

5-1995

Molecular and Electronic Structure of TiH₂

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Abstract

Ab initio electronic structure calculations using correlated wave functions have been performed to investigate the structure and energetics of TiH₂ in its low-lying electronic states. Several triplet states have been found to lie very close to each other in energy (within 5 kcal/mol) and nearly 1 eV below the lowest singlet state. The lowest quintet states appear to be considerably higher in energy. The ground state of TiH₂ is found to be bent ³B₁ in C_{2v} symmetry, with the ³A₁ state lying only 1 kcal/mol higher in energy. The lowest singlet state, ¹A₁, is found to be slightly bent, but with a very flat potential energy surface. The Ti–H bond in all TiH₂ electronic states is predicted to be strongly polarized Ti⁺H⁻. The use of state-averaged multiconfigurational self-consistent field wave functions is essential to obtain a consistent picture of all electronic states of interest.

Keywords

Wave functions, *Ab initio* electronic structure calculations, Electronic structure, Ground states, Potential energy surfaces

Disciplines

Chemistry

Comments

The following article appeared in *Journal of Chemical Physics* 102 (1995): 6806 and may be found at <http://dx.doi.org/10.1063/1.469152>.

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Citation: *The Journal of Chemical Physics* **102**, 6806 (1995); doi: 10.1063/1.469152

View online: <http://dx.doi.org/10.1063/1.469152>

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Molecular and electronic structure of TiH₂

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(Received 17 November 1994; accepted 26 January 1995)

Ab initio electronic structure calculations using correlated wave functions have been performed to investigate the structure and energetics of TiH₂ in its low-lying electronic states. Several triplet states have been found to lie very close to each other in energy (within 5 kcal/mol) and nearly 1 eV below the lowest singlet state. The lowest quintet states appear to be considerably higher in energy. The ground state of TiH₂ is found to be bent ³B₁ in C_{2v} symmetry, with the ³A₁ state lying only 1 kcal/mol higher in energy. The lowest singlet state, ¹A₁, is found to be slightly bent, but with a very flat potential energy surface. The Ti–H bond in all TiH₂ electronic states is predicted to be strongly polarized Ti⁺H[−]. The use of state-averaged multiconfigurational self-consistent field wave functions is essential to obtain a consistent picture of all electronic states of interest. © 1995 American Institute of Physics.

I. INTRODUCTION

TiH₂ is the prototypical divalent titanium compound, so it is important to accurately determine the structure and energetics of the low-lying manifold of electronic states for this species. This is particularly important in view of the important role of divalent titanium species as catalysts for such reactions as the hydrosilation reaction.¹ A few previous calculations have been performed on TiH₂. The band structure of TiH₂ has been studied using the augmented-plane wave (APW) method.² There have, in addition, been three *ab initio* electronic structure calculations on TiH₂. Demuyneck and Schaefer³ performed limited singles and doubles configuration interaction (CISD) calculations using a triple zeta +polarization (TZP) basis set on the ³A₁ state in C_{2v} symmetry. This state was predicted to be linear, albeit with a very flat bend potential. Tyrrell and Youakim^{4,5} performed Hartree–Fock calculations on the ³B₁ and ³A₁ states of TiH₂, using both all-electron and effective core potential (ECP) wave functions, and predict both states to be bent. Experimentally, Xiao *et al.* recently assigned the IR frequencies for TiH₂ based on a study of the reaction of molecular hydrogen with titanium in Kr and Ar matrices at 12 K.⁶ These authors predicted TiH₂ to be bent. Since it appears that the most stable molecular and electronic structures of this important molecule have still not been clearly established, a detailed, definitive theoretical study on TiH₂ is needed to provide essential insights into the nature of this species.⁷

In the present paper, we report the results of *ab initio* electronic structure calculations on the molecular and electronic structures in low-lying singlet and triplet spin states of TiH₂ using complete active space self-consistent field (CASSCF) wave functions augmented by multireference methods. Our primary concerns are to determine (1) the ground electronic state of TiH₂, and (2) the molecular structure of TiH₂ (linear or bent structure). Therefore, the geometry and energy order are emphasized throughout this paper.

II. COMPUTATIONAL METHODS

All geometries of TiH₂ in this study were first optimized at the CASSCF level of theory, using the GAMESS program.⁸ The CASSCF active space is summarized in Table I, where the notation (*m/n*) means *m* electrons and *n* orbitals are included in the active space. The C_∞ axis of the linear structure corresponds to the Z axis, while in the bent structure the Y axis is the C₂ axis and the X axis is perpendicular to the TiH₂ molecular plane. As seen from Table I, the 11 orbitals in the (6/11) active space are more than the full valence complement of Ti 4*s*, Ti 3*d*, and H 1*s*. Preliminary calculations suggested that the 4*p* orbitals on Ti play an important role in determining the order of the low-lying triplet linear states, although the effect of these orbitals on the geometries is relatively small. For this reason, these Ti 4*p* orbitals are included in the active space.

