

Potential energy curve of the ground state of the titanium dimer[☆]

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Abstract

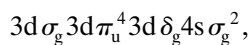
A global potential energy curve has been obtained for the ground state of the Ti dimer with state averaged complete-active-space self-consistent-field (CASSCF) and multi-reference (MR) configuration interaction (CI) calculations. The calculated potential curves have a large barrier at intermediate internuclear distances (R). The dissociation energy of the ground state was estimated and is in agreement with an experimental estimate. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Metal dimer; Global potential energy curve; State averaged CASSCF/MRCI; Dissociation energy

1. Introduction

The ground state of the Ti dimer was assigned as a $^3\Delta_g$ state by Bauschlicher et al. [1] by using a multi-reference configuration-interaction (MRCI) approach. Doverstål et al. [2] confirmed this assignment by resonant two-photon ionization spectroscopy and estimated the dissociation energy as

≥ 1.349 eV. The main configuration of the ground state is



which correlates diabatically with two excited atomic states 5F . The bonding in this state consists of a two-electron $4s-4s$ bond, a four-electron $3d\pi-3d\pi$ bond, and two one-electron $3d-3d$ bonds. This configuration is dominant in the bonding region because of the strong bonding. However, it is energetically unfavorable at large

[☆]Dedicated to Professor Keiji Morokuma in celebration of his 65th birthday.

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R because it must promote electrons in both Ti atoms. The configuration arising from the atomic ground state asymptote ${}^3F + {}^3F$ also generates a ${}^3\Delta_g$ state,

$$3d\pi_g 3d\pi_u 3d\delta_g 3d\delta_u 4s\sigma_g^2 4s\sigma_u^2,$$

having weaker bonds than the configuration discussed above. This configuration gives a lower total energy for larger R . From these considerations, we can expect configurational mixings in the potential energy curve of the ground state. The asymmetric asymptote ${}^3F + {}^5F$ also generates a ${}^3\Delta_g$ species. This configuration

$$3d\sigma_g 3d\pi_u^2 3d\delta_g 3d\delta_u 4s\sigma_g^2 4s\sigma_u$$

has a double bond character and is favored over the ${}^5F + {}^5F$ configuration at the dissociation limit, because it involves the excitation of a single Ti. Thus, this configuration is also expected to contribute to the description of the ground state.

In this work, we address ourselves to the problem of obtaining a reliable global potential energy curve for the ground state of the Ti dimer by considering a large number of quasi-degenerate states arising from the asymptotes mentioned above. In order to describe these states equivalently, we solved the state-averaged complete active space self-consistent field (SA-CASSCF) equations for these quasi-degenerate states and performed single and double excitation CI calculations. The dissociation energy (D_e) is another property of interest for us. Bauschlicher et al. [1] calculated the four lowest states of Ti_2 at various levels of calculation. They reported D_e only for the ${}^7\Sigma_u^+$ state as 0.79 eV obtained by an averaged coupled pair functionals (ACPF) calculation, but not for the ${}^3\Delta_g$ state. Experimentally [2], the long-lived state was observed at 10882 cm^{-1} above the ground state and D_e was estimated as $\geq 1.349\text{ eV}$.

All calculations were performed in $D_{\infty h}$ symmetry using the program system ALCHEMY II [3,4] where this symmetry is fully utilized.

