALCHEMY II [29], while for MRCPA we used the code developed by Tanaka and coworkers [19], which is combined with ALCHEMY II.

3 Results and discussion

3.1 Classification of the ground state

The total CASSCF energy of each electronic state at the nuclear distance of 4.5 au is listed in Table 1 together with the leading valence-shell configuration that has the largest CASSCF coefficient. The parentheses show the π and δ occupations in the C_{2v} expression for Π states. Note that the wave functions of the Π ($^5\Pi$, $^3\Pi$, and $^1\Pi$) states were contaminated with Φ states. This is because the orbital symmetries were broken during the CASSCF procedure, when we use C_{2v} point group for the $C_{\infty v}$ symmetry. For simplicity, however, these states are merely denoted as "Π" states in this study. These CASSCF results suggest that the Π ($^5\Pi$, $^3\Pi$, and $^1\Pi$) and Δ ($^5\Delta$, $^3\Delta$, and $^1\Delta$) states are energetically lowerthan the Σ^+ ($^7\Sigma^+$, $^5\Sigma^+$, $^3\Sigma^+$, and $^1\Sigma^+$) and Σ^- ($^5\Sigma^-$ and $^3\Sigma^-$) states. Thus, the Π and Δ states appear to be highly likely candidates for the ground state of the TiSi molecule.

We carried out MRSDCI calculations in which the dynamical correlation of eight valence electrons is taken into account (denoted as val CI in this study) for Π ($^5\Pi$, $^3\Pi$, and $^1\Pi$) states and Δ ($^5\Delta$, $^3\Delta$, and $^1\Delta$) states, and the $^7\Sigma^+$ state. The $^7\Sigma^+$ state is the lowest among the Σ^+ and Σ^- states. The numbers of reference configurations are 6, 3, 5, 9, 9, 9, and 1 for the $^5\Delta$, $^3\Delta$, $^1\Delta$, $^5\Pi$, $^3\Pi$, $^1\Pi$ and $^7\Sigma^+$ states, respectively, and the total numbers of CSFs are, respectively, 548,026, 573,961, 692,967, 855,396, 740,908, 425,327, and 776,64 for the $^5\Delta$, $^3\Delta$, $^1\Delta$, $^5\Pi$, $^3\Pi$, $^1\Pi$ and $^7\Sigma^+$ states. The reference configurations for the $^5\Delta$ and $^3\Pi$ states are shown next; the C_{2v} expressions of the π and δ occupations are given in parentheses.

$^5\Delta$ state

$...9\sigma^2 10\sigma^2 12\sigma^1 4\pi^2 1\delta^1$ $(...4b_1^1 4b_2^1 13a_1^1)$

$...9\sigma^2 11\sigma^2 12\sigma^1 4\pi^2 1\delta^1$ $(...4b_1^1 4b_2^1 13a_1^1)$

$...9\sigma^2 10\sigma^1 11\sigma^1 12\sigma^1 4\pi^2 1\delta^1$ $(...4b_1^1 4b_2^1 13a_1^1)$

$...9\sigma^2 11\sigma^1 12\sigma^2 4\pi^2 1\delta^1$ $(...4b_1^1 4b_2^1 13a_1^1)$

$...9\sigma^1 10\sigma^2 12\sigma^1 4\pi^2 1\delta^2$ $(...4b_1^2 13a_1^1 1a_2^1)$

$-(...4b_2^2 13a_1^1 1a_2^1)$

$^3\Pi$ state

$...9\sigma^2 10\sigma^2 4\pi^3 1\delta^1$ $(...4b_1^2 4b_2^1 1a_2^1)$

$...9\sigma^2 10\sigma^2 4\pi^1 5\pi^2 1\delta^1$ $(...5b_1^2 4b_2^1 1a_2^1)$

$...9\sigma^2 10\sigma^2 4\pi^2 5\pi^1 1\delta^1$ $(...4b_1^1 5b_1^1 4b_2^1 1a_2^1)$

$...9\sigma^2 11\sigma^2 4\pi^3 1\delta^1$ $(...4b_1^2 4b_2^1 1a_2^1)$

$...9\sigma^2 11\sigma^2 4\pi^1 5\pi^2 1\delta^1$ $(...5b_1^2 4b_2^1 1a_2^1)$

$...9\sigma^2 11\sigma^2 4\pi^2 5\pi^1 1\delta^1$ $(...4b_1^1 5b_1^1 4b_2^1 1a_2^1)$