Because several electronic states that may be in a small energy range are of interest here, state-averaged CASSCF (SA-CASSCF) wave functions^{9–13} have been employed in this work to provide a consistent treatment of excited states and radiative transitions, and to prevent variational collapse (root flipping). These SA-CASSCF calculations have been performed using the MOLPRO program.¹⁴ The active space used in the SA-CASSCF is the same (6/11) as discussed above for the CASSCF calculations. The stability of relative SA-CASSCF energies has been verified by adding additional, higher-lying, states to the set being averaged. This has a negligible effect on the relative energies of the lower states. Starting from the SA-CASSCF wave functions, final energies were estimated by performing multireference configuration interaction (MRCI)^{15–19} calculations (again using MOLPRO) in order to account for the effects of dynamic correlation.

For all of the aforementioned calculations, a triple-zeta valence basis set has been used. For Ti, the Wachters original Gaussian basis set (14*s*,11*p*,6*d*)²⁰ contracted to [10*s*,8*p*,3*d*] with some modification^{8,21} was used, while a contracted Gaussian basis set (5*s*)/[3*s*] augmented with a set of *p*-type functions ($\alpha_p=1.0$) was employed for H. In the GAMESS calculations, sets of 6*d* orbitals have been used, while 5*d* orbitals were used with MOLPRO.

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TABLE I. Active space used for the CASSCF and MRCI calculations on TiH₂.

| TiH ₂ | Orbital included | Size ^a |
|----------------------------------|---|-------------------|
| Linear (<i>D_{∞h}</i>) | 4σ _g (Ti-H), 3σ _u (H---H*), 1δ _g +(Ti 3d _{x²-y²), 1δ_g-(Ti 3d_{xy}), 1π_g+(Ti 3d_{xz}), 1π_g-(Ti 3d_{yz}), 5σ_g(Ti 3d_z²), 6σ_g(Ti 4s), 3π_u+(Ti 4p_x), 3π_u-(Ti 4p_y), 4σ_u(Ti 4p_z)} | (6/11) |
| Bent (<i>C_{2v}</i>) | 6a ₁ (Ti-H), 3b ₂ (H---H*), 7a ₁ (Ti 3d _{x²-y²), 3b₁(Ti 3d_{xy}), 3a₂(Ti 3d_{xz}), 4b₂(Ti 3d_{yz}), 8a₁(Ti 3d_z²), 9a₁(Ti 4s), 4b₁(Ti 4p_x), 10a₁(4p_y), 5b₂(Ti 4p_z)} | (6/11) |

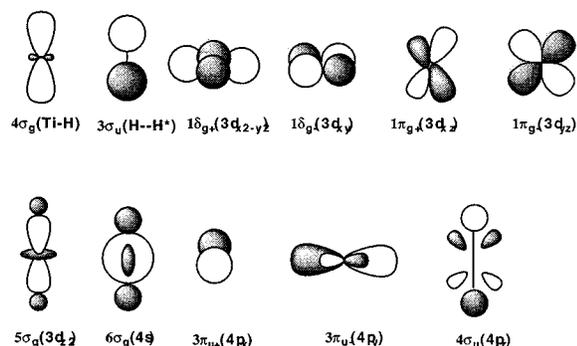
^aThe notation (*m/n*) denotes *m* electrons and *n* orbitals in the active space.

III. RESULTS AND DISCUSSION

A. Linear structures

1. Preliminary considerations

Before discussing the geometries and energies, we present schematic pictures of the orbitals involved in the active space:



There are five Ti 3*d* orbitals that are quite localized, but 5σ_g(3*d*_z²) has significant contributions from the H 1*s* orbitals. Such 1*s* orbital mixing is also seen in 6σ_g(4*s*) and 4σ_u(4*p*_z). On the other hand, the Ti 3*d*_z² orbital makes only a small contribution to 4σ_g(Ti-H), and Ti 4*p*_z contributes to 3σ_u(H---H*).

A preliminary estimate of the energy ordering and splittings was obtained with SA-CASSCF(6/11) calculations on the seven lowest states in both the singlet and triplet manifolds, as well as five quintet states. In keeping with the previous theoretical studies,³⁻⁵ we fixed the Ti-H bond length at 1.880 Å. The results are summarized in Table II, where it is seen that the triplet states are the most stable, while the quintet states are the least stable among the spin states. This is in contrast to the prediction that the heavier analogues, ZrH₂²² and HfH₂²³ have singlet ground states. The singlet, triplet, and quintet manifolds are well separated in energy at the SA-CASSCF level of theory (e.g., the lowest singlet state is ~1 eV higher than the lowest triplet state). However, the four lowest triplet states all lie within a 4 kcal/mol range. The vertical quintet states of TiH₂ lie considerably higher in energy than the lower spin states, so the remainder of this work is focused on the lower energy singlet and triplet states.