2. Method of calculations

2.1. Basis set

We used Slater-type functions (STFs) of double zeta quality prepared for the $3d^2 4s^2$ (3F) state by Clementi and Roetti [5]. One 3d STF with an exponent of 0.88 was added to improve the 3d atomic orbital of the $3d^3 4s$ (5F) state. The orbital exponent was determined for 5F by an MCSCF calculation with two configurations $3d^3 4s$ and $3d^2 4s^2$. We also added one 4p STF with an exponent of 1.2 for taking into account the near degeneracy effect of 4s and 4p orbitals. The exponent was optimized for the 3F state by an MCSCF calculation with two configurations $3d^2 4s^2$ and $3d^2 4p^2$. Two 4f STFs with exponents of 1.494 and 2.585 were also included to allow for correlation effects among the 3d electrons. The SDCI calculations from the HF configurations with the present basis (8s5p3d2f) gave 0.902 eV for the energy separation between 3F and 5F , while a recent valence CI calculation with an extended basis set gave 0.923 eV [6]. This shows that the present set is flexible enough to represent both the 3F and 5F atomic states. In addition, the Davidson correction [7] (denoted as Q-correction hereafter) increases the excitation energy to 0.983 eV which is larger than the experimental value by 0.177 eV [8]. This discrepancy originates from disregarding the inner-shell correlation effect and the relativistic effect. We also checked basis set superposition errors (BSSE) for the 5F atomic state by a counterpoise scheme [9] where a ghost set was put 3.0 a.u. apart from the Ti atom. The BSSE is less than 0.05 eV and 0.10 eV at the SCF, and CI levels, respectively. Thus, we decided not to make any correction for potential energy curves and spectroscopic constants.

2.2. CASSCF and MRSDCI calculations

Following our previous studies on Sc_2 [10], we performed the SA-CASSCF calculations, where the 3d and 4s electrons are active and 27 solutions, which correspond to molecular states arising

ing from low lying seven asymptotes, were solved. The MCSCF wavefunctions are spanned with 5808 configuration state functions (CSFs). The SA-CASSCF is adequate for obtaining an appropriate global potential energy curve which leads to the complicated state mixing and results in proper dissociation limit. The resultant state averaged MOs were used in the successive CI calculations.

We further performed multi-reference SDCI calculation (MRSDCI) for the ground state. Only the correlation effects of the 3d and 4s electrons were considered. As to the reference space, we selected the CSFs whose coefficients in the MCSCF wave functions of the lowest solution exceeded a threshold of 0.05 in absolute magnitude at each R . The dimension of the MRSDCI ranges from 518069 to 2029815 in the $D_{\infty h}$ symmetry. Balasubramanian et al. [11] suggested that the first order CI (FOCI), in which all single excitations from the complete active space (CAS) are taken into account, is extremely effective for describing a global potential curve of a metal dimer. The effect of disregarding single excitations in the above MRSDCI was studied by comparing CI energies of FOCI and a CI where double excitations to the external space were excluded from the MRSDCI mentioned above. We call the latter CI, MRSCI hereafter.

In addition, we performed a single excitation CI (FOCI(3p)) which contains only single excitations from the 3p electrons to the 3d and 4s MOs. These excitations are not allowed at the dissociation limits due to the conservation of parity but are allowed in the molecular system. It will be shown in the next section that these excitations increase the D_e of the Ti dimer.

3. Results and discussion

3.1. SA-CASSCF results

The results of SA-CASSCF calculations at the dissociation limit are shown in Table 1. The degeneracy of the atomic states is retained within 0.07 eV. The order of the asymptotes agrees with that of experiment except for $^3F + ^3F(II)$ and $^3F + ^1G$. The calculated excitation energies, however, are higher than the experimental values by

Table 1

Relative energies of 27 low lying states

	SCF	SA-CASSCF	Exp.
$3d^2 4s^2 ^3F + 3d^2 4s^2 ^3F$	0	0	0
$3d^2 4s^2 ^3F + 3d^3 4s ^5F$	0.554	1.09–1.13	0.81
$3d^2 4s^2 ^3F + 3d^2 4s^2 ^1D$	1.27	1.14–1.20	0.87
$3d^2 4s^2 ^3F + 3d^2 4s^2 ^3P$	1.54	1.37–1.42	1.03
$3d^2 4s^2 ^3F + 3d^3 4s ^3F(II)$	1.46	2.08–2.11	1.42
$3d^2 4s^2 ^3F + 3d^2 4s^2 ^1G$	1.98	1.81–1.88	1.47
$3d^3 4s ^5F + 3d^3 4s ^5F$	1.11	2.21–2.22	1.61

0.3–0.6 eV. The excitation energies of the asymptotes associated with $3d^3 4s$ configuration by SA-CASSCF are considerably higher than those by atomic SCF calculation, indicating that the obtained averaged MOs are favored over the $3d^2 4s^2$ configuration.

