
Ground States of BeC and MgC: A Comparative Multireference Brillouin–Wigner Coupled Cluster and Configuration Interaction Study

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ABSTRACT: The competing $X^3\Sigma^-$ and $^5\Sigma^-$ states of the experimentally unknown alkaline–earth metal carbides BeC and MgC are examined with the multireference Brillouin–Wigner coupled cluster method restricted to single and double excitations (MRBW-CCSD). The results are compared against the traditional single-reference CCSD approach, as well as with other single and multireference methods. In both molecules, the CCSD $^5\Sigma^- \leftarrow X^3\Sigma^-$ energy difference is underestimated, leading to an “erroneous” ground-state prediction in BeC. The MRBW-CCSD method corrects this anomalous behavior, leading to fair agreement with multireference configuration interaction (MR-CI) predictions. Our results at the highest levels of theory are extrapolated to the basis

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set limit, and the core/valence correlation is taken into account, leading to very accurate energetics and spectroscopic constants in both carbides. © 2004 Wiley Periodicals, Inc. *Int J Quantum Chem* 102: 762–774, 2005

Key words: carbides; spectroscopic constants; multireference configuration interaction; multireference coupled cluster

Introduction

The coupled-cluster (CC) method [1] has enjoyed considerable success in the accurate prediction of energetics and spectroscopic constants in small molecules. In the early 1980s, the CC variant including single and double excitations (SD) out of a single-reference (Hartree–Fock) wavefunction, CCSD, came forward as a size-extensive counterpart of configuration interaction methods (i.e., CISD) with comparable computational demands for small molecular systems [2]. Yet the “correlation” problem was still present in the quest for “chemically” accurate results. The significant contribution along this development by Pople and coworkers, the “noniterative” triple excitation correction to the CCSD expansion termed “CCSD(T)” [3], became one of the most popular and successful methods of choice for small molecule properties near their equilibrium geometries. This progress, together with the establishment of the correlation-consistent basis sets, have been termed by Dunning as the two recent advances responsible for the dramatic progress in the last decade in predicting with unprecedented accuracy a broad range of molecular properties, including molecular binding energies [4].

Even for equilibrium geometry properties, however, it is well known that single-reference treatments can be inadequate. The extra correlation energy gained by the (T) noniterative correction is sometimes not sufficient to cure the lack of “non-dynamical” correlation energy. Recent tests to such cases using a multireference coupled cluster approach [5] based on the use of the Brillouin–Wigner resolvent (MRBW-CCSD) have been successful so far [6, 7]. The diatomic alkaline–earth metal carbide (MC) diatomics and the isovalent carbides of group 12 of the periodic table have proven to be a good testing ground for multireference methods [7]. The reason lies behind the (*ns*, *np*) “near-degeneracy” of the M atomic orbitals, resulting in a multireference wavefunction with significant biexcited $ns^2 \rightarrow np^2$ character, even at the equilibrium geometry. In a recent paper, we employed the MRBW-CCSD

method in CaC and ZnC in order to compare its performance against conventional single-reference and multireference methods [8, 9]. In the most interesting case of CaC, upon inclusion of the “semi-core” $2s^2 2p^6$ electron correlation of Ca, the CCSD and CCSD(T) methods predicted a $^5\Sigma^-$ ground state differing from a competing $^3\Sigma^-$ state by at least 10 kcal/mol (CCSD level) [7]. The MRBW-CCSD results agreed with large MR-CI calculations predicting a $^3\Sigma^-$ ground state for CaC [8]. While our paper was in press, an experimental study by Ziurys and coworkers [10] in which the pure rotational spectrum of the CaC radical was recorded in the laboratory confirmed the $X^3\Sigma^-$ identity of its ground state.

