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The electronic structure of Ti$_2$ and Ti$_2^{+}$

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The Ti$_2$ and Ti$_2^{+}$ molecular systems have been studied through multireference variational and single reference coupled-cluster methods coupled with large basis sets. Potential energy curves have been constructed for 30 (Ti$_2$) and 2 (Ti$_2^{+}$) states and the usual spectroscopic parameters have been extracted. The main feature of the potential curves is the existence of van der Waals minima (Ti$_2$) around 7 bohr irrespective of the molecular symmetry, and 4s$^2$–4s$^1$ interactions (Ti$_2^{+}$) around 6 bohr. Numerous avoided crossings lead to stronger covalent bonds emanating from 4s$^1$–4s$^1$ atomic distributions. The X-state of the neutral species is formally a $3\Delta_g$ state with the first excited state lying within 1 kcal/mol. The removal of the symmetry defining e$^-$ leads to the X$^2\Sigma^+_g$ state of Ti$_2^{+}$.


I. INTRODUCTION

The purpose of the present study is to paint a comprehensive picture on the electronic structure and bonding of the Ti$_2$ and Ti$_2^{+}$ molecules. The severe computational and conceptual difficulties of the 3d–transition metal (M) containing compounds and, in particular, of the M$_2$ systems are well known (Refs. 1 and 2); but see also below.

The first experimental observation on Ti$_2$ was reported almost half a century ago by Kant and Strauss, via a combination of Knudsen equilibrium effusion techniques with mass-spectrometric analysis at high temperatures. By assuming an electronic state of $^1\Sigma$ symmetry, a bond distance twice the Pauling radius of Ti, and a harmonic frequency 1.25 times the Debye frequency of the element (ω = 331 cm$^{-1}$), an upper limit to the dissociation energy was obtained, D$_0^0$ < 52 kcal/mol. Five years later, Kant and Lin assuming as well a $^1\Sigma$ ground state gave a new set of indirectly obtained experimental values: r$_D$ = 2.65 Å, ω = 288 cm$^{-1}$ (using Bader’s rule), and D$_0^0$ = 28.3 ± 4 or 32.8 ± 5 kcal/mol depending on the approach followed, i.e., the second or third law, respectively. By considering a $^2\Delta$(2$\Sigma$) ground state the third law D$_0^0$ value becomes 32.8 ± 5 (36.7 ± 5) kcal/mol. Using resonance Raman spectroscopy in Ar matrices, Cossé et al. reported the harmonic and anharmonic frequencies of Ti$_2$, ω$_o$ = 407.9 and ω$_{x_0}$ = 1.08 cm$^{-1}$.

Bier et al. recalculated the dissociation energy of Ti$_2$ by employing more accurate r$_e$ and ω$_o$ values using the experimental results of Ref. 3. They obtained D$_0^0$ = 33.9, 48.4, or 24.2 kcal/mol depending on the approach used, i.e., the second-law, the third-law, or the Leroy–Bernstein method, respectively, a set of quite different values in conflict also with previously reported D$_0^0$ results; see also Ref. 8.