In Fig. 1, we show 27 potential energy curves of $^3\Delta_g$. We have obtained CASSCF solutions which consist of three characteristic constituents. The constituent (a) is a bunch of CSFs arising from low-lying asymptotes including states associated with the $^3F + ^3F$ asymptote which give repulsive potential curves. The constituent (b) arises from asymmetric asymptotes and has an attractive potential. The constituent (c) is associated to the $^5F + ^5F$ asymptote which forms a strong multi-bond. The mixing of these constituents makes the potential curves very complicated. In the ground state, the character of the wave function changes from group (a) to (c) via group (b) (see Fig. 2). We have a large barrier at the intermediate region of 5–6 a.u. The binding energy cannot be obtained at the CASSCF level. We recall that the averaged MOs are favoured over $3d^2 4s^2$. The present averaged MO set gives the excitation energy of $^5F + ^5F$ about 1.0 eV higher than the HF limit reflecting the character of MOs. Thus, reorganization of MO in CI calculation is expected to give a reasonable amount of binding energy.

3.2. MRSDCI calculations

The MRSDCI results for the ground state are shown in Fig. 3. A large barrier and irregularity of the potential energy curve were again obtained at an intermediate region. The reference comprises

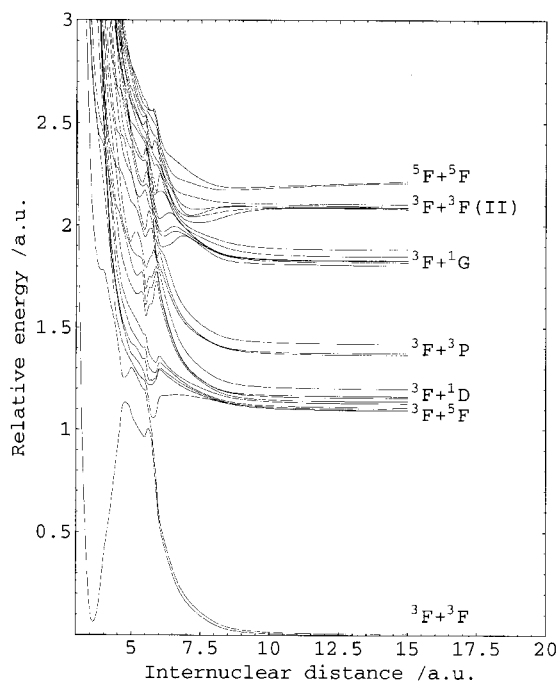


Fig. 1. SA-CASSCF potential energy curves of the lowest 27 states of $^3\Delta_g$ species.

85–87% of the CI wave function at the equilibrium region and the dissociation limit. The weight of reference space, however, decreases to 80% at the intermediate region. Though we included the largest number of reference configurations in this region, the resultant wave function shows insufficiency of accuracy. This imbalance of the quality of the wave function is the cause of irregularities in the CI potential energy curves with and without the Davidson correction.

The character of the CI wave function is nearly the same as that of the MCSCF wave function as shown in Fig. 2. At the equilibrium region, the ground state has $^5F+^5F$ character and dissociates to $^3F+^3F$ limit. At intermediate region, a drastic change of character occurs and the $^3F+^5F$ character becomes dominant. The MRSDCI calculation yielded positive D_e of 0.514 eV.