$...9\sigma^2 10\sigma^1 11\sigma^1 4\pi^3 1\delta^1$ $(...4b_1^2 4b_2^1 1a_2^1)$

$...9\sigma^2 10\sigma^1 11\sigma^1 4\pi^1 5\pi^2 1\delta^1$ $(...5b_1^2 4b_2^1 1a_2^1)$

$...9\sigma^2 10\sigma^1 11\sigma^1 4\pi^2 5\pi^1 1\delta^1$ $(...4b_1^1 5b_1^1 4b_2^1 1a_2^1)$

The total energies of val CI + Q for each electronic state at the nuclear distance of 4.5 au are also given in Table 1, and the potential-energy curves obtained using val CI + Q are displayed in Fig. 1, which indicates that the $^5\Delta$ state is the lowest energetically, but that the $^3\Pi$ state is the second lowest and lies slightly (0.184 eV using val CI + Q) higher. Thus, from these results, the $^3\Pi$ state cannot be eliminated as a possible ground-state candidate. According to the results of the val CI + Q calculations, other Π and Δ states distribute within 0.5 eV above the $^5\Delta$ state, while the $^7\Sigma^+$ state is located more than 1.0 eV above it.

More extensive MRSDCI calculations, in which the correlation between valence electrons and Ti 3*p* electrons was also taken into account, were performed for the lowest $^5\Delta$ and $^3\Pi$ states. In these calculations (labeled v-c CI in this study), the reference configurations were the same as those for the corresponding val CI, and the natural orbitals given by the corresponding val CI were used. To reduce the total number of CSFs, some external orbitals (19 MOs for the $^5\Delta$ state and 17 MOs for the $^3\Pi$ state) were cut off by a threshold for the occupation number in the val CI calculations. The total numbers of CSFs for v-c CI were 1,404,155 and 1,963,229 for the the $^5\Delta$ and $^3\Pi$ states, respectively. Furthermore, after v-c CI, we carried out MRCPA calculations on these states using the respective v-c CI natural orbitals. The results of v-c CI + Q and MRCPA(2), which is the second-order approximation in the MRCPA scheme, also indicate that the $^5\Delta$ state is the lowest and may be identified as the ground state. The lowest $^3\Pi$ state lies above the ground state by 0.167 eV (v-c CI + Q) or 0.120 eV [MRCPA(2)].

3.2 Bonding characteristics in the ground and low-lying states

In order to better understand the characteristics of the $^5\Delta$ ground and other low-lying states of TiSi, we analyzed the CASSCF wave functions because there were no large qualitative changes in the wave functions among the CASSCF, val CI, and v-c CI approaches. We further compared the wave functions with reported results of a study of the TiC molecule [16, 21], since we

Table 1. Total energy (E_{tot}) and the largest contributor in complete-active-space self-consistent-field (CASSCF) and E_{tot} from val CI + Q and v-c CI + Q for each state at a distance of 4.5 au. E_{tot} (CAS), E_{tot} (val CI + Q), and E_{tot} (v-c CI + Q) are relative to −1137.0 au