Through “mass-resolved resonant two photon ionization spectroscopy in a jet-cooled molecular beam (R2PI),” and assuming a $3\Delta_g$ ground state as suggested by theoretical calculations by Bauschlicher et al., Doverstål et al. were able to assign the observed rotational lines as the 0–0 band of the $^3\Pi_{0u}$ ← $^X^3\Delta_{1g}$ transition of Ti$_2$. They obtained r$_D$($^3\Delta_g$) = 1.9422 ± 0.0008 Å, r$_D$(3$\Pi_u$) = 1.997 ± 0.009 Å, ΔG$_{1/2}^0$ = 394.14 cm$^{-1}$, and D$_0^0$ ≥ 1.349 eV (=31.1 kcal/mol). In addition, based on the latter D$_0^0$ value and an approximate value of the ionization energy (IE) of Ti$_2$, IE = 6.125 eV, they estimated a lower limit of the dissociation energy of Ti$_2^{+}$, D$_0^0$ ≥ 2.052 eV. This value is consistent with an experimental D$_0^0$(Ti$_2^{+}$) result of 2.37 ± 0.07 eV measured by Armentrout and co-workers. In 1991, Russon et al. obtained an accurate dissociation energy of Ti$_2^{+}$, D$_0^0$ = 2.435 ± 0.002 eV (=56.15 ± 0.05 kcal/mol). The latter value combined with a better estimate of the ionization energy of Ti$_2$, IE = 5.93 ± 0.19 eV, gives D$_0^0$(Ti$_2^{+}$) = 1.54 ± 0.19 eV (=35.5 ± 4.4 kcal/mol). Three years later Doverstål et al. through the R2PI method extracted spectroscopic parameters for an upper $^3\Delta_u$ state, namely, r$_D$ = 0.2405(14) Å, T($^3\Delta_u$ ← X) = 9029.91(1) cm$^{-1}$, and A(spin-orbit constant) = 38.79 cm$^{-1}$. Recently, Himmel and Bihlmeyer employing UV–visible and resonance Raman spectra of Ti$_2$ in noble gas matrices, reported D$_e$(D$_0^0$) = 27.2 (26.6) kcal/mol, considerably lower than the 35.5 ± 4.4 kcal/mol of Russon et al. Finally, Hübner et al. in a combined experimental (visible absorption spectroscopy)–theoretical work, gave experimental ω$_o$, ω$_{x_0}$, and T$_e$ values for the upper $^1\Pi_u$, $^3\Phi_u$, $^2\Pi_u$, and $^2\Phi_u$ states of Ti$_2^{+}$.

The first non-empirical calculations on the 3d–M$_2$ (M = Sc–Cu) series at the Hartree–Fock level were done by Wolf and Schmidtke, who reported r$_e$($^1\Sigma_g^+$) = 1.87 Å and ω$_e$ = 580 cm$^{-1}$ for the Ti$_2$ dimer. A few years later, Walch and Bauschlicher performed multireference configuration interaction (MRCI) calculations on Ti$_2$. In 1991, Bauschlicher et al. reinvestigated the Ti$_2$ molecule; they examined four states $^3\Sigma^+_u$, $^1\Sigma^+_g$, $^3\Delta_g$, and $^3\Sigma^+_g$ by valence MRCI and AC柏 (averaged coupled pair functional)/[66p9d4f2/1g] methods. Core correlation effects of the 3f$^3$3p$^6$ subvalence electrons were estimated through MCPF (modified coupled
The present work is performed through the Davidson (vide supra) corrections. All calculations were done through single and double excitations out of the reference spaces. Core-valence (3\(s^2\)) effects at the CI level were unfeasible due to the ensuing sizes. The size of the valence (\(\text{ic}\)) MRCI expansions range from \(\sim 4.5 \times 10^6\) (quintets) to \(9.5 \times 10^6\) (triplets) configuration functions. Size non-extensivity errors estimated to be less than 10 m\(e_{\text{h}}\) were accounted for through the Davidson (+Q) correction.\(\text{Fe}^{3+}\) states \(3\Delta_g\), \(1\Sigma_g^+, 7\Sigma_u^+, \) and \(3\Sigma_u^+\) were also examined at the valence and core-valence (3\(s^2\)) coupled-cluster level of theory, RCCSD(T)/QC\(\xi\), and C-RCCSD(T)/QC\(\xi\) respectively. Scalar relativity was taken into account through the second order Douglas–Kroll–Hess (DKH2) approximation.\(\text{Fe}^{3+}\) calculations were performed by the MOLPRO program.\(\text{Fe}^{3+}\) III. THE COMPLEXITY OF THE Ti2 MOLECULE