Now we investigate the effect of single excitations which were not considered in the MRSDCI calculation but were included in the FO CI. In Fig. 4 the energy contributions from these configurations are plotted against R . The contribu-

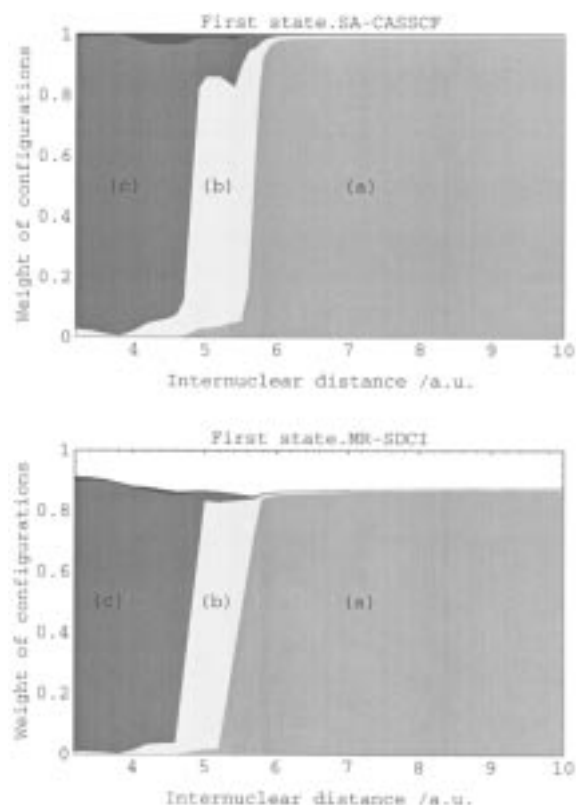


Fig. 2. Character of the wavefunctions. Each type is categorized by its asymptote from which the configuration arises. Constituent a: $(3d^24s^2)^3F + (3d^24s^2)^3F$. Constituent b: $(3d^24s^2)^3F + (3d^34s)^5F$. Constituent c: $(3d^34s)^5F + (3d^34s)^5F$.

tions show irregularities at the intermediate region of 4.5–6 a.u., indicating again the insufficiency of the reference configurations in this region. We have some doubt that the second minimum given by the Davidson correction arises from the inaccurate description of the reference configurations. This contribution increases D_e by 0.058 eV. We also investigated the effect of single excitations of the 3p electron to 3d and 4s which contribute to D_e directly, because these excitations are prohibited at the dissociation limit. The contribution was calculated as the difference of FO CI(3p) and CASSCF energies. As expected the effects of the 3p electron excitations monotonically decrease as R increases (see Fig. 5). This contribution gave another improvement of 0.172