In the current work, we focus on the lighter members of the series, namely, BeC and MgC. To the best of our knowledge, these two molecules are unknown experimentally; however, several theoretical studies have been devoted to them. In 1993, two groups published extended MR-CI studies on 13 and 23 low-lying states on BeC [11, 12]. In the first work, Borin and Ornellas [11] found a $^3\Sigma^-$ ground state with a binding energy, $D_e = 55.1$ kcal/mol, at a bond length $r_e = 1.667$ Å. The competing $^5\Sigma^-$ state was predicted to lie 5.1 kcal/mol above (T_e value) [11]. It is noted, however, that the D_e values in this work appear to be a bit overestimated (see below). In later papers, the authors studied in more detail the transition dynamics of BeC [13]. In the second work, Wright and Kolbuszewski predicted a somewhat weaker Be–C bond: $D_e = 47.0$ kcal/mol with $r_e = 1.693$ Å (MR-CI results). The T_e value for the first excited $^5\Sigma^-$ state was found to be 6.5 kcal/mol [12]. In 1996, da Silva et al. [14] predicted a $^5\Sigma^-$ ground state for BeC at the CISD and CISD+Q levels; however, the situation was reversed at the generalized valence-bond (GVB) CI and GVB-CI+Q levels with a calculated $^5\Sigma^- \leftarrow ^3\Sigma^-$ energy gap, $T_e = 1.63$ kcal/mol. In more recent work, Kalcher and Sax [15] found the $^5\Sigma^-$ state 5.0 kcal/mol above the $^3\Sigma^-$ at the multireference averaged coupled-pair functional (MRACPF)/aug-cc-pVQZ level of theory. Very recently, MR-CI results with a smaller basis set predicting a Be–C bond strength of $D_e = 49.3$ kcal/mol, and $r_e = 1.683$

Å were published by Pelegrini et al. [16], but no results were reported for the $^5\Sigma^-$ state.

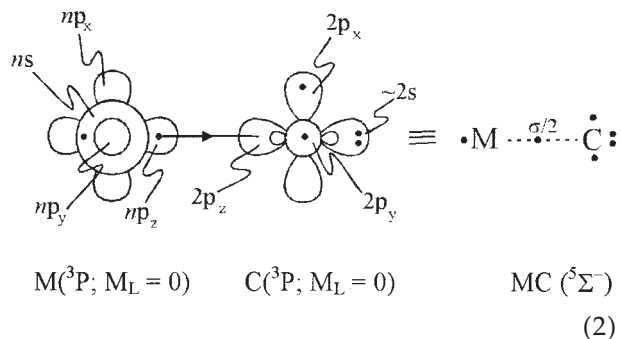
The most thorough work in the literature concerning the MgC molecule comes from the 1993 work of Bauschlicher, Langhoff, and Partridge [17]. These workers used the MR-CI method, as well, coupled with augmented triple and quadruple zeta basis sets for carbon and a corresponding basis set on magnesium with a suitable core polarization potential (CPP). They reported results for 20 low-lying states of MgC. According to their values, there is no doubt for the $^3\Sigma^-$ identity of the ground state of MgC ($D_e = 35.1$ kcal/mol, $r_e = 2.071$ Å), with the $^5\Sigma^-$ state being 10.1 kcal/mol higher [17]. Castro et al. [18] were the first to deal theoretically with the MgC molecule, and they published spectroscopic constants and dipole moments of three states (including the $^3\Sigma^-$ state) using the MP4 expansion. In later work, Castro and Canuto [19] re-examined some electric and spectroscopic properties of MgC at an analogous level of theory. The results of Boldyrev et al. [20] are quite similar to those of Bauschlicher et al. [17], employing similar methods but with the 6-311+G* basis set. For instance, the $T_e(^5\Sigma^- \leftarrow X^3\Sigma^-)$ energy gap of Boldyrev et al. [20] is predicted to be 9.9 and 11.4 kcal/mol at the MR-CI and MR-CI+Q levels of theory, respectively [20]. As with BeC, da Silva et al. [14] predicted a $^5\Sigma^-$ ground state at the CISD level of theory and a smaller, $^5\Sigma^- \leftarrow X^3\Sigma^-$ separation of 8.3 kcal/mol at the GVB-CI+Q level of theory. In subsequent work, the authors reported, however, erroneously, high (see above) binding energies of 89.2 ($X^3\Sigma^-$) and 112.0 ($^5\Sigma^-$) kcal/mol [21]. Kalcher and Sax [15] studied the $X^3\Sigma^-$ state, at the MRACPF/aug-cc-pVQZ level, predicting a bond length, $r_e = 2.089$ Å. Finally, results for the ground state of MgC were published in the aforementioned work of Pelegrini et al. [16], practically in agreement with the work of Bauschlicher et al. [17].

