

Theoretical Investigation of the Electronic States of Calcium Carbide, CaC

Aristotle Papakondylis*[†] and Aristides Mavridis*[‡]

Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, P.O. Box 64 004, 157 10 Zografou, Athens, Greece

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Using multireference methods and semiquantitative basis sets, we have computed nineteen potential energy curves and spectroscopic parameters of the calcium monocarbide system, CaC. For the much debated $^3\Sigma^-$ and $^5\Sigma^-$ states our calculations definitively show that the ground state is of $^3\Sigma^-$ symmetry with the $a^5\Sigma^-$ state lying 1500–2500 cm^{-1} higher. For the $X^3\Sigma^-$ state our best estimates for the binding energy and equilibrium bond length are 51 kcal/mol and 2.33 Å, respectively. All states are strongly ionic with a charge transfer of 0.5 to 0.7 e^- from Ca to C.

1. Introduction

In an effort to elucidate the electronic structure and bonding of the ground and low-lying states of the calcium monocarbide molecule (CaC), we present systematic ab initio calculations employing multireference methods in conjunction with adequate basis sets.

The alkaline earth metal carbides constitute an extremely complicated class of compounds,¹ the understanding of which could be helped considerably by a detailed examination of the corresponding diatomics. Theoretically, the most thorough investigation so far is the multireference work of Bauschlicher et al.² on the magnesium carbide, MgC. Concerning CaC, the first laboratory detection by recording its pure rotational spectrum was announced very recently by Ziurys and co-workers.³ It is interesting, however, to follow the history of the theoretical work on CaC, focused mainly on the elucidation of its ground state.

Castro et al.⁴ for the first time investigated theoretically the $^3\Sigma^-$, $^1\Sigma^+$, and $^3\Pi$ states of CaC by MP4 methods and moderate size basis sets, concluding that the ground state is of $^3\Sigma^-$ symmetry. Subsequent calculations of CaC, BeC, and MgC by Da Silva et al.,⁵ at the GVB+CI/[6s4p2d/c_a8s6p2d/c] level, suggested that the ground state of CaC is $^5\Sigma^-$, 3.2 kcal/mol lower than the $^3\Sigma^-$ state. The problem was revisited by Serrano and Canuto⁶ who, employing UCCSD(T)/[8s6p2d2f/c_a6s4p2d/c] methods, concluded that, indeed, there is a strongly competitive $^5\Sigma^-$ state, but located approximately 800 cm^{-1} higher than the $^3\Sigma^-$ state. It should be observed though that their single reference calculations⁶ suffer from serious spin contamination. In addition, the fact that the $^3\Sigma^-$ state correlates adiabatically to $\text{Ca}(4s^2;^1S) + \text{C}(^3P)$, whereas the $^5\Sigma^-$ correlates to $\text{Ca}(4s^14p^1;^3P) + \text{C}(^3P)$, means that the Ca energy separation $\Delta E(^3P \leftarrow ^1S) = 1.892 \text{ eV} (=43.63 \text{ kcal/mol})$ ⁷ should be taken into consideration if one is interested in resolving the question of the $^3\Sigma^- - ^5\Sigma^-$ ordering.

Recently, we published a study on the ground states of CaC and ZnC, testing a newly developed multireference coupled cluster method (MRBWCCSD).⁸ In this work, and for reasons of comparison, we also report some results from the present study, where it is clearly indicated that the ground state of CaC

is of $^3\Sigma^-$ symmetry (see also below). Interestingly, two more papers on CaC appeared at the same time as ref 8: the experimental one previously mentioned,³ and a theoretical work by Takada et al.⁹ These workers employed a multireference + singles + doubles configuration interaction approach coupled with a 6-311G(3d1f) basis, and a selection scheme of picking configurations. They report results on the disputed $^3\Sigma^-$ and $^5\Sigma^-$ states as well as on four higher states, namely, $^3\Pi$, $^1\Delta$, $^1\Pi$, and $^1\Sigma^+$. They concluded that the symmetry of the ground state is $^3\Sigma^-$, with $^5\Sigma^-$ lying 695 cm^{-1} higher, or 1156 cm^{-1} including the Davidson correction. Their results will be contrasted with ours in due course. Now, according to the experimentalists,³ the CaC microwave spectra show clear triplet patterns, evidence that the ground state of CaC is indeed $^3\Sigma^-$ as opposed to $^5\Sigma^-$.

The motivation of the present study, at the time it started, was the clarification of the CaC ground state question,⁸ as well as the examination of a series of low-lying excited states and their bonding nature. Although the first question does not seem to be an issue anymore, the accurate $a^5\Sigma^- - X^3\Sigma^-$ splitting is still debatable, as well as its bonding nature and a more systematic examination of its excited states. Toward this end, and using rather large basis sets and multireference variational methods, we have constructed potential energy curves (PEC) for a total of 19 states, obtaining dissociation energies, common spectroscopic constants, and dipole moments. We believe that the present study could be of considerable help in the experimental elucidation of the excited manifold of CaC.

2. Methodological Outline

Considering the ground ($4s^2; ^1S$) and the first excited state ($4s^14p^1; ^3P$) of Ca ($\Delta E = 15\,263.10 \text{ cm}^{-1} = 1.8924 \text{ eV}$)⁷ and the ground ($2s^22p^2; ^3P$) and the first excited state ($2s^22p^2; ^1D$) of C ($\Delta E = 10\,164.07 \text{ cm}^{-1} = 1.2602 \text{ eV}$)⁷, the following molecular states ($^{2S+1}|\Lambda|$) are obtained

$$\text{Ca}(^1S) \otimes \text{C}(^3P) = \text{CaC}(^3\Sigma^-, ^3\Pi),$$

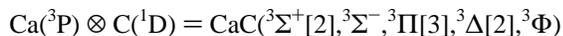
$$\text{Ca}(^1S) \otimes \text{C}(^1D) = \text{CaC}(^1\Sigma^+, ^1\Pi, ^1\Delta),$$

$$\text{Ca}(^3P) \otimes \text{C}(^3P) = \text{CaC}(^1,3,5\Sigma^+, ^1,3,5\Sigma^-[2], ^1,3,5\Pi [2], ^1,3,5\Delta),$$

[†] E-mail: papakondylis@chem.uoa.gr.

