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On the ground state of titanium phosphide, TiP: A theoretical investigation

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Using multireference variational and coupled cluster methods in conjunction with very large core-correlation-consistent basis sets, we have confirmed that the ground state of TiP is of $^2\Sigma^+$ symmetry with the first excited state $A\,^2\Delta$ no more than 3.5 kcal/mol higher. We also report full potential energy curves, dissociation energies, bond lengths, dipole moments, and the usual spectroscopic constants. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1768159]

I. INTRODUCTION

Understanding the bonding of first row transition metal (M) containing compounds is still a challenging task. Even diatomics of the type MX, where X is any atom of the second or third row of the periodic table, seem to defy our modern quantum mechanical weaponry. Very briefly, there are three main reasons of the origin of the many problems encountered in an accurate and detailed theoretical description of such systems. (a) In general, MX are highly open-shell systems, (b) the very high density of M states dictating multireference molecular wave functions, and (c) the perennial correlation problem which becomes particularly nasty in transition metal containing systems, due to the significant importance of the "semicore" $3s^2 3p^6$ electrons of the M atom in the energetics of the MX molecules (see also Ref. 1).

In the present paper we try to pinpoint the ground state symmetry of the titanium phosphide molecule, TiP, using multireference and coupled cluster methods and very large basis sets. It is interesting that no experimental results exist for the entire MP (M=Sc to Cu) series, and only three theoretical studies: one on ScP,[2] one on TiP,[3] and a very recent density functional (B3LYP) study on the MP (M=Sc to Cu) sequence.[4] This latter work was the motivation to reexamine[3] the identity of the ground TiP state, given the existence of the large correlation consistent (cc)-type basis sets for the Ti atom.[5]

In our previous study on TiP using multireference generalized valence bond (GVB) and/or complete active space (CAS) wave functions+single+double replacements [GVB+1+2, CAS+1+2=multireference configuration interaction(MRCI)] and modest size basis sets ($[5s4p3d/_{\mathrm{Ti}}\,5s5p2d/_{\mathrm{P}}]$), we have found that TiP has a ground state of $^2\Sigma^+$ symmetry with a $^2\Delta$ state located 4.9 kcal/mol higher, in both GVB+1+2 and MRCI approximations.[3] However, the recent B3LYP/$[8s7p4d1f/_{\mathrm{Ti}}\,6s5p3d2f/_{\mathrm{P}}]$ calculations of Tong *et al.*[4] predict a $^2\Delta$ ground state with the $^2\Sigma^+$ 1.86 kcal/mol higher.

Presently we focus on the $^2\Sigma^+$ and $^2\Delta$ states. For the Ti atom we employ the core-valence cc-pCV5Z basis set of Bauschlicher[5] ($21s16p9d5f4g3h1i$), while for the P atom the augmented core-valence aug-cc-pCVQZ of Dunning[6] ($20s15p7d5f3g$) was used, both generally contracted to $[(7s8p6d5f4g3h1i)_{\mathrm{Ti}}/(10s9p7d5f3g)_{\mathrm{P}}]$, numbering 178 +134=312 spherical Gaussian functions. The purpose of using this very large basis set carrying core-correlation functions ($3s^2 3p^6/_{\mathrm{Ti}} 2s^2 2p^6/_{\mathrm{P}}$) at all levels of calculation was to eliminate as much as possible the one-electron basis set correlation error and to ensure an overall consistent treatment. Our reference CAS wave functions are generated by distributing seven "valence" (active) electrons ($3d^2 4s^2$ on Ti $+3p^3$ on P) among nine orbitals (one $4s$ and five $3d$ on Ti+three $3p$ on P) under C_{2v} geometrical and axial Σ or Δ constraints. The $3s^2\ e^-$ of P were frozen in the CASSCF procedure for purely technical reasons. The CAS zeroth order functions comprise 1536 and 1488 configuration functions (CF) of $^2A_1(^2\Sigma^+, {}^2\Delta)$ and $^2A_2(^2\Delta)$ symmetries, respectively. The valence MRCI expansions (including now $3s^2\ e^-$ on P) consists of 260×10^6 ($^2A_1$) and 259×10^6 ($^2A_2$) CFs, reduced to about 3.5×10^6 CFs using the internal contraction scheme (ic MRCI) as implemented in the MOLPRO2002 package.[7]

To estimate core-correlation effects stemming in essence from the Ti atom ($3s^2 3p^6$), icMRCI calculations were performed including the Ti $3s^2 3p^6$ core electrons in the CI procedure (C-MRCI). The C-MRCI (icC-MRCI) expansions of $^2A_1$ and $^2A_2$ symmetries contain about 2×10^9 (35.5×10^6) CFs. Our computational resources did not allow the inclusion of the $2s^2 2p^6$ core electrons of P in the configuration interaction calculations (but see below). In addition, the inclusion of the $2s^2 2p^6\ e^-$ would undermine the quality of the multireference wave function due to the dramatic increase of the size-nonextensivity errors.