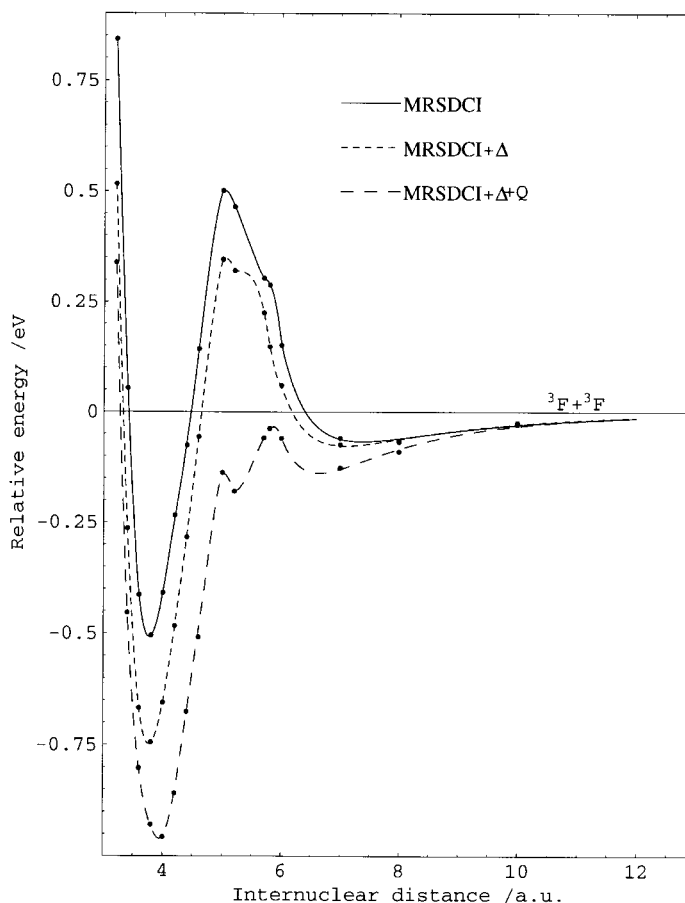


Fig. 3. Potential energy curves by MRSDCI, MRSDCI with single excitation corrections Δ , and MRSDCI with Δ and Q correction. Δ consists of the energy lowering of the single excitations of 4s and 3d like electrons in SA-CAS space given in Fig. 4 and those of 3p excitations given in Fig. 5. Q refers to Davidson correction and the correction was performed on the MRSDCI total energies augmented with Δ .

eV for D_e and we obtained 0.744 eV. Adding the Q-correction yielded 0.960 eV. At the dissociation limit, the SDCI + Q treatment gave an excitation energy of 5F which is higher by 0.18 eV than the experimental value due to disregarding contributions from inner core correlation and the relativistic effects. These effects may increase the dissociation energy, because the ground state has $^5F + ^5F$ character at the equilibrium geometry. From these considerations, we may estimate D_e to be 1.32 eV. Experimentally, the long-lived state 10882 cm^{-1} above the ground state suggests that D_e is greater than 1.349 eV [2]. The present result is consistent with experiment.

In Table 2, we summarize spectroscopic constants along with available experimental values. The present vibrational constants are smaller than the previous theoretical values and the experimental ones. The present calculations show irregularities just outside the equilibrium region. This may have influence on the spectroscopic constants.

4. Summary

We have investigated the Ti dimer with the SA-CASSCF and MRSDCI calculations. Although SA-CASSCF failed to give the stable

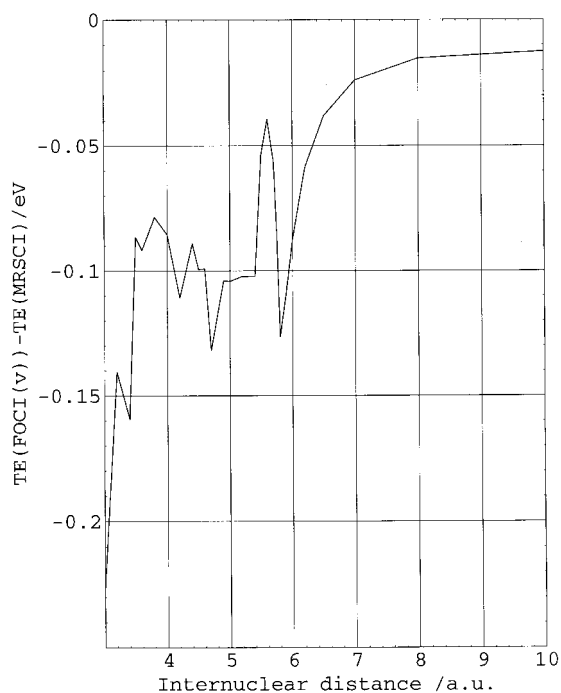


Fig. 4. Effects of single excitations from 4s and 3d in SA-CAS space. We estimated this subtracting the total energy (TE) given by MRSDCI, where the double excitations to the external space were excluded from the MRSDCI, from TE given by FOCI where the references are SA-CAS space; $TE(FOCI(SA-CAS)) - TE(MRSDCI)$ is plotted against R .