Although \(3d-M_2\) dimers are chemically “naive” systems, that is, diatomic molecules with a rather small number of electrons, the combined orbital and spin angular momenta give rise to incomodically complex electronic molecular distributions defying all current computational methods.\(\text{Fe}^{3+}\) The Ti2 molecule with 8 outer (4\(s\)^2\(d^2\) \times 2) and 16 subvalence (3\(s^2\)) \(3\Sigma^+\) \times 2) electrons, is a most characteristic case. For instance, within an energy range of 13 000 cm\(^{-1}\) (1.612 eV) there are 6 atomic 25\(s^1\)L Ti terms, namely, a\(^1\)F(4\(s^2\)3\(d^2\)), a\(^3\)F(4\(s^2\)3\(d^2\)), a\(^1\)D(4\(s^2\)3\(d^2\)), a\(^3\)P(4\(s^2\)3\(d^2\)), b\(^1\)F(4\(s^2\)3\(d^2\)), and a\(^1\)G(4\(s^2\)3\(d^2\)).\(\text{Fe}^{3+}\) Starting from the energetically lowest asymptote a\(^1\)F + a\(^3\)F and up to a\(^1\)F + a\(^1\)F asymptote there are 7 dissociating channels [a\(^1\)F + (a\(^1\)F, a\(^3\)F, a\(^1\)D, a\(^3\)P, b\(^1\)F, a\(^1\)G)] resulting overall to 762 (4984) \(|\Delta\Sigma\rangle \langle \Omega\rangle\) molecular Ti2 states, a real challenge for every existing method of solving the eigenvalue Schrödinger equation. Considering that the energy range of molecular Ti2 states is more-or-less the same with the asymptotic energy range \(\Delta E \sim 13 000 \text{ cm}^{-1}\), the mean energy separation per state is \(\sim 13 000/762 = 17 (|\Delta\Sigma\rangle)\) or 13 000/4984 = 2.6 (|\(\Omega\rangle\)) cm\(^{-1}\). The symmetries of all 762 \(|\Delta\Sigma\rangle\) states resulting from the 7 channels, a\(^1\)F + (a\(^1\)F, a\(^3\)F, a\(^1\)D, a\(^3\)P, b\(^1\)F, a\(^1\)G) are (singlets to nonets)\(\Sigma^\pm, \Pi, \Delta, \Phi, \Gamma, H, I, K\)\text{g,w}. Therefore, it is obvious that obtaining either experimental or theoretical
reliable results for a Ti_{2}+ like system is an arduous task indeed. Even the concept of the ground state seems to lose its physical meaning in an almost continuous manifold of states.

Presently, we have constructed PECs for 30 states at the MRCl+Q/Qx level, 10 singlets 1(Σ←−gs, Π←−gs, Λ←−gs, Φ←−g, Γ←−g), 13 triplets 3(Σ←−gt, Σ←−gt, Π←−gt, Π←−gt, Λ←−gt, Φ←−g, Φ←−g, Γ←−gt, H←−g, 6 quintets 5(Π←−g, Π←−g, Φ←−g, H←−g, H←−g), and one seplet 2(Σ←−gs, Δ←−g) for the Ti_{2}+ cation.

All examined states but the 7Σ←−gs correlate adiabatically to the ground state atoms (a^2F + a^2F), whereas the 7Σ←−gs correlates to a^2F + a^2F. It is interesting to mention that the two lowest and practically degenerate states according to the present work, 3Δ←−g and 1Σ←−gs, correlate diabatically to two excited a^2F Ti atoms (vide infra).

IV. RESULTS AND DISCUSSION

A. Ti_{2}

Table I lists numerical results of the first four states of Ti_{2} in a variety of methods, whereas Table II collects results for 26 higher states at the MRCl+Q/Qx level; Figures 1 and 2 display MRCl+Q/Qx PECs and a relative energy level diagram of the 30 states presently examined. Between “infinity” (=12 bohr) and the repulsive part of the PECs we can distinguish three interacting regions: a van der Waals (vdW) around 7.0 boh, a very “messy” one between 7 and 5 boh, and the equilibrium region between 4.7 and 3.6 boh. The vdW PECs originate from the a^2F(4s^23d^2) + a^2F(4s^23d^2) channel, with interactions ranging from 8.0(1Γ←−g) to 4.0(2Σ←−gs) mE_{h}. The number of vdW states shown in Figure 1 is 24 (12 singlets, 6 triplets,
TABLE II. Bond distances $r_e$(Å), dissociation energies $D_e$(kcal/mol), harmonic frequencies $\omega_e$(cm$^{-1}$), and energy separations $T_e$(kcal/mol) of 26 higher states of Ti$_2$ at the MRCI+Q/Qζ level of theory.

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<th>State</th>
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<th>$D_e$</th>
<th>$\omega_e$</th>
<th>$T_e$</th>
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<td>238</td>
<td>26.02</td>
</tr>
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</table>

$^a$With respect to adiabatic ($a^3F + a^5F$) ground state [adiabatic] atoms.