[‡] E-mail: mavridis@chem.uoa.gr.

and



a total of 32 molecular states. Seventeen of them are presently examined, namely, all 5 states of the first two groups, and the $^3\Sigma^+$, $^1\Sigma^-[2]$, $^3,5\Sigma^+$, $^1,3\Pi[2]$, $^5\Pi$, and $^1,3\Delta$ of the third group. Four quintets of the third group ($^5\Sigma^\pm$, $^5\Pi$, and $^5\Delta$) that were not considered, are expected to be of repulsive character, similar to the corresponding states of MgC.² States correlating to $\text{Ca}(^3\text{P}) + \text{C}(^1\text{D})$ (fourth group) were not considered, due to technical difficulties caused by intervening states of the asymptote $\text{Ca}(^3\text{D}) + \text{C}(^3\text{P})$, lower in energy than $\text{Ca}(^3\text{P}) + \text{C}(^1\text{D})$ by 0.628 eV.⁷ Also two more states possibly correlating to $\text{Ca}(^3\text{D}) + \text{C}(^3\text{P})$ were partially examined.

For the C atom we employed the triple and quadruple augmented correlation consistent basis sets of Dunning,¹⁰ aug-cc-pVxZ, (x = T, Q), generally contracted to [5s4p3d2f] and [6s5p4d3f2g], respectively; the latter was used only for the two lower states, $^3\Sigma^-$ and $^5\Sigma^-$. The use of diffuse functions was deemed as necessary because the carbon atom is expected to acquire a negative charge upon bonding. For the Ca atom we started with the 23s16p basis of Partridge,¹¹ extended with 9d and 6f Gaussians, taken from the ANO basis set of Sc(Z=21)¹² and scaled by 0.875 and 1.250, respectively, the scaling factors being determined by optimizing the total energy of $\text{Ca}(^1\text{S})$ at the CISD level. To obtain satisfactorily the atomic energy separation $\text{Ca}(^3\text{P}\leftarrow^1\text{S})$, an additional diffuse p function (exponent = 0.05) was found as necessary. This basis set was generally contracted to [7s5p4d3f]. The complete CaC basis (with aug-cc-pVTZ on C) contains 109 spherical Gaussian functions.

Our computational strategy consists of a multireference CISD approach based on a CASSCF zero order function. The complete active space (CAS) was generated by allowing the six "atomic" valence electrons of CaC ($4s^2 + 2s^2p^2$) to be distributed among 13 orbitals corresponding to the "active" space of the Ca- ($4s+4p+3d$) and C($2s+2p$) atoms. Such an allotment produces about 3800 configuration functions (CF) for the quintets, 9700 CFs for the triplets, and 6500 CFs for the singlets. Additional correlation was obtained by single and double excitations of the six valence electrons out of the zeroth-order space (CASSCF+1+2=MRCI), keeping always the "core" orbitals C($\sim 1s^2$) and Ca($\sim 1s^2 2s^2 2p^6 3s^2 3p^6$) fully occupied. The MRCI expansions contain about 4.3×10^6 , 8.8×10^6 , and 5.2×10^6 CFs; these numbers were further reduced to about 400 000 (quintets), 700 000 (triplets), and 1 100 000 (singlets) by applying the internal contraction technique as implemented in the MOLPRO package.¹³

To test the adequacy of the Ca basis set, we run MRCI calculations for the $X^3\Sigma^-$ and $a^5\Sigma^-$ states only, using the newly developed cc-pV5Z basis for Ca by Peterson¹⁴ in conjunction with the aug-cc-pV5Z of C.¹⁰ The MRCI expansions, using these large basis sets (195 contracted spherical Gaussians), contain about 2×10^6 and 1.4×10^6 internally contracted CFs for the $X^3\Sigma^-$ and $a^5\Sigma^-$ states, respectively.

Around equilibrium the $^3\Sigma^-$ and $^5\Sigma^-$ states were also examined by including the $3s^2 3p^6$ outer core electrons of Ca in the CISD procedure in conjunction with the x=T basis of C (C-MRCI), reducing at the same time the reference space to 8 active orbitals by excluding the Ca 3d functions to keep the calculations tractable.

The following total atomic energies and splittings were obtained at the MRCI level of theory, and the triple- ζ basis on