State	E_{tot} (CAS)	Primary config. in CASSCF[a]	Coefficients of the primary configuration[b]	E_{tot} (val CI + Q)	E_{tot} (v-c CI + Q)
$^5\Delta$	−0.31556	$9\sigma^2 10\sigma^2 12\sigma^1 4\pi^2 1\delta^1$	0.85	−0.43512	−0.53142
$^3\Delta$	−0.31222	$9\sigma^2 10\sigma^2 12\sigma^1 4\pi^2 1\delta^1$	0.70, 0.46	−0.42452	
$^1\Delta$	−0.30530	$9\sigma^2 10\sigma^2 12\sigma^1 4\pi^2 1\delta^1$	0.84	−0.42145	
$^5\Pi$[b]	−0.29316	$9\sigma^2 10\sigma^1 11\sigma^1 4\pi^3 1\delta^1$ $(4b_1^2 4b_2^1 1a_2^1)$	0.81	−0.42297	
$^3\Pi$[b]	−0.31589	$9\sigma^2 10\sigma^2 4\pi^3 1\delta^1$ $(4b_1^2 4b_2^1 1a_2^1)$	0.70	−0.42929	−0.53064
$^1\Pi$[b]	−0.30782	$9\sigma^2 10\sigma^2 4\pi^3 1\delta^1$ $(4b_1^2 4b_2^1 1a_2^1)$	0.71	−0.42396	
$^7\Sigma^+$	−0.28077	$9\sigma^2 10\sigma^1 11\sigma^1 4\pi^2 1\delta^2$	0.97	−0.39932	
$^5\Sigma^+$	−0.27990	$9\sigma^2 10\sigma^2 4\pi^2 1\delta^2$	0.81		
$^3\Sigma^+$	−0.27372	$9\sigma^2 10\sigma^2 4\pi^2 1\delta^2$	0.79		
$^1\Sigma^+$	−0.27137	$9\sigma^2 10\sigma^2 4\pi^2 1\delta^2$	0.80		
$^5\Sigma^-$	−0.27990	$9\sigma^2 10\sigma^2 11\sigma^1 12\sigma^1 4\pi^2$	0.82		
$^3\Sigma^-$	−0.25627	$9\sigma^2 10\sigma^2 11\sigma^2 4\pi^2$	0.73		
cf. dissociation limit[c]	−0.27916			–0.36679	−0.44586

[a] Only the configuration with the largest coefficient(s) is given for each state

[b] All calculations were performed using C_{2v} symmetry and, as a result, the $^5\Pi$, $^3\Pi$ and, $^1\Pi$ states were obtained as a mixture of Π and Φ states. In the π space, the b_1 and b_2 orbitals are not degenerate

[c] The Si ^{3}P ($3s^2 3p^2$) + Ti ^{3}F ($3d^2 4s^2$) asymptote is assumed as the dissociation limit