$^b$With respect to diabatic atoms $a^3F + a^5F$.

$^c$MRCI + s.r. + Q.

$^d$C–MRCI + Q.

$^e$MRCI + Q.

$^f$r$_e$ values are calculated indirectly by the present authors according to the relation $r_e = r(X^3\Lambda_g)^{10} + \Delta r_e$, where $\Delta r_e$ are experimentally determined values in Ref. 15.

$^g$With respect to diabatic atoms $a^3F + a^5F$.

$^h$With respect to diabatic atoms $a^3F + b^3F$.

$^i$The $21^3\Sigma^+_l$ features two minima, a global, and a local.
6 quintets), out of a possible 84 \(\Lambda \Sigma\) states correlating to \(a^3F + a^3F\) Ti atoms. Certainly, all 84 states would show similar vdw interactions and minima close to 7 b, approximately twice the \(3d^2(\Sigma F)4s^2\) atomic Ti radius of \(\sim 3.8\) b.  

The “messy” region between 7 and 5 b is the result of numerous avoided crossings of the repulsive part of the vdw PECs, with incoming strongly attractive PECs of the same symmetry emanating from higher channels; see Figure 1. We turn now to the discussion of the first four states of \(Tl_2\).

1. \(X^3\Delta_g, 1^1\Sigma_g^+, 2^3\Sigma_u^+, \) and \(3^3\Sigma_u^+\)

As was already discussed two ground state \(a^3F\) Ti atoms lead only to non-covalent \(4s^2 - 4s^2\) vdw interactions. Attractive interactions are expected from higher channels, e.g., \(4s^2 3d^3(\Sigma F)4s^3 3d^4(\Sigma G)\) and \(4s^3 3d^4(\Sigma F)4s^3 3d^3(\Sigma F)\). The first two, practically degenerate states according to our calculations (vide infra), \(X^3\Delta_g\) and \(1^1\Sigma_g^+\), correlate diabatically to two \(a^3F\) Ti atoms, whereas the next two states, \(2^3\Sigma_u^+\) and \(3^3\Sigma_u^+\), are related to \(a^3F + a^3F\) atoms. The leading equilibrium CASSCF configurations and corresponding Mulliken densities of the first two states are (valence electrons only)

\[
\begin{align*}
|X^3\Delta_g\rangle & \approx 0.86 |1\sigma^2_1\pi^2_1\sigma^1_1\pi^1_1\Delta^1_1\rangle \\
|4s^{0.094}4p^{0.020}3d^{0.494}4p^{0.064}p^{0.063}d^{0.02}c^{0.02}d^{0.50}\rangle & \\
|1^1\Sigma_g^+\rangle & \approx 0.81 |1\sigma^2_2\pi^2_2\pi^1_1\pi^1_1\sigma^1_1\rangle \\
|4s^{0.094}4p^{0.103}3d^{0.888}4p^{0.074}p^{0.073}d^{0.04}c^{0.04}d^{0.90}\rangle
\end{align*}
\]

Taking into consideration that the ratio of the 4s and 3d radii is \((4s)/(3d) = 2.6, 30\) the bonding of the \(1^1\Sigma_g^+\) state is captured by the following valence-bond-Lewis (vBL) icon:

\[\tau\]

The diagram above suggests four bonds, two \(\sigma\) \((1\sigma_g, 2\sigma_g)\) and two \(\pi\) \((1\pi_u, 1\pi_y)\). However, the two \(\pi\) \((3d_{xz} - 3d_{yz})\) and the one \(\sigma\) \((3d_{z^2} - 3d_{x^2})\) singlet coupled distributions are energetically ineffective due to miniscule overlaps. In the \(X^3\Delta_g\) state the bonding can be represented with a similar vBL diagram, the difference being the transfer of a \(3d_{xz} - 3d_{yz}(2\sigma_g)\) electron to a \(\delta_{z^2}\) distribution. This bonding similarity between the \(X^3\Delta_g\) and \(1^1\Sigma_g^+\) states is reflected to the same bond distances and bond energies (Table I).