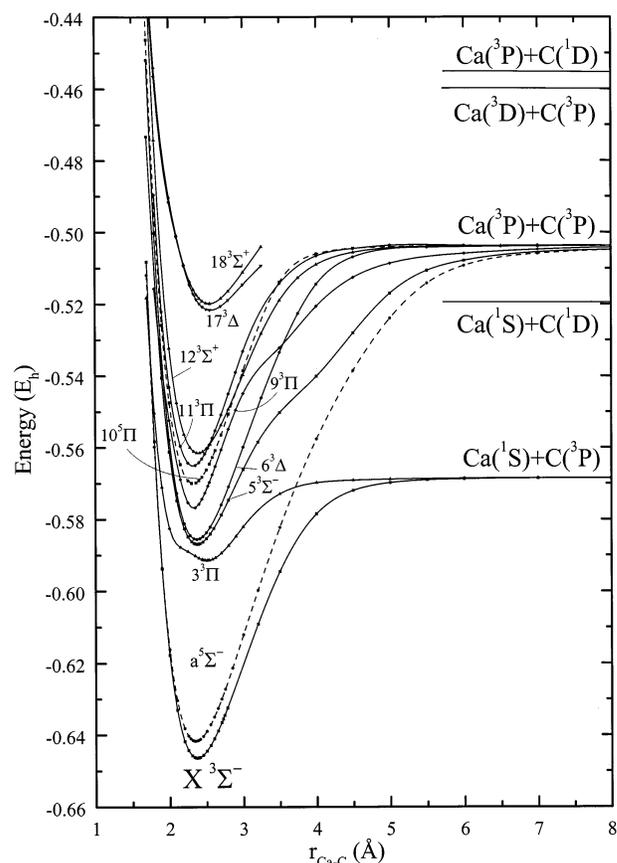


Figure 1. Potential energy curves of nine triplets and two quintets of CaC obtained at the MRCI/[5s4p3d2f/c_aaug-cc-pVTZ/c] level of theory.

the carbon atom (experimental results in parentheses⁷):

$$\text{C: } E(^3\text{P}) = -37.78046 E_h, \quad E(^1\text{D}) = -37.73261 E_h, \\ \Delta E(^1\text{D}\leftarrow^3\text{P}) = 1.302 \text{ eV} (1.260 \text{ eV}, \bar{M}_J)$$

$$\text{Ca: } E(^1\text{S}) = -676.78700 E_h, \quad E(^3\text{P}) = -676.72223 E_h, \\ \Delta E(^3\text{P}\leftarrow^1\text{S}) = 1.762 \text{ eV} (1.892 \text{ eV})$$

Including the Ca $3s^2 3p^6$ core electrons the $^3\text{P}\leftarrow^1\text{S}$ separation improves only slightly becoming 1.770 eV. Notice that the $\text{Ca}(^3\text{P}\leftarrow^1\text{S})$ gap is predicted to be *smaller* than the experimental one by 0.130 eV (=1049 cm^{-1}). With the cc-pV5Z basis set,¹⁴ the CISD $^3\text{P}\leftarrow^1\text{S}$ Ca splitting is 1.667 eV, confirming that our ad hoc constructed Ca basis performs rather well.

All our molecular calculations show a modest size-extensivity error of 0.5–2.0 mE_h at the MRCI level, but becoming significant at the C-MRCI level, clearly indicating the deterioration of the quality of the wave function. The counterpoise correction for the basis set superposition error was calculated to be less than 0.5 mE_h at the equilibrium distance of the $^3\Sigma^-$ state, so it was not considered any further.

All electronic structure calculations were performed with the MOLPRO2000 program,¹³ whereas spectroscopic constants for all states were extracted from the $G(v) + F_v(J)$ energy levels of the corresponding potential wells by solving numerically the one-dimensional rovibrational Schrödinger equation.¹⁵

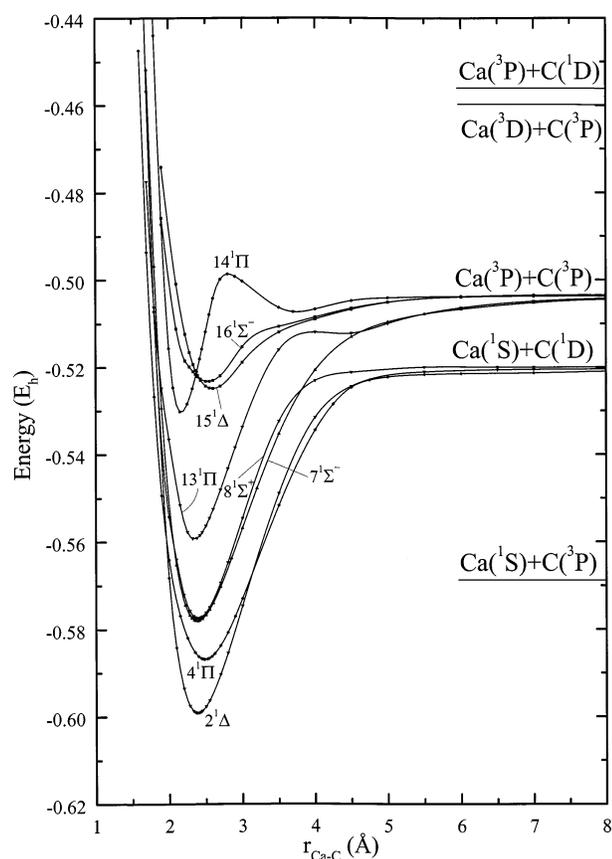
3. Results and Discussion

Potential energy curves (PEC) of the triplets and quintets are shown in Figure 1, singlets are depicted in Figure 2. Table 1 lists total energies, dissociation energies (D_e), interatomic

TABLE 1: Total Energies E (hartree), Dissociation Energies D_e (kcal/mol), Bond Distances r_e (Å), Spectroscopic Constants ω_e , $\omega_e x_e$, α_e , and \bar{D}_e (cm^{-1}), Dipole Moments μ (Debye), Mulliken Charges q_{Ca} , and Separation Energies T_e (eV) of the Ground and Excited States of the CaC Molecule at the MRCI Level of Theory