The electronic configurations are also listed in Table II. The most stable singlet and triplet electronic states are ¹Σ_g⁺

TABLE II. Total (hartree) and relative (kcal/mol) SA-CASSCF(6/11) energies and electronic configurations of linear TiH₂ in singlet, triplet, and quintet spin states. The numbers of averaged states are seven (singlet and triplet) and five (quintet). The Ti-H length is fixed at 1.880 Å in all cases.

| State | <i>E</i> _{tot} | <i>E</i> _{rel} | Configuration ^a and weight (%) |
|--|-------------------------|-------------------------|---|
| ¹ Σ _g ⁺ | -849.522 01 | 22.8 | 4σ _g ² 3σ _u ² 1δ _g ² ₊ (32), 4σ _g ² 3σ _u ² 1δ _g ² ₋ (32), 4σ _g ² 3σ _u ² 5σ _g ² (23), 4σ _g ² 3σ _u ² 1π _g ² ₊ (5), 4σ _g ² 3σ _u ² 1π _g ² ₋ (5) |
| ¹ Π _g | -849.515 00 | 27.2 | 4σ _g ² 3σ _u ² 1δ _g ² ₊ +1π _g ² ₊ (41), 4σ _g ² 3σ _u ² 1δ _g ² ₋ +1π _g ² ₋ (41), 4σ _g ² 3σ _u ² 1π _g ² ₊ +5σ _g ² (14) |
| ¹ Γ _g | -849.506 16 | 32.7 | 4σ _g ² 3σ _u ² 1δ _g ² ₊ (48), 4σ _g ² 3σ _u ² 1δ _g ² ₋ (48) |
| ¹ Δ _g | -849.503 48 | 34.4 | 4σ _g ² 3σ _u ² 1δ _g ² ₊ +5σ _g ² (85), 4σ _g ² 3σ _u ² 1π _g ² ₊ (5), 4σ _g ² 3σ _u ² 1π _g ² ₋ (5) |
| ³ Φ _g | -849.558 30 | 0.0 | 4σ _g ² 3σ _u ² 1δ _g ² ₊ +1π _g ² ₊ (48), 4σ _g ² 3σ _u ² 1δ _g ² ₋ +1π _g ² ₋ (48) |
| ³ Δ _g | -849.556 17 | 1.3 | 4σ _g ² 3σ _u ² 1δ _g ² ₊ +5σ _g ² (96) |
| ³ Σ _g ⁻ | -849.553 14 | 3.2 | 4σ _g ² 3σ _u ² 1δ _g ² ₋ +1π _g ² ₋ (48), 4σ _g ² 3σ _u ² 1π _g ² ₊ +1π _g ² ₋ (48) |
| ³ Π _g | -849.551 86 | 4.0 | 4σ _g ² 3σ _u ² 1δ _g ² ₊ +1π _g ² ₊ (35), 4σ _g ² 3σ _u ² 1δ _g ² ₋ +1π _g ² ₋ (35), 4σ _g ² 3σ _u ² 1π _g ² ₊ +5σ _g ² (27) |
| ⁵ Φ _u | -849.451 27 | 67.2 | 4σ _g ² 3σ _u ² 5σ _g ² 1δ _g ² ₋ +1π _g ² ₋ (46), 4σ _g ² 3σ _u ² 5σ _g ² 1δ _g ² ₊ +1π _g ² ₊ (46), 4σ _g ² 3σ _u ² 5σ _g ² 1δ _g ² ₋ +1π _g ² ₋ +6σ _g ² (1), 4σ _g ² 3σ _u ² 5σ _g ² 1δ _g ² ₊ +1π _g ² ₊ +6σ _g ² (1) |
| ⁵ Σ _u ⁻ | -849.446 72 | 70.0 | 4σ _g ² 3σ _u ² 5σ _g ² 1π _g ² ₊ +1π _g ² ₋ (53), 4σ _g ² 3σ _u ² 5σ _g ² 1δ _g ² ₊ +1δ _g ² ₋ (39) 4σ _g ² 3σ _u ² 5σ _g ² 1π _g ² ₋ +1π _g ² ₊ +6σ _g ² (1), 4σ _g ² 3σ _u ² 5σ _g ² 1δ _g ² ₊ +1δ _g ² ₋ +6σ _g ² (1) |
| ⁵ Π _u | -849.436 48 | 76.4 | 4σ _g ² 3σ _u ² 5σ _g ² 1δ _g ² ₋ +1π _g ² ₋ (43), 4σ _g ² 3σ _u ² 5σ _g ² 1δ _g ² ₊ +1π _g ² ₊ (43), 4σ _g ² 3σ _u ² 1δ _g ² ₊ +1δ _g ² ₋ +1π _g ² ₋ (6), 4σ _g ² 3σ _u ² 5σ _g ² 1δ _g ² ₋ +1π _g ² ₋ +6σ _g ² (1), 4σ _g ² 3σ _u ² 5σ _g ² 1δ _g ² ₊ +1π _g ² ₊ +6σ _g ² (1) |