Despite the extensive size of the present calculations our numerical results are not, in general, very satisfactory the inherent difficulties of the \(3d\)-M2 systems. At the valence level the MRClQ+ (ACPF) [CClSSD(T)] bond length is \(r_c = 2.009\) (2.008) [1.976] Å; including scalar relativity \(r_c\) changes by \(\delta r_c = 0.01\) [0.01] [-0.01] Å, respectively. Calculating the correlation of the \(3s^23p^6\) valence electrons at the MRCl level was proved unfeasible due to the enormous size of the ensuing expansions. Core effects at the RCCSSD(T) level \((C^-RCCSSD(T))\) decrease the bond length by \(\delta r_c = 0.077\) Å. Assuming transferability of core effects we obtain \(r_c = 2.019\) (MRCl–DKH2+Q) – 0.077 \((\delta r_c) = 1.942\) Å, identical to the experimental value (Table I). At the \(C^-\text{RCCSSD(T)}\) level, however, \(r_c\) is predicted shorter by 0.035 Å than the experimental value. Following the same reasoning, the dissociation energy with respect to the ground state atoms is estimated to be \(D^0 = D^0\) (MRCl–DKH2+Q) + \([D^0(C^-\text{RCCSSD(T)}) - D^0(\text{RCCSSD(T)})] = 14.6 + [30.6 - 15.8] = 29.4\) kcal/mol vs 26.1 kcal/mol at the MRCl+Q (MRCl–DKH2+Q) [C^-RCCSSD(T)–DKH2 level. It is worth mentioning at this point that scalar relativistic effects at all methods reduce the binding energy by 4–5 kcal/mol, while core effects increase the binding energy by the surprising amount of 15 kcal/mol.

For the \(1^1\Sigma_g^+\) state scalar relativistic and core effects show the same trends as in the \(X^3\Delta_g\) state: the former reduce \((+\text{increase})\) the binding energy \((\text{bond length})\) by 2–4 kcal/mol \((\sim 0.016)\), while the latter increase the binding energy by 14 kcal/mol, decreasing at the same time the bond distances by 0.064 Å; see Table I. Following the same line of thinking as before, we obtain \(r_c = r_c\) (MRCl–DKH2+Q) + \(\delta r_c = 2.025\) (2.064) Å, and \(D^0 = D^0\) (MRCl–DKH2+Q) + \([D^0(C^-\text{RCCSSD(T)}) - D^0(\text{RCCSSD(T)})] = 13.6 + [29.2 - 14.8] = 28.0\) kcal/mol as compared to 26.6 kcal/mol at the \(C^-\text{RCCSSD(T)}\)–DKH2 level, very similar to the \(D^0\) of the \(X^3\Delta_g\) state. This means that the \(X^3\Delta_g\) and \(1^1\Sigma_g^+\) states are degenerate within 1 kcal/mol. This energy separation \(T_c = 0.0\) ± 1 kcal/mol is corroborated at all levels of theory presently employed. As a matter of fact at the \(C^-\text{RCCSSD(T)}\)–DKH2 level, the \(1^1\Sigma_g^+\) state becomes the ground state by \(-\sim 1\) kcal/mol; see Table I.

The main equilibrium CASSCF configurations and Mulliken populations of the next two states are

\[
\begin{align*}
|2^2\Sigma_u^+\rangle & \approx 1\sigma^2_2\pi^2_1\sigma^1_1\pi^1_1\pi^1_1(0.72)\Delta^{1,2}_1 + (0.45)\Delta^{1,2}_2 \\
|4s^{0.094}4p^{0.253}3d^{0.500}4p^{0.064}p^{0.063}d^{0.02}c^{0.02}d^{0.50}\rangle & \\
|3\Sigma_u^+\rangle & \approx 0.87 |1\sigma^2_2\pi^2_1\sigma^1_1\pi^1_1\pi^1_1\rangle \\
|4s^{0.314}4p^{0.222}3d^{0.500}4p^{0.064}p^{0.063}d^{0.02}c^{0.02}d^{0.92}\rangle
\end{align*}
\]

The \(2^2\Sigma_u^+\) correlates diabatically (adiabatically) to the mixed channel \(a^3F + a^3F\) \((a^3F + a^3F)\), while the \(2^1\Sigma_u^+\) dissociates uniquely to \(a^3F + a^3F\). The bonding in the \(3\Sigma_u^+\) state can be captured by the vBL diagram below:

\[\tau\]