state	$-E$	D_e^a	r_e	ω_e	$\omega_e x_e$	$\alpha_e \times 10^{-3}$	$\bar{D}_e \times 10^{-6}$	μ	q_{Ca}	T_e
$X^3\Sigma^-$	714.64639	48.9	2.369	460.8	2.89	2.6	0.65	3.64	+0.64	0
$X^3\Sigma^-b$	714.65246	51.1	2.363	458.5				3.45	+0.75	0
$X^3\Sigma^-c$	714.82335		2.346	468.6				3.08	+0.61	0
$X^3\Sigma^-d$	714.65558	50.9	2.353	464.6				3.51	+0.65	0
$X^3\Sigma^-e$			2.3015				0.7			
$a^5\Sigma^-$	714.64166	86.1	2.346	472.2	2.34	2.5	0.61	3.49	+0.61	0.1287
$a^5\Sigma^-b$	714.64571	86.2	2.346	472.2				3.65	+0.69	0.1837
$a^5\Sigma^-c$	714.81854		2.320	477.2				3.04	+0.58	0.1309
$a^5\Sigma^-d$	714.65099	86.0	2.331	474.8				3.37	+0.64	0.1248
$2^1\Delta$	714.59911	49.4	2.385	452.2	2.51	2.6	0.67	4.38	+0.59	1.287
$3^3\Pi$	714.59137	14.4	2.505	309.4	12.86	10.9	2.26	3.85	+0.52	1.497
$4^1\Pi$	714.58686	41.4	2.486	359.5	3.35	0.9	0.79	3.85	+0.56	1.620
$5^3\Sigma^-$	714.58685	51.7	2.373	427.3	3.06	3.0	0.75	4.39	+0.59	1.620
$6^3\Delta$	714.58592	51.4	2.367	454.1	2.33	2.6	0.67	3.22	+0.57	1.656
$7^1\Sigma^-$	714.57806	46.4	2.384	423.8	2.74	2.9	0.75	3.45	+0.61	1.859
$8^1\Sigma^+$	714.57744	36.1	2.391	438.7	4.06	2.5	0.75	4.87	+0.56	1.876
$9^3\Pi$	714.57680	45.6	2.337	629.6	25.70	1.2	0.40	7.99	+0.64	1.894
$10^5\Pi$	714.56999	41.5	2.314	485.3	3.00	2.7	0.66	3.03	+0.79	2.079
$11^3\Pi$	714.56510	38.5	2.329	506.7	3.54	3.1	0.61			2.212
$12^3\Sigma^+$	714.56153	36.3	2.382	433.1	2.97	2.6	0.73	3.09	+0.53	2.309
$13^1\Pi$	714.55931	34.7	2.335	498.6	3.23	3.7	0.58	5.08	+0.61	2.370
$14^1\Pi_G^f$	714.53034	16.7	2.162	763.3	29.66	6.3	0.44	8.31	+0.66	3.158
$14^1\Pi_L^g$	714.50735	2.3	3.698	133.7	4.48	1.5	0.48			3.783
$15^1\Delta$	714.52490	13.5	2.599	286.7						3.306
$16^1\Sigma^-$	714.52326	12.5	2.543	266.7						3.351
$17^3\Delta$	714.52165	41.4	2.556	324.1	3.60	2.9	0.85	2.42	+0.56	3.394
$18^3\Sigma^+$	714.51985	40.3	2.546	335.0	2.57	2.4	0.85	2.52	+0.58	3.443

^a With respect to asymptotic products. ^b aug-cc-pVQZ on the carbon atom. ^c Core electrons of Ca ($3s^2 3p^6$) included in the MRCI (C-MRCI) procedure, aug-cc-pVTZ on carbon atom. ^d cc-pV5Z on Ca, and aug-cc-pV5Z on C. ^e Experimentally determined $X^3\Sigma^-$ state, bond distance r_0 , and centrifugal distortion constant \bar{D}_0 , ref 3. ^f Global minimum. ^g Local minimum.

**Figure 2.** Potential energy curves of eight singlets of CaC obtained at the MRCI/[5s4p3d2f/c_aaug-cc-pVTZ/c] level of theory.

distances (r_e), spectroscopic constants (ω_e , $\omega_e x_e$, α_e , \bar{D}_e), total Mulliken MRCI charges on Ca (q_{Ca}), dipole moments (μ)

obtained as expectation values, and separation energies (T_e) of all states studied.

3a. $X^3\Sigma^-$, $a^5\Sigma^-$ States. As was already mentioned it is clear by now that the ground state of CaC is of $^3\Sigma^-$ symmetry.^{3,8,9} Table 1 shows that at the MRCI level $X^3\Sigma^-$ is lower than $^5\Sigma^-$ by 0.1287 eV (=1038 cm^{-1}); including core-correlation effects from the $3s^2 3p^6$ electrons of Ca (C-MRCI) the $X^3\Sigma^- - a^5\Sigma^-$ remains practically unaffected, $T_e = 1056 \text{ cm}^{-1}$. However, by increasing the carbon basis set alone from triple to quadruple, the T_e increases substantially becoming 0.1837 eV (=1482 cm^{-1}) or 1500 cm^{-1} at the C-MRCI level, assuming additivity of core correlation effects. The multireference Davidson correction changes only slightly this number to 1519 cm^{-1} . Now from Figure 1 we observe that though the $X^3\Sigma^-$ state traces its origin to the ground-state atoms, the $^5\Sigma^-$ state correlates to $\text{Ca}(^3\text{P}) + \text{C}(^3\text{P})$, i.e., to the first excited state of Ca. At the CISD level our $\text{Ca}(^3\text{P} \leftarrow ^1\text{S})$ separation is 1.762 eV, 0.130 eV (=1048 cm^{-1}) lower than the experimental one; thus there is no doubt that $^3\Sigma^-$ is the ground state of CaC. Shifting upward the $^3\Sigma^-$ energy uniformly by 0.130 eV, to match the experimental CaC ($^3\text{P} \leftarrow ^1\text{S}$) energy splitting, the energy separation becomes 1500 + 1048 = 2548 cm^{-1} , suggesting that the T_e ($a^5\Sigma^- \leftarrow X^3\Sigma^-$) is bracketed between 1500 and 2548 cm^{-1} . The corresponding UCCSD(T) result of Serrano and Canuto⁶ is 800 cm^{-1} , and the MRCI of Takada et al.,⁹ 695 cm^{-1} . In the MgC system the ground state is also of $^3\Sigma^-$ symmetry, the energy separation T_e ($^5\Sigma^- \leftarrow ^3\Sigma^-$) being 3545 cm^{-1} at the MRCI + Davidson correction level.² Because the $^5\Sigma^- D_0 = 84.9 \text{ kcal/mol}$ of MgC is practically equal to that of the CaC $a^5\Sigma^-$ state ($D_0 = 85.5 \text{ kcal/mol}$), the larger T_e ($^5\Sigma^- \leftarrow ^3\Sigma^-$) value of MgC is due to the interplay between the much larger $\text{Mg}(^3\text{P} \leftarrow ^1\text{S}) = 2.714 \text{ eV}$ splitting,⁷ and the smaller binding energy of the $\text{MgC } ^3\Sigma^-$ state (35.0 kcal/mol²), as compared to the Ca $T_e(^3\text{P} \leftarrow ^1\text{S})$ and $\text{CaC}(X^3\Sigma^-) D_e$ values, respectively.