Larger MRCI calculations were also performed by including the three $4p$ orbitals of Ti in the CASSCF procedure, referred to as L-MRCI. These L-MRCI(icL-MRCI) expansions contain about 1.8×10^9 (27.3×10^6) CFs.

For reasons of comparison we have also performed coupled cluster singles and doubles with perturbative triples calculations, based on restricted valence open shell Hartree-Fock orbitals [RCCSD(T)], and C-RCCSD(T), CC-RCCSD(T) including the core $3s^2 3p^6$ (Ti), and both the core $3s^2 3p^6$ (Ti) and $2s^2 2p^6$ (P) electrons, respectively.

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TABLE I. Absolute energies E (hartree), bond lengths r_e (Å), binding energies D_e (kcal/mol), harmonic frequencies, and anharmonic corrections ω_e, $\omega_e x_e$ (cm^{-1}), rotational vibrational couplings α_e (cm^{-1}), centrifugal distortions $\overline{D}_e$ (cm^{-1}), Mulliken charges on Ti q_{Ti}, dipole moments μ (D), and energy differences T_e (kcal/mol) of the TiP molecule. Literature results are also included.

Methods	$-E$	r_e	D_e	ω_e	$\omega_e x_e$	$\alpha_e(10^{-3})$	$\overline{D}_e(10^{-7})$	$+q_{\mathrm{Ti}}$	$\langle\mu\rangle$[a]	μ_{FF}[b]	T_e
$X\,^2\Sigma^+$											
CASSCF[c]	1189.185 24	2.144	39.0	471.4	3.45	1.33	1.33	0.40	3.41	3.72	0.0
MRCI	1189.368 70	2.118	59.9	508.8	2.64	1.11	1.23	0.44	3.79	4.71	0.0
MRCI+Q[d]	1189.387 7	2.119	61								0.0
ACPF[e]	1189.384 79	2.119	60.0	509.1	2.62	1.11	1.22	0.43	4.09	4.70	0.0
L-CASSCF[c,f]	1189.212 59	2.144	36.3	459.9	1.45	1.31	1.40	0.42	4.10	4.05	0.0
L-MRCI[f]	1189.376 58	2.120	59.3	498.6	2.60	1.22	1.28	0.45	4.21	4.63	0.0
L-MRCI+Q[d,f]	1189.392 9	2.117	63								0.0
C-MRCI[g]	1189.691 60	2.097	63.0	521.6	3.25	1.19	1.24	0.43	3.46	4.85	0.0
C-MRCI+Q[d,g]	1189.753 3	2.095	67								0.0
RCCSD(T)	1189.386 02	2.100	59.3	525.8	3.06	1.11	1.22			4.79	0.0
C-RCCSD(T)[g]	1189.762 92	2.074	65.0	540.1	3.43	1.12	1.24			4.64	0.0
CC-RCCSD(T)[h]	1190.088 60	2.070	65.6	541.3	3.56	1.10	1.25			4.60	0.0
MRCI[i]	1189.234 33	2.158	47	465				0.48	4.4		0.0
B3LYP[j]		2.078	59.7	483					4.55		0.0
$A\,^2\Delta$											
CASSCF[c]	1189.174 51	2.212	31.1	437.1	2.19	1.09	1.28	0.52	5.89	5.75	6.73
MRCI	1189.361 80	2.176	54.6	473.9	2.00	0.984	1.21	0.51	6.21	6.93	4.33
MRCI+Q[d]	1189.381 9	2.178	56								3.6
ACPF[e]	1189.378 68	2.178	55.1	471.1	2.09	0.980	1.22	0.47	6.17	7.04	3.83
L-CASSCF[c,f]	1189.199 94	2.206	27.2	400.7	7.14	2.44	1.54	0.57	7.21	7.24	7.93
L-MRCI[f]	1189.36971	2.183	54.0	460.5	0.27	0.813	1.25	0.52	6.88	6.75	4.31
L-MRCI+Q[d,f]	1189.387 2	2.182	59								3.5
C-MRCI[g]	1189.685 22	2.150	58.7	491.1	1.87	0.967	1.21	0.51	5.91	6.97	4.00
C-MRCI+Q[d,g]	1189.748 0	2.148	64								3.3
RCCSD(T)	1189.381 25	2.168	54.8	478.6	3.00	1.12	1.21			6.93	3.00
C-RCCSD(T)[g]	1189.758 84	2.139	58.8	502.7	2.74	1.05	1.19			6.61	2.56
CC-RCCSD(T)[h]	1190.084 30	2.135	59.20	505.1	4.76	0.961	1.19			6.62	2.69
MRCI[i]	1189.226 59	2.217	42	434				0.45	7.2		4.86
B3LYP[j]		2.139	61.6	454				0.49	6.35		−1.85

[a] Dipole moments obtained as expectation values.