The bonding comprises three bonds, two formal ineffective \(\pi\) \((3d_{xz} - 3d_{yz})\) and one strong \(\sigma\) \((1\sigma_g)\) \((4s - 4s)\), and two electrons coupled into a triplet are distributed to \(2\sigma_g \approx 0.96|3d_{xz} - 3d_{yz}|\) and \(1\sigma_u \approx 0.70|4s - 4s| - 0.37|4p_x - 4p_z|\) orbitals.
By uncoupling the two $\pi_u$ bonds and distributing the four electrons coupled into a quintet to the four singly occupied $1\delta_u$ and $1\sigma_u$ orbitals, the $2^3\Sigma^+_u$ state is obtained, bound through a single $\sigma$ (1$\sigma_g^2$) bond. This bonding description is in complete conformity with the main equilibrium configurations and the population analysis given above.

There are no experimental results for the $2^7\Sigma^+_u$ and $3^3\Sigma^+_u$ states. According to Table I at the valence level the MRCI–DKH2+Q (ACPF–DKH2) bond distance of the $2^3\Sigma^+_g$ state is 2.556 (2.561) Å, with a $T_e = 0.0 \pm 1$ kcal/mol. However, the results of Ref. 15 suggest that including the $3p^6$ subvalence electrons at the MRCI + scalar relativity + Q level reduces the bond distance by ~0.1 Å and increases $T_e$ by 7–8 kcal/mol. Including the $3z^23p^6$ e$^-$ at the C–RCCSD(T) level, our results indicate similar trends with those of Ref. 15, i.e., a reduction of bond length and a considerable increase in the $T_e(2^3\Sigma^+_g^-3\Delta_g)$ gap, although the severe multireference character of the $2^3\Sigma^+_g$ state (vide supra) does not allow for quantitative conclusions at the C–RCCSD(T) level. Nevertheless, it is rather safe to conclude that the $2^3\Sigma^+_g$ state is separated from the first two states by some 5–10 kcal/mol with a recommended $r_e = 2.45$ Å.

In the $3^3\Sigma^+_g$ state the MRCI–DKH2+Q (ACPF–DKH2) [RCCSD(T)–DKH2], $r_e = 2.162$ (2.159) [2.116] Å and $T_e = 2.26$ (2.33) [3.23] kcal/mol. Correcting the MRCI–DKH2+Q results for core-correlation effects obtained at the CC level, $\delta r_e = -0.097$ Å and $\delta T_e = +5.1$ kcal/mol, we get $r_e = 2.162-0.097 = 2.065$ Å and $T_e = 2.26 + 5.1 = 7.4$ kcal/mol, as contrasted to 2.029 Å and 9.27 kcal/mol at the C–RCCSD(T)–DKH2 level of theory: $r_e$ and $T_e$ values by Hübner et al.15 are comparable with the present calculations; see Table I.

### 2. Higher states

Table II collects $r_e$, $D_e$, $\omega_e$, and $T_e$ values of 26 higher states of Ti$_2$ calculated at the MRCI+Q/QM level and within an energy range of less than 20 kcal/mol. Observe that all states are strongly bound with respect to their diatomic channels, whereas about half of them are also bound with respect to the ground state atoms. According to the results of the first four states previously discussed, core (3$s^23p^6$) effects reduce uniformly the bond lengths by $0.10 \pm 0.01$ Å; see also Ref. 2. In addition, although core effects are of importance to the $T_e$ separations for the first four states, their influence seems to diminish for the higher states as is evidenced from the results of Ref. 15 and the limited experimental values; see Table II. Therefore, we can claim with some confidence that MRCI+Q bond distances should be very close to reality if reduced by about 0.10 Å; on the other hand $T_e$ separations can be considered of a semi-quantitative value. This is corroborated by contrasting theoretical and existing experimental values (in parenthesis) of $r_e$ (after reduction by 0.10 Å) and $T_e$ for the $6^3\Pi_u$, $7^3\Phi_u$, $17^3\Pi_u$, and $28^3\Phi_u$ states: $r_e = 2.02$ (2.00), 2.03 (2.04), 2.08 (2.07), 2.08 (2.07) Å and $T_e = 10.1 (11.5)$, 10.7 (12.4), 17.6 (20.3), 22.5 (23.7) kcal/mol, respectively; see Table II.