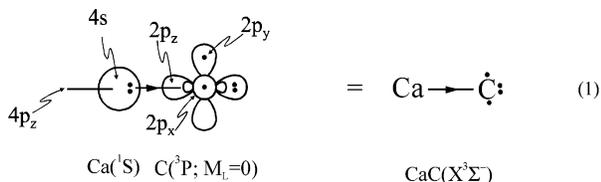
The leading CASSCF equilibrium CFs and the atomic Mulliken populations (Ca/C) of the $X^3\Sigma^-$ state are

$$|X^3\Sigma^- \rangle \sim 0.74|7\sigma^2 8\sigma^2 3\pi_x^1 3\pi_y^1 \rangle - 0.42|7\sigma^2 9\sigma^2 3\pi_x^1 3\pi_y^1 \rangle - 0.37|7\sigma^2 8\sigma^1 9\sigma^1 3\pi_x^1 3\pi_y^1 \rangle$$

and

$$4s^{0.92} 4p_z^{0.21} 4p_x^{0.02} 4p_y^{0.02} 3d_{z^2}^{0.09} 3d^{0.08} / 2s^{1.82} 2p_z^{0.90} 2p_x^{0.93} 2p_y^{0.93}$$

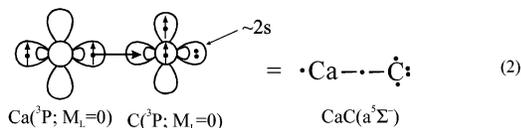
The bonding can be succinctly represented by the following valence bond–Lewis (vBL) diagram



suggesting a single σ bond due to the transfer of about $0.7 e^-$ from the $4s4p_z$ hybrid on Ca to the empty $2p_z$ orbital on C. At the MRCI(+Davidson correction)/aug-cc-pVQZ(on C) level, we obtain $D_e = 51.1$ (51.5) kcal/mol at $r_e = 2.363$ Å (Table 1). Including the $3s^2 3p^6$ Ca “core” electrons in the MRCI (=C-MRCI) procedure shortens the bond distance by 0.023 Å, but the induced size nonextensivity errors prevented a reliable estimation of D_e at this level. At the MRCI/cc-pV5Z/C_aaug-cc-pV5Z/C level the D_e remains the same but the bond length decreases significantly to $r_e = 2.353$ Å. Assuming additivity of core-correlation effects with respect to the bond distance, our final estimate is $r_e = 2.353 - 0.023 = 2.33$ Å now in better agreement with the recently determined experimental value,³ $r_0 = 2.3015$ Å.

Corresponding theoretical values from refs 6 and 9 are 45.9 kcal/mol, 2.348 Å and 45.4 kcal/mol, 2.368 Å, respectively. Our total energies of $X^3\Sigma^-$ and $a^5\Sigma^-$ states are 29 and 26 mE_h lower than those reported in ref 9.

The $a^5\Sigma^-$ state traces its lineage to $Ca(^3P) + C(^3P)$, it is dominated by a single reference wave function along the entire potential curve (Figure 1), and its bonding is uniquely determined by the symmetry of the atoms at infinity. The following bonding picture



suggesting a $1/2 \sigma$ bond, is entirely consistent with the equilibrium configuration

$$|a^5\Sigma^- \rangle \sim 0.96|7\sigma^2 8\sigma^1 9\sigma^1 3\pi_x^1 3\pi_y^1 \rangle$$

and the relevant Mulliken distributions:

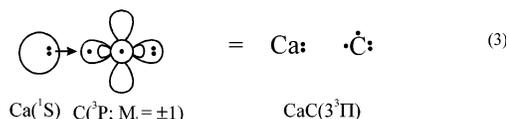
$$4s^{0.91} 4p_z^{0.22} 4p_x^{0.02} 4p_y^{0.02} 3d^{0.20} / 2s^{1.80} 2p_z^{0.90} 2p_x^{0.93} 2p_y^{0.93}$$

About $0.7 e^-$ are transferred via the σ -frame from Ca to the empty $2p_z$ C orbital creating the $1/2 \sigma$ bond. It is remarkable that this half σ bond is worth 86 kcal/mol with respect to the adiabatic atoms in all basis sets used (Table 1), the strongest bond of all states studied and with a bond length shorter by 0.02 Å than the X-state. The bonding similarity between the

$X^3\Sigma^-$ and $a^5\Sigma^-$ states is obvious (electron transfer through the σ frame to the empty $2p_z$ orbital), therefore attributing the much larger stabilization of the latter to exchange correlation effects. Hypothesizing again additivity of the core effects with respect to the bond distance, our best estimate for r_e is $2.331 - 0.026 = 2.305$ Å. Relative results obtained from ref 9 are $D_e = 83.7$ kcal/mol and $r_e = 2.341$ Å at the MRCI level of theory.