^aOnly one configuration is indicated for degenerate states and the different combinations of spins [e.g., α(1)β(2), or β(1)α(2)] are not distinguished for the singlet states.

and ³Φ_g, respectively. The two outermost valence electrons are distributed among the five Ti *d* orbitals in the ¹Σ_g⁺ state, with three important configurations. The contributions of *d*δ (*d*_{x²-y²} and *d*_{xy}) and *d*π(*d*_{xz} and *d*_{yz}) are important for the ³Φ_g state. It is noteworthy that the two degenerate states in the second triplet (³Δ_g) are dominated by the configuration with one electron each in *d*σ (*d*_z²) and *d*δ. These are essentially identical to the *C*_{2*v*} configurations that dominate the ³A₁ and ³B₁ states examined by Demuyneck and Schaefer³ and Tyrrell and Youakim.^{4,5}

2. Geometries and energies

The SA-CASSCF optimized geometries (obtained using a parabolic fit) are shown in Table III, together with single point MRCI relative energies at the SA-CASSCF geometries. The SA-CASSCF Ti-H bond lengths in all states except ¹Δ_g are in the narrow range 1.90–1.92 Å. The bond length in ¹Δ_g is 0.02 Å shorter. The 1.902 Å bond length predicted for the ³Δ_g state is only a bit longer than the 1.874 Å (Ref. 5) estimated for ³A₁ at the SCF level, reflecting the fact that the leading configurations have large coefficients. At the MRCI level of theory, the four triplet states lie within a 3.5 kcal/mol (0.15 eV) range, with ³Δ_g predicted to be very slightly lower in energy than ³Φ_g. The singlet states are well separated from the triplet manifold, with the lowest singlet state lying

TABLE III. SA-CASSCF geometries (Å) and energies (hartree, kcal/mol) of TiH₂ in various linear states.

| State | R(Ti-H) | SA-CASSCF ^a | | MRCI ^b | |
|--|---------|------------------------|-------------------------|-------------------|-------------|
| | | E | ΔE | E | ΔE |
| ³ Φ _g | 1.920 | -849.558 74 | 0.0 | -849.595 24 | 0.0 |
| ³ Δ _g | 1.902 | -849.556 31 | 1.5 | -849.595 60 | -0.2 |
| ³ Σ _g ⁻ | 1.909 | -849.553 54 | 3.3 | -849.591 13 | 2.6 |
| ³ Π _g | 1.917 | -849.552 24 | 4.1 | -849.589 71 | 3.5 |
| ¹ Σ _g ⁺ | 1.905 | -849.526 39 | 20.3 (0.0) ^c | -849.564 94 | 19.0 (0.0) |
| ¹ Γ _g | 1.907 | -849.514 83 | 27.6 (7.3) | -849.549 03 | 29.0 (10.0) |
| ¹ Π _g | 1.904 | -849.513 50 | 28.4 (8.1) | -849.557 90 | 23.4 (4.4) |
| ¹ Δ _g | 1.877 | -849.503 22 | 34.8 (14.5) | -849.549 38 | 28.8 (9.8) |

^aThese calculations have been done independently for the singlets and triplets, and the number of states (equally averaged) is seven for both spin states.

^bThe MRCI values based on the SA-CASSCF wave functions.

^cThe values in parentheses are the energies relative to ¹Σ_g⁺.

more than 15 kcal/mol (0.65 eV) above the highest of the four triplet states examined. Dynamic correlation does have an appreciable effect within each manifold. The MRCI calculations stabilize ³Δ_g relative to ³Φ_g, reversing the order of these two states relative the SA-CASSCF results. Similarly, all singlet states are preferentially stabilized by MRCI relative to ¹Γ_g, so the ¹Γ_g state is predicted to be the least stable in the singlet manifold considered here.

In summary, the ground state of linear TiH₂ is predicted to be ³Δ_g and the lowest singlet state is ¹Σ_g⁺.