### B. Ti$_2^+$

We return now to the vBL diagram of the neutral Ti$_2$ 1$^1\Sigma^+_g$ state, practically degenerate to the X$^1\Delta_g$. By removing one electron from the $2\sigma_g(3d_{2z} - 3d_{dz})$ orbital the $2^2\Sigma^+_g$ state obtains, while by removing one electron from the $2\sigma_g$ orbital and transferring the other to a $3d_{yz}$ atomic distribution, we get a $2^4\Delta_g$ state of Ti$_2^+$. The decongestion of the $\sigma$ frame of Ti$_2$ by removing one electron and the resulting stabilization of the one electron $2\sigma_g$ bond suggests that the ground state of Ti$_2^+$ is $2^2\Sigma^+_g$. Indeed, preliminary MRCI calculations indicate that the ground state of Ti$_2^+$ is of $2^2\Sigma^+_g$ symmetry. Table III lists numerical results for the $2^2\Sigma^+_g$ and $2^4\Delta_g$ states, and Figure 3 displays the corresponding PECs. The main MRCI equilibrium configurations and Mulliken populations of the $X^3\Sigma^+_g^+$ and $2\Delta_g$ states are given below:

\[
\begin{align*}
|X^3\Sigma^+_g^+⟩ &\approx 0.85 |1\sigma_g^2 2\sigma_u^1 1\pi_u^2 1\pi_u^2⟩ \\
&\pm 0.14 |1\sigma_g^2 2\sigma_u^1 3\delta_u^2 1\pi_u^2⟩ \\
|2\Delta_g⟩ &\approx 0.84 |1\sigma_g^2 1\pi_u^2 1\pi_u^2 1\pi_u^2⟩ \\
&\pm 0.16 |1\sigma_g^2 3\delta_u^2 1\pi_u^2 1\pi_u^2⟩
\end{align*}
\]

The bonding of the X-state is captured by the following vBL diagram:

![vBL Diagram](image)

As in the $X^3\Delta_g$ state of the neutral species, the bonding comprises of a strong $\sigma$ bond ($1\sigma_g \sim 3s^24s$) a weak half $\pi$ bond ($2\sigma_g \sim 3d_{xy}+3d_{yz}$), and two $\pi$ ($1\pi_u^u, 1\pi_u^u$) weak bonds. By moving the $2\sigma_g$ single electron to a $3d_{yz}$ orbital, the $2\Delta_g$ is formed some 5 kcal/mol above the X$^3\Sigma^+_g^+$ state. Both states correlate adiabatically to the ground state fragments $a^3(F(4s^23d^2)+a^3(F(4s^23d^2)$.

Following the MRCI PECs from infinity towards equilibrium, a first (local) minimum is observed at 3.3 Å for both states due to a $4s^2(4s^2)4s(4s^2)$ interaction, amounting to a 2 center–3 electron bonding of 30 kcal/mol (see Figure 3); see also Ref. 2. Moving to the left and after the avoided crossing with states coming from Ti($a^3F$) + Ti($a^3F$), the global minima of the X$^3\Sigma^+_g^+$ and $2\Delta_g$ are reached at 2.10 and 1.85 Å, respectively. Observe that between the local (3.30 Å) and global (1.85 Å) minima of the $2\Delta_g$ state, there is a middle minimum (2.44 Å) practically isoeenergetic to the global one at the MRCI+Q level.

Let us examine now our numerical results listed in Table III. The C–RCCSD(T)–DKH2 binding energy is $D_e(D_0) = 53.2(52.7)$ kcal/mol, in fair agreement with the experimental value $D_e(0) = 56.2 \pm 0.05$ kcal/mol.12 At the valence MRCI–DKH2+Q (ACPF–DKH2) the binding energy is 47.1 (46.8) kcal/mol. Adding core $3s^23p^6$ effects...
TABLE III. Energies E(\text{e} \text{V}) \), bond distances \( r_e (\text{Å}) \), dissociation energies \( D_e \)(kcal/mol), harmonics and anharmonics frequencies \( \omega_e, \omega_e \times_e (\text{cm}^{-1}) \), and energy separations \( T_e \)(kcal/mol) of the first two states of Ti\(_2^+\).