A final comment should be added concerning the dipole moments of the X and a states: including the $3s^2 3p^6$ electrons of Ca in the MRCI (C-MRCI) procedure diminishes both dipole moments by 0.5 D, reflecting the deterioration of the quality of the wave function due to the significant by now size non-extensivity errors (see also ref 16).

3b. Excited Triplets. From Figure 1 we observe that the first excited triplet is of Π symmetry ($3^3\Pi$), correlating to the ground-state atoms $Ca(^1S) + C(^3P)$ and pictured by the following vBL diagram



implying a rather repulsive, or a weakly attractive interaction. Indeed, and according to Table 1, $D_e = 14.4$ kcal/mol and $r_e = 2.505$ Å at the MRCI level ($D_e = 10.8$ kcal/mol, $r_e = 2.538$ Å from ref 9). For the analogous $3^3\Pi$ state of the MgC molecule, and at approximately the same level of theory, Bauschlicher et al.² report $D_e = 7$ kcal/mol.

The topology of the $3^3\Pi$ potential energy curve (PEC) implies an interaction with the $9^3\Pi$ and $11^3\Pi$ states located 0.396 and 0.715 eV above the $3^3\Pi$ state at the MRCI level. The dominant CASSCF equilibrium configurations and the Mulliken distributions (Ca/C)

$$|3^3\Pi \rangle \sim 0.84|7\sigma^2 8\sigma^2 9\sigma^1 3\pi^1 \rangle - 0.35|7\sigma^2 9\sigma^1 3\pi^3 \rangle$$

$$4s^{1.04} 4p_z^{0.21} 4p_x^{0.03} 4p_y^{0.03} 3d_{z^2}^{0.09} 3d^{0.07} / 2s^{1.88} 2p_z^{1.26} 2p_x^{0.66} 2p_y^{0.66}$$

corroborate the “bonding” scheme (3), sometimes described as “three-electron two-center ($3e^- - 2c$) bond”.

From the 7 remaining triplets, the first 5 correlate adiabatically to $Ca(4s^1 4p^1; ^3P) + C(^3P)$, but we were not able to calculate full PECs for the highest two, $17^3\Delta$ and $18^3\Sigma^+$, states (Figure 1). The dominant CASSCF equilibrium CFs of these 7 triplets, in ascending energy order, are

$$|5^3\Sigma^- \rangle \sim 0.59|7\sigma^2 8\sigma^1 9\sigma^1 3\pi_x^1 3\pi_y^1 \rangle + 0.60|7\sigma^2 8\sigma^1 9\sigma^1 3\pi_x^1 3\pi_y^1 \rangle + 0.44|7\sigma^2 8\sigma^2 3\pi_x^1 3\pi_y^1 \rangle$$

$$|6^3\Delta \rangle \sim 0.67|(7\sigma^2 8\sigma^1 9\sigma^1)(3\pi_x^2 - 3\pi_y^2)$$

$$|9^3\Pi \rangle \sim 0.66|7\sigma^2 8\sigma^1 9\sigma^1 3\pi^3 \rangle - 0.55|7\sigma^2 8\sigma^2 9\sigma^1 3\pi^1 \rangle - 0.27|7\sigma^2 8\sigma^2 3\pi^1 4\pi^1 \rangle$$

$$|11^3\Pi \rangle \sim 0.77|7\sigma^2 8\sigma^1 3\pi^2 4\pi^1 \rangle + 0.30|7\sigma^2 8\sigma^2 9\sigma^1 3\pi^1 \rangle - 0.27|7\sigma^2 8\sigma^1 3\pi^3 \rangle$$

$$|12^3\Sigma^+ \rangle \sim 0.66|(7\sigma^2 8\sigma^1 9\sigma^1)(3\pi_x^2 + 3\pi_y^2)$$

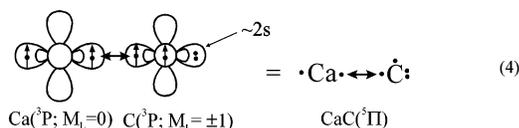
$$|17^3\Delta \rangle \sim 0.64|7\sigma^2 8\sigma^2(3\pi_x^1 4\pi_x^1 - 3\pi_y^1 4\pi_y^1)$$

$$|19^3\Sigma^- \rangle \sim 0.63|7\sigma^2 8\sigma^2(3\pi_x^1 4\pi_x^1 + 3\pi_y^1 4\pi_y^1)$$

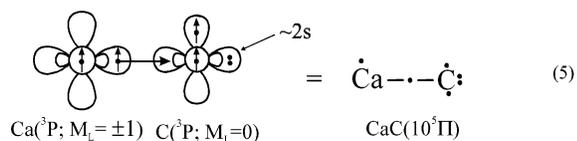
With the exception of the $17^3\Delta$ and $18^3\Sigma^+$ states whose asymptotic products we are not sure about, Table 1 lists dissociation energies and common spectroscopic constants for the rest of the 5 triplets given above.