B. Bent structures

1. Overview

For each of the states discussed above, a key question is whether the molecule has a linear or a bent structure. The SA-CASSCF TiH₂ bend potentials at $R=1.880$ Å for singlet and triplet states are shown in Figs. 1(a) and 1(b), respectively. As is seen from these figures, upon bending the H-Ti-H angle, the seven linear singlet states split into three A₁, two B₁, one B₂, and one A₂ states, while the seven triplets split into one A₁, two B₁, two B₂, and two A₂ states. In the singlet manifold, the SA-CASSCF potential energy curve for the most stable ¹A₁ (originating from ¹Σ_g⁺) is extremely flat in the region 140°–180°. While the potential energy curve of ³A₁ (¹Δ_g) has a minimum near 140°, that of ²A₁ (¹Γ_g) is almost parallel to the lowest ¹A₁ state. There is an avoided crossing around 120° between the two ¹B₁ states originating from ¹Γ_g (¹B₁) and ¹Δ_g (²B₁). In this region the weights of the two electronic configurations, $6a_1^2 3b_2^2 7a_1^1 3b_1^1$ and $6a_1^2 3b_2^2 8a_1^1 3b_1^1$, are found to be almost equal. This results in a minimum on the ²B₁ surface at a H-Ti-H angle of 100°, while ¹B₁ has a minimum at a larger angle. In contrast, the potential energies of the lowest ¹B₂ and ¹A₂ states that originate from ¹Π_g increase monotonically as the angle decreases.

In the triplet manifold, it appears that the ³A₁ and ³B₁ states originating from ³Δ_g both have a local minimum near 140°. The potential energy curves of the ³A₂ and ³B₂ states that originate from ³Φ_g have very shallow minima around 160°, while the potential energies of the higher-lying states increase monotonically as the H-Ti-H angle decreases.

2. Geometries and energies

The SA-CASSCF results in Fig. 1 are for a fixed Ti-H bond length. The SA-CASSCF bent C_{2v} structures for both singlet and triplet states, starting from the results in Fig. 1 were obtained using three-point parabolic fits for the Ti-H bond length and H-Ti-H bond angle. The geometries and energies of these structures are collected in Table IV. The originating linear states are ³Δ_g for both ³A₁ and ³B₁, ¹Σ_g⁺ for the lowest ¹A₁, ¹Δ_g for the lowest ¹B₁ and ¹Γ_g for the second ¹B₁. All structures are more stable than the parent

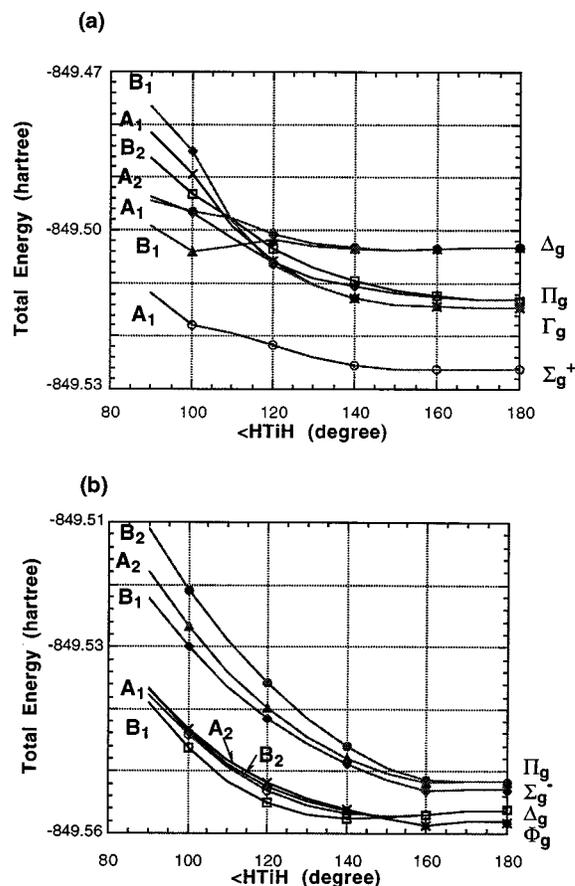


FIG. 1. TiH₂ bend potentials ($D_{\infty h} \rightarrow C_{2v}$) using SA-CASSCF(6/11)/TZVP. (a) Singlets, (b) triplets.

TABLE IV. SA-CASSCF geometries (Å, degree) and energies (hartree) of TiH₂ in bent states.

| State(origin) | R(Ti-H) | A(HTiH) | SA-CASSCF ^a | ΔE^b | MRCI/SA-CASSCF | ΔE^b |
|--|---------|---------|------------------------|--------------|----------------|--------------|
| ³ A ₁ (³ Δ _g) | 1.881 | 150.6 | -849.557 21 | -0.6 | -849.597 93 | -1.5 |
| ³ B ₁ (³ Δ _g) | 1.863 | 140.7 | -849.557 70 | -0.9 | -849.598 82 | -2.0 |
| ¹ A ₁ (¹ Σ _g ⁺) | 1.899 | 168.4 | -849.526 38 | 0.0 | -849.565 47 | -0.3 |
| ¹ A ₁ (¹ Δ _g) | 1.858 | 147.3 | -849.503 91 | -0.4 | -849.552 68 | -2.1 |
| ¹ B ₁ (¹ Δ _g) | 1.785 | 108.2 | -849.509 47 | -3.9 | -849.550 88 | -0.9 |
| ¹ B ₁ (¹ Γ _g) | 1.855 | 152.5 | -849.503 87 | 6.9 | -849.552 29 | -2.0 |

^aThese calculations were done independently for the singlet and triplet manifolds; the number of states averaged is seven for both spin states.