<table>
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<tr>
<th>State</th>
<th>Method</th>
<th>( -E )</th>
<th>( r_e )</th>
<th>( D_e )</th>
<th>( \omega_e )</th>
<th>( \omega_e \times_e )</th>
<th>( T_e )</th>
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<td>( \chi^2 \Sigma_g^+ )</td>
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<td>C–RCCSD(T)–DKH2</td>
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<td>356</td>
<td>2.60</td>
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</tr>
</tbody>
</table>

Expt. (D\(_00\), Ref. 12)  56.2

\( \delta r_e = 0.123 \text{ Å} \) at the RCCSD(T) level, there-fore \( r_e(MRCI–DKH2+Q) - \delta r_e = 2.140-0.123 = 2.017 \text{ Å} \) as contrasted to the C–RCCSD(T)–DKH2 value of 1.981 Å.

Our recommended bond distance is \( r_e = (2.017+1.981)/2 = 2.00 \text{ Å} \). The experimental IE of Ti\(_2^+\) is 5.93 ± 0.19 eV\(^{12}\) in acceptable agreement with the C–RCCSD(T)–DKH2 result of 5.64 eV.

For the \( ^2\Delta_g \) state, taking into consideration the \( 3s^23p^6 \) core effects at the CC level, the recommended bond distance is \( r_e = r_e(MRCI–DKH2+Q) + \delta r_e = 1.851-0.042 = 1.81 \text{ Å} \), as compared to 1.77 Å at the C–RCCSD(T)–DKH2 level. According to Table III the C–RCCSD(T)–DKH2 \( T_e = 5.6 \text{ kcal/mol} \) is in agreement with the MRCI–DKH2+Q value after the inclusion of the subvalence core effects at the CC level, \( T_e = 13.3–7.1 = 6.2 \text{ kcal/mol} \).

V. FINAL REMARKS

Using MRCI and single reference CC methods combined with large basis sets, we have studied the electronic structure of Ti\(_2^+\) and Ti\(_2^+\). In particular, we have constructed (valence) MRCI+Q PECs for Si (Ti\(_2^+\)) and \( ^2\Delta_g \) states, whereas for the lowest 4 states of Ti\(_2^+\) and the 2 states of Ti\(_2^+\), scalar relativistic and subvalence (\( 3s^23p^6 \)) core correlation effects have been taken into account. We have to confess, however, that although our calculations are the best and most systematic so far in the literature, the results cannot be deemed as satisfactory, in other words do not reflect our strenuous efforts put in this project. As already stated, the almost insurmountable computational and conceptual difficulties of the \( 3d–M_2 \) systems are due to the extremely dense manifold of the \( \Lambda–\Sigma \) states.

The ground state of Ti\(_2^+\) was considered to be up to now, rather “traditionally,” of the \( ^3\Delta_g \) symmetry; the present calculations, although do not prove, suggest as well that this is very probably true. Recommended “best” theoretical bond distance and dissociation energy for the \( X^2\Sigma_g^+ \) state are (experimental values in parenthesis), \( r_e = 1.942 (r_0 = 1.9422 ± 0.0008) \text{ Å} \) (Ref. 10) and \( D_0^\text{ex} = 29.0 (35.5 ± 4.4) \text{ kcal/mol} \) (Ref. 12). Formally, the two Ti atoms are held together by one

![FIG. 3. MRCI/Q\(_x\) PECs of 2 states of Ti\(_2^+\). Energies have been shifted by +1696.0 E\(_{\text{h}}\).](image-url)
and a half σ and two π bonds. Our calculations indicate, but again do not prove, that the first excited state, $1\Sigma_g^+$, is within 1 kcal/mol of the $X^3\Delta_g$ state.

By removing the symmetry defining $d$ electron from the $X^1\Delta_g$ state of Ti$_2$, the $X^2\Sigma_g^+$ state of Ti$_2$ is obtained, with the first excited state of $2\Delta_g$ symmetry about 6 kcal/mol higher.

Finally, in addition to the first four states of Ti$_2$ more thoroughly calculated, numerical results of quasi-quantitative accuracy for 26 higher states are also given. We believe that the present study is a step towards a better understanding of the electronic structure of Ti$_2$, and of some use to the scientific community.