Of the triplet states presented in this section, the two lower being dipole connected to the ground $X^3\Sigma^-$ state are $3^3\Pi$ and $5^3\Sigma^-$. The respective transitions according to the $\Delta\Lambda = 0, \pm 1$ selection rule (Hund cases (a) and (b)), $3^3\Pi \leftarrow X^3\Sigma^-$ (12 075 cm^{-1}) and $5^3\Sigma^- \leftarrow X^3\Sigma^-$ (13 068 cm^{-1}) might be useful in detecting the CaC species. Because the $X^3\Sigma^-$, $5^3\Sigma^-$ PECs are almost parallel, the $5^3\Sigma^- \leftarrow X^3\Sigma^-$ transitions are strongly Franck-Condon favored, the 0-0, 1-1, and 2-2 FC factors being 0.997, 0.990, and 0.976, respectively. This is not the case for the $3^3\Pi \leftarrow X^3\Sigma^-$ transition, with 0-0, 0-1, 0-2, and 0-3 FC factors of 0.460, 0.442, 0.078, and 0.007, respectively.

3c. Quintets. The $\text{Ca}(4s^1 4p^1; ^3P) + \text{C}(^3P)$ asymptote gives rise to 5 quintets, namely, $^5\Sigma^-$ [2], $^5\Sigma^+$, and $^5\Pi$ [2], three of which ($^5\Sigma^-$, $^5\Sigma^+$, $^5\Pi$), are expected to be repulsive (vide supra) and were not examined. From the remaining two, the $a^5\Sigma^-$ was previously discussed in connection with the $X^3\Sigma^-$ state. We can comprehend why one of the $^5\Pi$ states is (Pauli) repulsive if we take a look at its vbL diagram,



Exchanging the M_L values (0, ± 1) to (± 1 , 0) one expects a bound state according to the following vbL scheme:



A single configuration describes the equilibrium adequately,

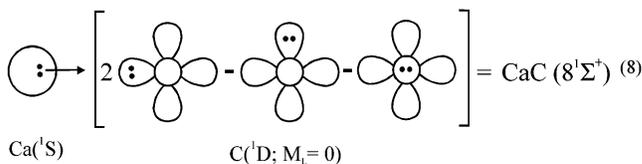
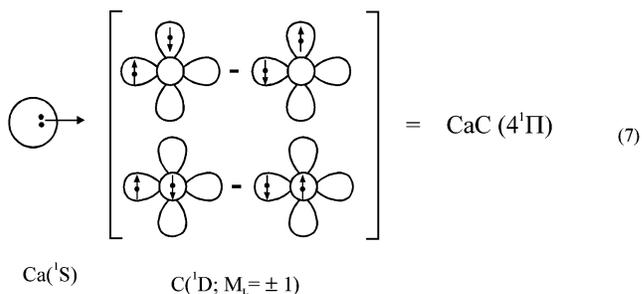
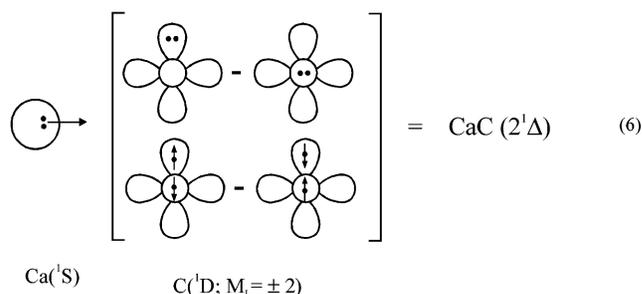
$$|10^5\Pi\rangle \sim 0.97|7\sigma^2 8\sigma^1 3\pi_x^1 3\pi_y^1 4\pi^1\rangle$$

but the Mulliken CASSCF atomic distributions,

$$4s^{0.11} 4p_z^{0.05} 4p_x^{0.02} 4p_y^{0.45} 3d_{z^2}^{0.10} 3d_{xz}^{0.05} 3d_{yz}^{0.42} / 2s^{1.83} 2p_z^{0.86} 2p_x^{1.02} 2p_y^{1.02}$$

reveal a slight complication. Indeed, the two $2p_\pi$ electrons are entirely localized on the C atom, and the $1/2 \sigma$ bond is formed by the migration of about $0.7 e^-$ through the σ skeleton from Ca to C filling its $2p_z$ orbital. However, the significant population ($0.42 e^-$) of the $3d_{yz}$ orbital of Ca is indicative of an interaction with a higher $^5\Pi$ state correlating to the $\text{Ca } ^3D(4s^1 3d^1; M_L=\pm 1)$ state, located 5093.5 cm^{-1} above the $^3P(4s^1 3p^1)$ state.⁷ At the MRCI level we calculate $D_e = 41.5 \text{ kcal/mol}$ at $r_e = 2.314 \text{ \AA}$, 0.055 \AA shorter than the r_e of the $X^3\Sigma^-$ at the same level of theory.

3d. Singlets. Figure 2 shows the PECs of 8 singlet states stemming from two asymptotic channels: $\text{Ca}(^1S) + \text{C}(^1D)$ and $\text{Ca}(^3P) + \text{C}(^3P)$. The first channel gives rise to 3 states of symmetries $^1\Delta$, $^1\Pi$, and $^1\Sigma^+$, whose asymptotic representations are depicted below, icons (6), (7), and (8)



Diagrams (6) and (8) predict bound states through σ -electron transfer from Ca to the empty available $2p_z$ C orbital, a binding mechanism similar to that of the $X^3\Sigma^-$ state, scheme (1). Indeed, atomic equilibrium Mulliken distributions are in conformity with the diagrams above and very similar to those of the X state.

$$|2^1\Delta\rangle: 4s^{0.96} 4p_z^{0.13} 4p_x^{0.05} 4p_y^{0.05} 3d^{0.20} / 2s^{1.85} 2p_z^{0.93} 2p_x^{0.87} 2p_y^{0.87}$$

$$|8^1\Sigma^+\rangle: 4s^{0.93} 4p_z^{0.10} 4p_x^{0.08} 4p_y^{0.08} 3d^{0.23} / 2s^{1.83} 2p_z^{0.94} 2p_x^{0.86} 2p_y^{0.86}$$

This bonding rationalization is finally confirmed by contrasting MRCI D_e and r_e values, 49.4 kcal/mol , 2.385 \AA ($2^1\Delta$), and 36.1 kcal/mol , 2.391 \AA ($8^1\Sigma^+$) to the corresponding values of the X state.