^bEnergy (kcal/mol) relative to the parent linear state.

linear states (Table IV). The H-Ti-H bond angles in all states are estimated to be less than 180°. While the bend angles are smaller in ³A₁ and ³B₁ than in ¹A₁, the triplet surfaces are clearly flatter at the SA-CASSCF level, based on the energy gain due to bending. All six states shown in Table IV are also predicted to be bent at the MRCI level of theory.

While the two C_{2v} components of D_{∞h}(³Δ_g) are both predicted to bend, the ³A₁ state is closer to linear, as predicted by Demuyck and Schaefer³ with a very flat bend potential, while the ³B₁ state appears to be strongly bent.^{4,5} Although the contribution of Ti 3d_{yz}(4b₂) in the electronic configurations of ³A₁ and ³B₁ is small, the bent structure is consistent with the prediction by Tyrrell and Youakim⁵ that a bent structure is expected for transition-metal dihydrides when an empty metal 3d_{yz}(π) orbital and an occupied metal 3d_z²(σ) orbital are present.

In Table V the relative energies of all linear and bent structures are compared at the MRCI/SA-CASSCF level. TiH₂ is predicted to have a bent structure in the triplet ground state (³B₁) and lowest singlet state (¹A₁). However, the potential energy surfaces for bending in these states are extremely flat. At all levels of calculation, ³B₁ is slightly more stable than ³A₁.

TABLE V. MRCI/SA-CASSCF total (hartree) and relative (kcal/mol) energies of TiH₂ in various electronic states.

| State | MRCI ^a | |
|--|-------------------|-------------------------|
| | E | ΔE |
| ³ Δ _g | -849.595 60 | 0.0 |
| ³ Φ _g | -849.595 24 | 0.2 |
| ³ Σ _g ⁻ | -849.591 13 | 2.8 |
| ³ Π _g | -849.589 71 | 3.7 |
| ³ A ₁ (³ Δ _g) ^b | -849.597 93 | -1.5 |
| ³ B ₁ (³ Δ _g) | -849.598 82 | -2.0 |
| ¹ Σ _g ⁺ | -849.564 94 | 19.2 (0.0) ^c |
| ¹ Π _g | -849.557 90 | 23.7 (4.4) |
| ¹ Δ _g | -849.549 38 | 29.0 (9.8) |
| ¹ Γ _g | -849.549 03 | 29.2 (10.0) |
| ¹ A ₁ (¹ Σ _g ⁺) | -849.565 47 | 18.9 (-0.3) |
| ¹ A ₁ (¹ Δ _g) | -849.552 68 | 26.9 (7.7) |
| ¹ B ₁ (¹ Γ _g) | -849.552 29 | 27.2 (7.9) |
| ¹ B ₁ (¹ Δ _g) | -849.550 88 | 28.1 (8.8) |

^aThe MRCI values using the SA-CASSCF wave functions.

^bThe original linear state.

^cThe values in parentheses are the energies relative to ¹Σ_g⁺.

It is useful to compare our results for the ³B₁ state using separate CASSCF calculations with the IR spectroscopic experiments in low temperature Kr and Ar matrices.⁷ (Note that this state actually distorts slightly from C_{2v} ³B₁ to C_s ³A'' at this level of theory.) The calculated frequencies (cm⁻¹) are 1481 (sym stretching), 1461 (asym stretching), and 245 (bending). These may be compared with the corresponding values in Kr (Ar) of 1477.9 (1483.2), 1412.1 (1435.5), and 496.1 (376.5) cm⁻¹, respectively. The two predicted stretching frequencies are in excellent agreement with experiment, while the bending frequency is somewhat underestimated. This is not so surprising for a rather flat potential energy surface, where one expects large amplitude motions and significant contributions from anharmonic effects. The calculated H-Ti-H angles are in very good agreement with the estimated experimental angle of 145°±5°.

C. Mulliken populations and dipole moments

In Table VI Mulliken population analyses are collected for several electronic states of TiH₂ obtained from the MRCI/SA-CASSCF natural orbitals. A large amount of electron transfer (~0.7e) is found to occur from Ti to the hydrogens in every state, indicating the Ti-H bond in TiH₂ is quite ionic (Ti^{δ+}-H^{δ-}). Also noteworthy is the significant reduction of Ti 4s population and the large Ti 4p population, compared to what one would expect from the formal s²d² electronic configuration of the ground state of the Ti atom. It is found that more than 0.5 electron resides in 4p in each electronic state. This suggests that the electron transfer from Ti to H occurs mainly from the Ti 4s orbital.