[b] Dipole moments obtained by the finite-field approach.

[c] State averaged over the two states.

[d] $+Q$ refers to the multireference Davidson correction.

[e] Averaged coupled pair functional, Ref. 10.

[f] Active space enlarged by the three $4p$ orbitals of Ti, see text.

[g] The $3s^2 3p^6$ core e^- of Ti are included in the CI procedure.

[h] The Ti $3s^2 3p^6$ and P $2s^2 2p^6$ core electrons are included.

[i] Reference 3.

[j] Reference 4.

For both states, $^2\Sigma^+$ and $^2\Delta$, we have constructed MRCI potential energy curves reporting total energies, bond distances, dissociation energies, usual spectroscopic parameters, and dipole moments. The latter have been obtained either as expectation values ($\langle\mu\rangle$), or using the finite-field approach (μ_{FF}), applying electric fields of about 10^{-4} a.u. along both directions of the internuclear axis and taking the average value.

II. RESULTS AND DISCUSSION

Table I lists our numerical results, while MRCI potential curves of the $^2\Sigma^+$ and $^2\Delta$ states are depicted in Fig. 1. A glance in Table I and Fig. 1 confirms that the ground state of TiP is of $^2\Sigma^+$ symmetry in accord with our previous inference,[3] and at variance with the DFT-B3LYP results of Tong *et al.*[4]

Let us examine now the character of the $X\,^2\Sigma^+$ and $A\,^2\Delta$ wave functions. The dominant equilibrium CASSCF configurations and atomic Mulliken distributions (Ti/P) are

$$|X\,^2\Sigma^+\rangle_{A_1} \approx (\sim|1\sigma^2[(0.83)2\sigma^2 3\sigma^1 + (0.24)2\sigma^1 3\sigma^2]1\pi_x^2 1\pi_y^2\rangle,$$

$$4s^{0.90}4p_z^{0.18}3d_{z^2}^{0.77}3d_{xz}^{0.81}4p_x^{0.05}3d_{yz}^{0.81}4p_y^{0.05}3d_{x^2-y^2}^{0.02} \times 3d_{xy}^{0.02}/3s^{1.95}3p_z^{1.19}3p_x^{1.10}3p_y^{1.10},$$

$$|A\,^2\Delta\rangle_{A_1+A_2} \approx (\sim 0.88|1/\sqrt{2}(1\sigma^2 2\sigma^2 1\pi_x^2 1\pi_y^2) \times (1\delta_+^1 + 1\delta_-^1)\rangle,$$

$$4s^{0.68}4p_z^{0.07}3d_{z^2}^{0.27}3d_{xz}^{0.69}4p_x^{0.04}3d_{yz}^{0.69}4p_y^{0.04} \times (3d_{x^2-y^2}3d_{xy})^{1.00}/3s^{1.93}3p_z^{1.05}3p_x^{1.24}3p_y^{1.24}.$$

Note that our orbital notation refers only to the nine valence electrons, i.e., we do not count the eight σ and six π doubly occupied ‘‘internal’’ orbitals. Pictorially, and consistent with

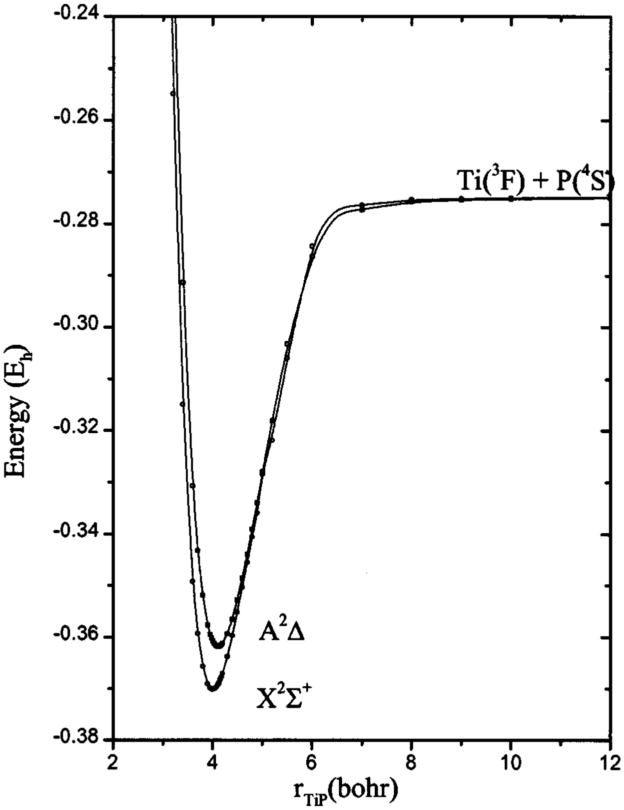
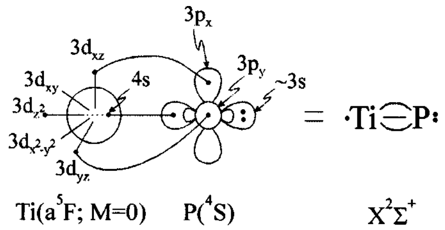
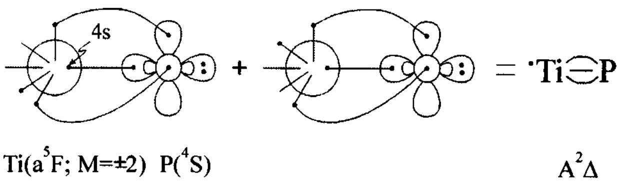