For the $4^1\Pi$ state, scheme (7) suggests a rather repulsive interaction; nevertheless, our calculations predict a binding energy of 41.4 kcal/mol at $r_e = 2.486 \text{ \AA}$ (Table 1). The equilibrium Mulliken analysis (Ca/C)

$$4s^{0.95} 4p_z^{0.25} 4p_x^{0.02} 4p_y^{0.02} 3d_{z^2}^{0.11} 3d_{xz}^{0.07} / 2s^{1.89} 2p_z^{1.26} 2p_x^{0.68} 2p_y^{0.08}$$

indicates that the bonding is caused by the transfer of about $0.5 e^-$ from a $4s 4p_z 3d_{z^2}$ hybrid on Ca to the $2p_\sigma$, $2p_\pi$ orbitals of the C atom, through the interaction of the $13^1\Pi$ state correlating to $\text{Ca}(4s^1 4p^1; ^3P) + \text{C}(^3P)$, Figure 2. This is also suggested by the leading CASSCF equilibrium configurations of the $4^1\Pi$ state:

$$|4^1\Pi\rangle \sim 0.74|7\sigma^2 8\sigma^2 9\sigma^1 3\pi^1\rangle - 0.23|7\sigma^2 8\sigma^1 3\pi^3\rangle - 0.54|7\sigma^2 9\sigma^1 3\pi^3\rangle$$

For those 3 singlets $2^1\Delta$, $4^1\Pi$, and $8^1\Sigma^+$, Takada et al.⁹ obtained practically the same internuclear distances and energy separations (T_e) as those listed in Table 1, whereas their D_e values are smaller than ours by 4.0, 2.6, and 4.8 kcal/mol, respectively.

We now turn to the remaining 5 singlets, which, in ascending energy order are $7^1\Sigma^-$, $13^1\Pi$, $14^1\Pi$, $15^1\Delta$, and $16^1\Sigma^-$. The

$7^1\Sigma^-$ state is degenerate with the $8^1\Sigma^+$ state, correlates to $\text{Ca}(^3\text{P}) + \text{C}(^3\text{P})$, and its equilibrium CASSCF configuration ($\sim 0.97|7\sigma^2 8\sigma^1 9\sigma^1 3\pi_x^1 3\pi_y^1\rangle$) and bonding are identical to those of the $a^5\Sigma^-$ state, but with the four open electrons coupled into a singlet. Pictorially, the bonding is described by scheme (2) consisting of a $1/2 \sigma$ bond, due to $0.6 e^-$ transfer from Ca to the empty $2p_z$ orbital of the C atom according to the Mulliken distributions,

$$4s^{0.85} 4p_z^{0.23} p_x^{0.03} 4p_y^{0.03} 3d^{0.22}/2s^{1.86} 2p_z^{0.87} 2p_x^{0.91} 2p_y^{0.91}$$

At the MRCI level, we predict $D_e = 46.4$ kcal/mol at $r_e = 2.384$ Å.

Both $13^1\Pi$ and $14^1\Pi$ correlate adiabatically to $\text{Ca}(^3\text{P}) + \text{C}(^3\text{P})$ suffering an avoided crossing between themselves at about 3.7 Å, Figure 2. $13^1\Pi$ has a significant binding energy of 34.7 kcal/mol at $r_e = 2.335$ Å, but its binding mode is obfuscated because of its strong multireference character. Now, the $14^1\Pi$ state presents two minima, a shallow one (local) at 3.7 Å, as a result of its interaction with the $13^1\Pi$ state, and a global one at $r_e = 2.162$ Å, the shortest bond length of all states studied. The hump between the two minima is 20 kcal/mol high with respect to the global minimum, the result of an avoided crossing with an incoming $^1\Pi$ (not calculated) state correlating to $\text{Ca}(^3\text{D}) + \text{C}(^3\text{P})$, Figure 2. Although the binding energy of the $14^1\Pi_G$ state is only 16.7 kcal/mol with respect to $\text{Ca}(^3\text{P}) + \text{C}(^3\text{P})$, it is strongly bound with respect to the diabatic fragments $\text{Ca}(^3\text{D}) + \text{C}(^3\text{P})$.

Finally, not much can be said about the two highest singlets $15^1\Delta$ and $16^1\Sigma^-$. Both correlate to $\text{Ca}(^3\text{P}) + \text{C}(^3\text{P})$, and have small binding energies of 13.5 and 12.5 kcal/mol, respectively, at relative large bond distances, 2.599 ($15^1\Delta$) and 2.543 Å ($16^1\Sigma^-$).

4. Synopsis

The electronic states of CaC have been studied by multireference methods (CASCF+1+2=MRCI) using semiquantitative basis sets. Potential energy curves have been constructed for

19 states covering an energy range of about 3.5 eV. A ten-year debate on the identity of the ground state can be considered as over, confirming beyond any doubt that the ground state is of $X^3\Sigma^-$ symmetry, and in accordance with recent experimental results; the $a^5\Sigma^-$ state is calculated to be 1500 to 2500 cm^{-1} higher.

With the exception of the $a^5\Sigma^-$ state, which has a binding energy of 86 kcal/mol, the rest of the states examined are relatively weakly bound with their binding energies ranging between 13 and 50 kcal/mol. All states show strong ionic character with an electron transfer of $0.5\text{--}0.7 e^-$ from Ca to C.

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- (14) We thank Dr. K. A. Peterson for making available to us these newly developed basis sets before publication.
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