In order to estimate the contribution of the Ti in-plane 3dπ orbital to the bent structures, the populations of the 4b₂ orbital for several bent structures were calculated. The calculated values of 0.113 (³A₁), 0.184 (³B₁), 0.110 [¹A₁(¹Σ_g⁺)], and 0.510 [¹B₁(¹Δ_g)] indicate that as the bond angle decreases, the population of the Ti 3dπ increases, as expected.

The calculated dipole moments are listed in Table VII. The dipole moment in ¹A₁ (0.953 D) is slightly larger than the previous theoretical values of 0.738 D for ZrH₂²² and 0.31 D for HfH₂,²³ suggesting the polarity of the group IV metal-hydrogen decreases as one descends the periodic table. The dipole moment in the ³B₁ ground state is almost three times larger than that in ¹A₁.

TABLE VI. Mulliken population analyses for TiH₂ states.

| State | Gross atomic charge | | | | Net atomic charge | | |
|--|-------------------------------|--------------------------------|----------------|--------|-------------------|--------|--------|
| | Ti(<i>s</i>) | Ti(<i>p</i>) | Ti(<i>d</i>) | Ti | H | Ti | H |
| ³ Δ _g | 6.681 (0.694) ^a | 12.578 (0.595) ^b | 2.014 | 21.274 | 1.363 | +0.726 | -0.363 |
| ³ Φ _g | 6.488 (0.498) | 12.576 (0.595) | 2.211 | 21.275 | 1.363 | +0.725 | -0.363 |
| ³ Σ _g ⁻ | 6.483 (0.492) | 12.575 (0.594) | 2.217 | 21.275 | 1.362 | +0.725 | -0.362 |
| ³ Π _g | 6.555 (0.566) | 12.586 (0.605) | 2.143 | 21.284 | 1.358 | +0.716 | -0.358 |
| ¹ Σ _g ⁺ | 6.586 (0.596) | 12.575 (0.588) | 2.134 | 21.295 | 1.353 | +0.705 | -0.353 |
| ¹ Π _g | 6.532 (0.540) | 12.591 (0.606) | 2.190 | 21.312 | 1.344 | +0.688 | -0.344 |
| ¹ Γ _g | 6.453 (0.460) | 12.557 (0.571) | 2.281 | 21.291 | 1.354 | +0.709 | -0.354 |
| ¹ Δ _g | 6.664 (0.677) | 12.593 (0.605) | 2.017 | 21.274 | 1.363 | +0.726 | -0.363 |
| ³ A ₁ | 6.687 (0.701) | 12.520 (0.540) | 2.095 | 21.302 | 1.349 | +0.698 | -0.349 |
| ³ B ₁ | 6.684 (0.698) | 12.483 (0.505) | 2.147 | 21.314 | 1.343 | +0.686 | -0.343 |
| ¹ A ₁ (¹ Σ _g ⁺) | 6.580 (0.591) | 12.562 (0.577) | 2.156 | 21.297 | 1.341 | +0.703 | -0.351 |
| ¹ A ₁ (¹ Δ _g) | 6.689 (0.703) | 12.520 (0.539) | 2.107 | 21.317 | 1.342 | +0.683 | -0.342 |
| ¹ B ₁ (¹ Γ _g) | 6.677 (0.690) | 12.536 (0.553) | 2.090 | 21.303 | 1.349 | +0.697 | -0.349 |
| ¹ B ₁ (¹ Δ _g) | 6.694 (0.706) | 12.461 (0.485) | 2.245 | 21.400 | 1.300 | +0.600 | -0.300 |

^aPopulations of Ti 4*s* orbital estimated by summing the populations on the two outermost *s* shells (Refs. 8 and 24).

^bPopulations of the Ti 4*p* orbital estimated by summing the populations on the two outermost *s* shells (Ref. 8).

IV. CONCLUDING REMARKS

Based on MRCI/SA-CASSCF calculations, the ground state of TiH₂ is predicted to be ³B₁ with an H–Ti–H angle of about 140°. The second triplet state, ³A₁, is also predicted to be bent with an angle of about 150°. In view of the flatness of these potential energy surfaces, the predicted angles are likely to have larger than usual error bars, on the order of 10° or more. The two lowest triplets, ³B₁ and ³A₁ are found to be very close in energy (within 1 kcal/mol), with ³B₁ slightly lower. It is quite possible that the order of these two states may be reversed if one could perform a full configuration interaction calculation with larger basis sets. In the singlet manifold, the lowest state (¹A₁) lies 21 kcal/mol above the triplet ground state at the MRCI level of theory. This state

TABLE VII. Dipole moments (Debye) of bent TiH₂ states.

| State | μ ^a |
|---|----------------|
| ³ A ₁ | 2.268 |
| ³ B ₁ | 2.934 |
| ¹ A ₁ (¹ Σ _g ⁺) ^b | 0.953 |
| ¹ A ₁ (¹ Δ _g) | 2.128 |
| ¹ B ₁ (¹ Γ _g) | 1.836 |
| ¹ B ₁ (¹ Δ _g) | 3.255 |

^aPositive polarity indicates Ti⁺H⁻.