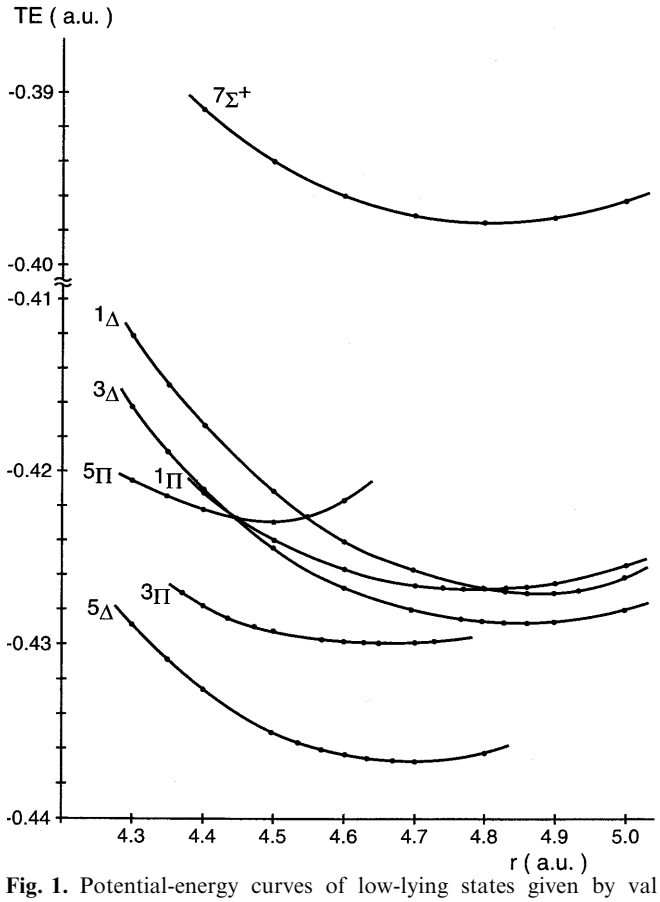

Fig. 1. Potential-energy curves of low-lying states given by val CI + Q

found that the bonding in the $^5\Delta$ ground state of TiSi is weaker than that in the $^3\Sigma^+$ ground state of TiC: the present val CI + Q level calculation gives a D_e of 1.90 eV for the $^5\Delta$ state, whereas the reported D_e for the $^3\Sigma^+$ state of TiC is 3.08 eV [16]. Before we describe the bonding nature of TiSi, let us briefly introduce the CASSCF wave functions of TiC [16]. The ground state of TiC is $7\sigma^2 3\pi^4 8\sigma^1 9\sigma^1\ ^3\Sigma^+$ and the lowest $^1\Sigma^+$ state lies 0.053 eV above it, where the $^1\Sigma^+$ state is described mostly by two configurations, $7\sigma^2 3\pi^4 8\sigma^2$ and $7\sigma^2 3\pi^4 9\sigma^2$. In both the $^3\Sigma^+$ and the $^1\Sigma^+$states, the 7σ orbital is mostly C 2*s* and has some Ti character and the 3π orbital is clearly a Ti 3*d*–C 2*p* bond. In the $^3\Sigma^+$ ground state of TiC, the open-shell 8σ is mostly Ti 4s and 4p and the open-shell 9σ is mostly on C and has a small amount of $3d\sigma$; thus the bonding nature in the ground state is described as a strong bonding, i.e., a double bond in π space plus some σ bond. In contrast, the $^1\Sigma^+$state is not a singlet analogue of the $^3\Sigma^+$state, because the coefficients for the two configurations are not equal and the characteristics of the 8σ and 9σ orbitals are different from those in the ground state. Bauschlicher and Siegbahn reported [16] that the 8σ and 9σ orbitals are neither the same orbitals as for the $^3\Sigma^+$ state nor are they a classic bonding and antibonding orbital.

For TiSi, the $^5\Delta$ ground state has a totally different bonding nature from the $^3\Sigma^+$ ground state of TiC [16, 21]. The $^5\Delta$ ground and other Δ states with different spin multiplicities are primarily represented by an occupation of $9\sigma^2 4\pi^2 1\delta^1(10\sigma,11\sigma)^2 12\sigma^1$. The three dominant configurations and their coefficients of the $^5\Delta$ ground state at $R = 4.5$ au are

$$...9\sigma^2 10\sigma^2 12\sigma^1 4\pi^2 1\delta^1: 0.85$$

$$...9\sigma^2 11\sigma^2 12\sigma^1 4\pi^2 1\delta^1: -0.28$$

$$...9\sigma^2 10\sigma^1 11\sigma^1 12\sigma^1 4\pi^2 1\delta^1: -0.32$$

Note that for the third configuration, only the largest coefficient of its component spin coupling is given here. The 9σ orbital is the essentially doubly occupied atomic Si 3*s* in all the states considered, and it corresponds to the 7σ orbital of TiC [16, 21]. The 1δ is the Ti $3d\delta$ atomic orbital, and the open-shell 4π is mostly the Si $3p\pi$ orbital. The character of the 4π orbital is in clear contrast to that of the corresponding 3π orbitals of TiC, since the 3π orbital of TiC is the Ti 3*d*–C 2*p* bonding orbital [16, 21]. The open-shell 12σ orbital is composed mainly of Ti 4*s* and $3d\sigma$ orbitals. Among the eight valence electrons, the six electrons in the orbitals explained earlier essentially do not contribute to the bonding. Only the two remaining electrons distributed in the 10σ and 11σ orbitals contribute to the bonding, but the bonding does not appear to be strong. That is, the 10σ and 11σ natural orbitals are, roughly speaking, bonding-type and antibonding-type orbitals between Ti 4*s*4*p* and Si 3*s*3*p*, respectively; however, they are not ordinary classic bonding and antibonding orbitals. Both orbitals also have large amplitudes in the outer bonding region, and their shape resembles that of the 8σ and 9σ orbitals in the $^1\Sigma^+$ state of TiC [16]. Furthermore, the occupation numbers of the natural orbitals (1.7 for 10σ and 0.3 for 11σ) also suggest that there is not a strong σ bond.