molecule relative to the atomic ground state of ${}^3F + {}^3F$, the potential energy curve for the ground state has a deep local minimum followed with a high hump. The electronic configuration for the ground state is $3d\sigma_g 3d\pi_u^4 3d\delta_g 4s\sigma_g^2$ for $R < 4.5$ a.u. including the minimum, is $3d\pi_g 3d\pi_u 3d\delta_g 3d\delta_u 4s\sigma_g^2 4s\sigma_u$ for $4.5 < R < 5.5$ a.u. including the waved hump, and is $3d\sigma_g 3d\pi_u^2 3d\delta_g 4s\sigma_g^2 4s\sigma_u^2$ for $R > 5.5$ a.u. correlating to ${}^3F + {}^3F$. The first MRSDCI solution for the ground state holds the characteristics of the MCSCF wave function and has a positive dissociation energy of 0.51 eV, and it becomes 0.96 eV after some corrections were added. The value is reasonably close to estimated experimental D_e of 1.35 eV. The calculated equilibrium internuclear distance is 3.96 a.u., compared with experimental value of 3.67 a.u. The potential energy curve for the ground state obtained with Davidson correction has one deep and two shallow minima segregated by a deep and

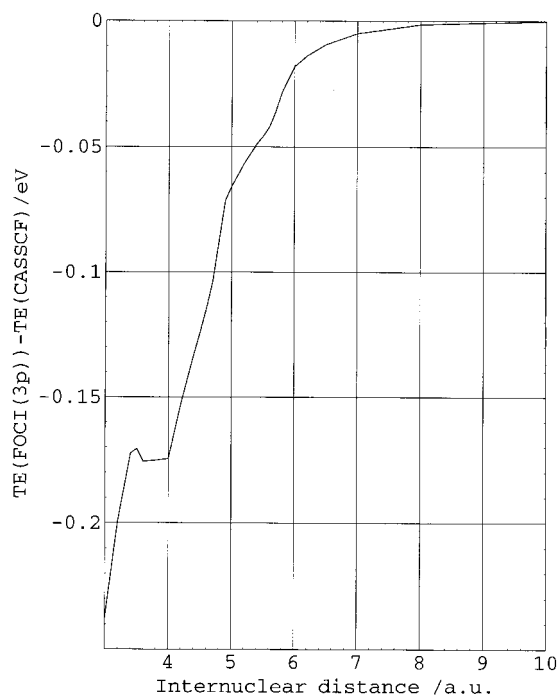


Fig. 5. Effects of single excitations from 3p in SA-CAS space. We estimated this subtracting the SA-CAS total energy ($TE(SA-CAS)$) from TE given by FOCI where the references are SA-CAS and active electrons are only 3p; $TE(FOCI(3p)) - TE(SA-CAS)$ is plotted against R .

narrow barrier and a low and wide barrier. We have some doubt on the second minimum; we suspect that the insufficiency of the reference

Table 2
Spectroscopic constants for the ground state of Ti_2

	ω_e/cm^{-1}	R_e/a_0	D_e/eV
SA-CASSCF	591	3.622	-0.053
MRSDCI	489	3.770	0.514
+ Δ_v^a	435	3.766	0.572
+ Δ_{3p}^b	419	3.771	0.744
+Q	320	3.961	0.960
MRSDCI ^c	404	3.719	(0.79) ^d
+Q ^c	373	3.769	—
Exp.	407.9 ^e	3.67006 ^f	$\geq 1.349^f$

^a $\Delta_v = TE(FOCI) - TE(MRSDCI)$.

^b $\Delta_{3p} = TE(FOCI(3p)) - TE(SA-CAS)$.

^cRef. [1].

^d D_e for ${}^7\Sigma_u^+$ by ACPF.

^eRef. [12].

^fRef. [2].

configurations in this region triggers this minimum. We, however, believe that there exists at least one hump which probably causes the irregularities. This hypothesis could be tested if the higher vibrational levels could be more closely investigated experimentally.

Acknowledgements

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