^bOriginal linear state.

also prefers a slightly bent structure (H–Ti–H angle ≈ 170°), but since the potential energy surface for bending is predicted to be quite flat, the error in the angle may again be quite large. Based on the results presented here, TiH₂ is expected to easily distort to bent C_{2v} or to antisymmetric C_{∞v} or C_s structures very easily in its low-lying electronic states.

In molecules such as TiH₂, in which multiconfiguration-based wave functions are critical, it is very important to design an underlying MCSCF active space that treats all electronic states in a consistent manner. For this reason, we consider the MRCI/SA-CASSCF wave functions and energies to be the most reliable of those used in the present work. The effect of the state averaging is relatively small for the geometries of TiH₂, but it is found to be important for investigating the energetics of several electronic states that are very close to each other in energy.

More than 0.5 electron resides in the 4*p* orbital in each electronic state of TiH₂, suggesting a significant contribution of Ti 4*p* orbitals for this molecule.

ACKNOWLEDGMENTS

We would like to thank Dr. Michael Schmidt for valuable discussions and Professor Tsuneo Hirano at Ochanomizu University and Keisaku Ishii at the University of Tokyo for their helpful suggestions. This work was supported in

part by a grant from the National Science Foundation (No. CHE-93173317). The calculations described in this work were performed on IBM RS 6000 computers generously provided by Iowa State University.

- ¹T. J. Barton and P. Boudjouk, in *Organosilicon Chemistry—A Brief Overview, Advances in Chemistry*, edited by T. Ziegler (American Chemical Society, Washington, DC, 1990); M. R. Kesti and R. M. Waymouth, *Organometallics* **11**, 1095 (1992); J. F. Harrod, T. Ziegler, and V. Tschinke, *ibid.* **9**, 897 (1990); B. Bode, P. N. Day, and M. S. Gordon (unpublished).
- ²A. Fujimori and N. Tsuda, *Solid State Commun.* **41**, 491 (1982).
- ³J. Demuynck and H. F. Schaefer, *J. Chem. Phys.* **72**, 311 (1980).
- ⁴J. Tyrrell and A. Youakim, *J. Phys. Chem.* **84**, 3568 (1980).
- ⁵J. Tyrrell and A. Youakim, *J. Phys. Chem.* **85**, 3614 (1981).
- ⁶Z. L. Xiao, H. Hauge, and J. L. Margrave, *J. Phys. Chem.* **95**, 2696 (1991).
- ⁷At the August 21–25, 1994 ACS meeting in Washington, DC, B. Ma, B. J. DeLeeuw, and H. F. Schaefer presented a poster “*Ab initio* study of the MH_4 (M=Ti, V and Cr) systems: Tetrahydrides and Dihydrogen Complexes,” in which they find the ground state of TiH_2 to be bent 3B_1 based on CISD optimization, followed by CCSD single point calculations. This is in agreement with our results.
- ⁸GAMESS: M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.* **14**, 1347 (1993).
- ⁹J. Hinze, *J. Chem. Phys.* **59**, 6424 (1973).
- ¹⁰K. Docken and J. Hinze, *J. Chem. Phys.* **47**, 4928 (1972).
- ¹¹C. C. J. Roothaan, J. H. Detrich, and D. G. Hopper, *Int. J. Quantum Chem. Symp.* **13**, 93 (1979).
- ¹²L. M. Cheung, T. S. Elbert, and K. Ruedenberg, *Int. J. Quantum Chem.* **16**, 1069 (1979).
- ¹³H.-J. Werner and W. Meyer, *J. Chem. Phys.* **74**, 5794 (1981); **74**, 5802 (1981).
- ¹⁴MOLPRO: H.-J. Werner and P. J. Knowles, University of Sussez, 1991. See also (a) H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **82**, 5053 (1985); (b) P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **115**, 259 (1985).
- ¹⁵P. J. Knowles and H.-J. Werner, *Theor. Chim. Acta* **84**, 95 (1992).
- ¹⁶H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **89**, 5803 (1988).
- ¹⁷P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **145**, 514 (1988).
- ¹⁸H.-J. Werner and E. A. Reinsh, *J. Chem. Phys.* **76**, 3144 (1982).
- ¹⁹H.-J. Werner, *Adv. Chem. Phys.* **LXIX**, 1 (1987).
- ²⁰A. J. H. Wachters, *J. Chem. Phys.* **52**, 1033 (1970).
- ²¹A. K. Rappe, T. A. Smedley, and W. A. Goddard, *J. Phys. Chem.* **85**, 2607 (1981).
- ²²J. Z. Wang, K. K. Das, and K. Balasubramanian, *Mol. Phys.* **69**, 147 (1990).
- ²³K. K. Das and K. Balasubramanian, *J. Phys. Chem.* **95**, 3979 (1991).