The Π ($^5\Pi$, $^3\Pi$ and $^1\Pi$) states are represented by the configuration $9\sigma^2(4\pi,5\pi)^3 1\delta^1(10\sigma,11\sigma)^2$, where the 1δ MO is the Ti $3d\delta$. As noted before, we obtained the Π states as a mixture of Π and Φ states. In the $^3\Pi$ state, 4π orbitals are not degenerate; the singly occupied 4π orbital, $4b_2$ in C_{2v}, is mostly Si $3p\pi$, similar to the 4π orbital in the Δ states, whereas the doubly occupied 4π ($+5\pi$) orbital, $4b_1$ ($+5b_1$) in C_{2v}, is dominated by the Si $3p\pi$ and Ti $3d\pi$ and is analogous to the 3π bonding MO of TiC. This doubly occupied 4π orbital contributes to the bonding. However, the occupation number of the antibonding orbital in π space, the 5π natural orbital, is substantial (0.4 for $5b_1$ and 1.6 for $4b_1$); therefore, the bonding in the π space does not appear to be very strong in comparison with the π bond in the $^3\Sigma^+$ and $^1\Sigma^+$ states of TiC. The weak bonding in σ space originates from the two electrons distributed in the 10σ and 11σ orbitals, which are similar to the 10σ and 11σ orbitals in the Δ states. The Σ^+ ($^1\Sigma^+$, $^3\Sigma^+$, $^5\Sigma^+$, and $^7\Sigma^+$) and Σ^- ($^3\Sigma^-$ and $^5\Sigma^-$) states have a leading occupation of $9\sigma^2 4\pi^2 1\delta^2\ (10\sigma,\ 11\sigma)^2$, where the 1δ and 4π orbitals are similar to those in the Δ states. The Σ^+ states, except for the $^7\Sigma^+$ state, which is essentially represented by an SCF configuration, have a weak σ bonding similar to the Δ states. The reason is that this bonding originates from the two electrons distributed in the 10σ and 11σ orbitals,

which are similar to those MOs in the Δ states. Note that the $^1\Sigma^+$ and $^3\Sigma^+$ states led by $9\sigma^2 4\pi^4(10\sigma,11\sigma)^2$ configurations, which correspond to the two lowest states of TiC, are energetically higher in TiSi.

3.3 Spectroscopic constants

The values of R_e, D_e, ω_e, and μ estimated by val CI + Q and c-v CI + Q are listed in Table 2, where μ was evaluated with the MRSDCI wave function at R_e. The results from the MRCPA(2) for the $^5\Delta$ ground and the lowest $^3\Pi$ states, denoted as v-c MRCPA(2), and those from CASSCF are also given in the table.

The R_e given by the CASSCF calculations was presumed to be longer than 2.65 Å (5.0 au) for all the states considered, but we did not perform a CASSCF calculation in the case of a bond length being longer than 2.65 Å because the nearest Si–Ti distances in solid $TiSi_2$ are 2.64 and 2.54 Å in the stable C49 and metastable C54 phases, respectively [5]. The R_e can be shortened considerably by taking into consideration the dynamical correlation in all the states examined. The R_e values estimated by val CI + Q were about 2.5–2.6 Å for the $^5\Delta$ ground and other low-lying states, except for the $^5\Pi$ state, which had a slightly shorter R_e of around 2.4 Å. The ω_e value obtained for each state was about 300 cm^{-1}, except for the $^5\Pi$ state, which had an ω_e value of 520.8 cm^{-1}. Such small ω_e values reflect the shallow potential-energy curves seen in Fig. 1 and the weak bonding in TiSi as described in the previous subsection. The estimated μ values of all the states examined were 2.6–3.8 D, polarizing as $Ti^{\delta+}Si^{\delta-}$, as is the case in the polarization of low-lying states of TiC, i.e., $Ti^{\delta+}C^{\delta-}$ [16].

By taking core–valence correlation into account (c-v CI + Q), the R_e values were shortened by 0.06–0.09 Å, ω_e increased by 20–30 cm^{-1}, and μ decreased slightly in comparison with the val CI + Q results. Furthermore, the core–valence correlation increases D_e by 0.4–0.5 eV, which reflects the importance of the inner-shell correlation to D_e [17, 18]. For the ground $^5\Delta$ state, the most reliable calculation in this study, v-c MRCPA(2), gave D_e of 3.00 eV, R_e of 2.41 Å, μ of 2.02 D, and ω_e of 366.6 cm^{-1}. For the $^3\Pi$ state, v-c MRCPA(2) gave values of 2.88 eV, 2.41 Å, 2.19 D, and 318.3 cm^{-1} for D_e, R_e, μ and ω_e, respectively. This is, however, core–core correlation that is not taken into account in this study. As was pointed out, R_e might be increased and D_e might be decreased slightly [18] if core–core correlation were included.