FIG. 1. Potential energy curves of the $X\,^2\Sigma^+$ and $A\,^2\Delta$ states of TiP at the MRCI level. Energies have been shifted by $+1189.0\ E_\mathrm{h}$.

the populations above, the bonding is captured by the following valence-bond-Lewis (vbL) diagrams:





Clearly, in both states the atoms interact through two π and one σ bond forming a genuine triple bond. A total of about 0.4 ($X\,^2\Sigma^+$) and 0.5 e^- ($A\,^2\Delta$) are transferred from Ti to P mainly through the π system in the $A\,^2\Delta$ case. *Both* $X\,^2\Sigma^+$ and $A\,^2\Delta$ states correlate adiabatically to the ground state atoms (Fig. 1), Ti($4s^2 3d^2$; $a\,^3$F)+P(^{4}S), obviously not appropriately "prepared" for a triple bond-like interaction. Indeed, the *in situ a* ^{5}F character of Ti atom 0.806 eV higher than the ground $a\,^3$F term[8] (calculated 0.947 eV at the L-MRCI level), is the result of avoided crossings around 5.2 ($X\,^2\Sigma^+$) and 5.5 bohr ($A\,^2\Delta$), with the corresponding excited states of the same symmetry originating from Ti($a\,^5$F)+P(^{4}S).

From Table I it is observed that at all levels of calculation the $^2\Sigma^+$ is calculated to be the ground state. Specifically, as we move from the (plain) MRCI($+Q$) to L-MRCI ($+Q$) to C-MRCI($+Q$), the $\Delta E(^2\Delta \leftarrow {}^2\Sigma^+)$ separation becomes 4.33(3.6), 4.31(3.5), and 4.00(3.3) kcal/mol, respectively, practically independent of the calculational level. Similar results are obtained at the R-CCSD(T), C-RCCSD(T), and CC-RCCSD(T) level being, 3.00, 2.56, and 2.69 kcal/mol, respectively. Hence it is rather certain that $^2\Sigma^+$ is the ground state of TiP with the first excited $A\,^2\Delta$ state bracketed between 3.5 and 2.5 kcal/mol higher. The C-MRCI+Q binding energy of the $X\,^2\Sigma^+$ (D_e) is close to 67 kcal/mol with slightly smaller values at the C-RCCSD(T), CC-RCCSD(T) levels, at r_e=2.095, 2.074, and 2.070 Å, respectively. Corresponding r_e values for the $A\,^2\Delta$ state are 2.148, 2.139, and 2.135 Å.

Considering the complexity of the TiP system, it is fair to say that the DFT-B3LYP results are surprisingly good:[4] $\Delta E(^2\Delta \leftarrow {}^2\Sigma^+) = -1.85$ kcal/mol, D_e= 59.7 kcal/mol ($^2\Sigma^+$), and r_e=2.078 ($^2\Sigma^+$) and 2.139 Å ($^2\Delta$).

A final comment is needed for the dipole moments. Assuming that finite-field dipole moment values (μ_FF) are more reliable (see also Ref. 9), what is interesting is the significant difference between the dipole moments of $X\,^2\Sigma^+$ and $A\,^2\Delta$ states, the latter's being larger by about 2 D (Table I). This large difference can be attributed mainly to the symmetry carrying $\sigma(d_{z^2})$ e^- distributed on the back and away from the Ti atom in the $X\,^2\Sigma^+$ state, as opposed to the $\delta(d_{xy}, d_{x^2-y^2})$ e^- distribution of the $A\,^2\Delta$ state the centroid of which is essentially at the Ti atom.[3]

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