Table 2. Spectroscopic constants of the various states evaluated

	R_e (Å)	D_e (eV)[a]	ω_e (cm^{-1})	μ (D)
$^5\Delta$ state				
CASSCF	> 2.54	> 1.19		
val CI + Q	2.488	1.901	328.6	3.04
v-c CI + Q	2.428	2.338	353.1	3.00
v-c MRCPA(2)	2.410	2.997	366.6	2.02
$^3\Delta$ state				
CASSCF	> 2.65	> 1.21		
val CI + Q	2.559	1.685	297.6	3.45
$^1\Delta$ state				
CASSCF	> 2.65	> 1.20		
val CI + Q	2.592	1.642	287.0	3.76
$^5\Pi$ state[b]				
CASSCF	> 2.43	> 0.45		
val CI + Q	2.377	1.529	520.8	3.09
$^3\Pi$ state[b]				
CASSCF	> 2.50	> 0.92		
val CI + Q	2.453	1.717	301.3	3.04
v-c CI + Q	2.368	2.308	348.1	2.93
v-c MRCPA(2)	2.408	2.877	318.3	2.19
$^1\Pi$ state[b]				
CASSCF	> 2.65	> 1.04		
val CI + Q	2.535	1.634	294.5	3.31
$^7\Sigma^+$ state				
CASSCF	> 2.65	> 0.29		
val CI + Q	2.540	0.837	309.9	2.60

[a] The Si ^3P ($3s^2 3p^2$) + Ti ^3F ($3d^2 4s^2$) asymptote was assumed
[b] See footnote b in Table 1

4 Conclusions

The electronic structure of the TiSi molecule was investigated by MRSDCI + Q calculations and MRCPA calculations. The results strongly suggest that the $^5\Delta$ state is the ground state and that the first excited state is a $^3\Pi$ state (a mixture of Π and Φ states) lying 0.12 eV above the ground state according to the c-v MRCPA(2) calculations. The spectroscopic data of both states are very close, and this can be considered the reason these states are not easy to identify experimentally. In addition to the $^3\Pi$ state, there are $^3\Delta$, $^1\Pi$, $^5\Pi$, and $^1\Delta$ states within 0.5 eV (at the val CI + Q level) above the $^5\Delta$ state. Many Σ^+ and Σ^- states also exist above these states.

The $^5\Delta$ ground state has an occupation of $(\sigma)^5(\pi)^2(\delta)^1$and does not have a strong covalent bond. In this state, six of the eight valence electrons (two σ electrons from Si 3*s*, two π electrons from Si 3*p*, one Ti 3*dδ* electron, and one σ electron of Ti 4*s* and 3*dσ*) essentially do not contribute to the bonding. The two remaining σ electrons, which are distributed in peculiar bonding-type and antibonding-type orbitals between the Ti 4*s*3*dσ* and Si 3*s*3*pσ*, give a weak σ bond. Thus, the bonding in the TiSi diatomic molecule is interestingly in contrast to that in bulk $TiSi_2$, in which the interaction between Ti *d* and Si *p* contributes to chemical bonding. The $^3\Pi$ state has an occupation of $(\sigma)^4(\pi)^3(\delta)^1$ and the bonding in the state is also not very strong. In addition to the weak σ bond, which is similar to that in the $^5\Delta$ state, a weak bonding exists in the π space, between Si 3*pπ* and Ti 3*dπ*. The nature of the bonding in these states is quite different from that in the TiC molecule, which has multiple covalent bonds, including a strong π double bond and some σ bonding. The differences in the bonding between TiC and TiSi originate from different behavior associated with Ti 3*d* between the C 2*p* and Si 3*p* electrons. In TiC, C 2*p* makes a bond with Ti 3*d*, and the four-electron occupation in this bonding orbital

produces a strong π double bond. In TiSi, however, Si 3*p* is isolated in the Si atom and does bond with Ti 3*d*. This can be understood because the C 2*p* level is close to the Ti 3*d* level; thus, bonding between C 2*p* and Ti 3*d* is easy, while the Si 3*p* level is far higher than the Ti 3*d* level. Despite the weak bonding characteristic in the TiSi molecule, the not-so-small D_e value of 3.00 eV, estimated by c-v MRCPA(2), suggests a large correlation contribution, especially from the inner-shell (Ti 3*p*), to the bonding in TiSi.

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