The reason single-reference methods tend to underestimate the $^5\Sigma^- \leftarrow ^3\Sigma^-$ gap in alkaline earth metal (and the other isovalent) carbides, leading even to a ground-state character change, for example, in BeC and CaC (see above), can be traced to the nature of these competing states [7, 8]. The quintet state originates from the $M(^3P; M_L = 0) + C(^3P; M_L = 0)$ components ($M = \text{Be, Mg}$) and is adequately described by the configuration

$$|^5\Sigma^- \rangle \sim |1\sigma^2 2\sigma^1 3\sigma^1 1\pi_x^1 1\pi_y^1 \rangle, \quad (1)$$

where the numbers in front of the molecular orbitals (MOs) refer to the ordering within the valence

space of each molecule. A qualitative view of the bonding can be captured by the following valence-bond–Lewis (vbL) icon:

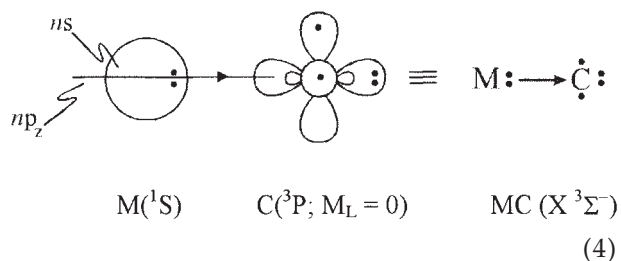


indicating that the M(Be/Mg) and C atoms are “nominally” kept together by a “half” (one-electron) bond, because Mulliken population analysis indicates negligible charge transfer along the π frame. Naturally, the configuration (1) dominates the full-valence (fv) complete active space self-consistent field (CAS-SCF) wavefunction(s) of BeC and MgC.

On the other hand, the triplet state emanates from the $M(^1S) + C(^3P; M_L = 0)$ channel, with the full-valence CAS-SCF wavefunction composed by the following six significantly contributing Slater determinants:

$$\begin{aligned} X^3|\Sigma^- \rangle \sim & C_0|1\sigma^2 2\sigma^2 1\pi_x^1 1\pi_y^1 \rangle + C_1|1\sigma^2 3\sigma^2 1\pi_x^1 1\pi_y^1 \rangle \\ & + C_2|1\sigma^2 \overline{2\sigma^1} 3\sigma^1 1\pi_x^1 1\pi_y^1 + 2\sigma^1 \overline{3\sigma^1} 1\pi_x^1 1\pi_y^1 \\ & + 2\sigma^1 \overline{3\sigma^1} 1\pi_x^1 1\pi_y^1 + 2\sigma^1 3\sigma^1 1\pi_x^1 \overline{1\pi_y^1} \rangle. \quad (3) \end{aligned}$$

At the equilibrium M—C distance(s), the coefficients C_0 , C_1 , and C_2 are equal to 0.80, -0.40 , and 0.20 for BeC and 0.82, -0.37 , and 0.20 for MgC, whereas at infinity $C_2 = 0$, and the 2σ and 3σ MOs correspond to the ns and np_z atomic orbitals of M ($n = 2$ for Be, $n = 3$ for Mg). The qualitative features of the bonding can be depicted succinctly through the vbL icon:



suggesting a pure “dative” bond.

The $X^3\Sigma^-$ state owes its multireference character mainly to the doubly excited ($2\sigma^2 \rightarrow 3\sigma^2$) Slater determinant $|1\sigma^2 3\sigma^2 1\pi_x^1 1\pi_y^1\rangle$ with coefficient C_1 [Eq. (3)], or in other words to the near degeneracy of the ns and $np(np_z)$ orbitals of the M atom. As expected, this state is not adequately described by single-reference methods; indeed, in BeC, this inadequacy becomes so large that in CISD and CCSD, and independently of the basis set size, the ordering of the two states is reversed and the ground state is predicted to be of $^5\Sigma^-$ symmetry.

The principal aim of the current work is to compare the results of the traditional CCSD method with the ones from the MRBW-CCSD. To monitor the results, we compare them with values obtained by fvMR-CI calculations. Furthermore, and in order to obtain very accurate energetics and spectroscopic constants, these will be extrapolated to the basis set limit, and the inner core electron correlation will be added. In this way, we hope to establish very accurate values in order to aid experimentalists in detecting these unobserved diatomics.

Methods

For both molecules, full-potential energy curves were calculated for the $X^3\Sigma^-$ and $^5\Sigma^-$ states in a hierarchy of single-reference and multireference methods, namely, restricted open-shell Hartree-Fock (ROHF), CISD, CISD+Q (= CISD + Davidson correction), RCCSD, MRBW-CCSD, RCCSD(T), fvCAS-SCF, fvMR-CI (internally contracted fvCAS-SCF + single + double replacements) and fvMR-CI+Q (= fvMR-CI + multireference Davidson correction), in conjunction with the correlation-consistent basis sets of Dunning and coworkers of quadruple- ζ quality, cc-pVQZ [22]. For the C atom specifically, this set was augmented by a set of diffuse functions, aug-cc-pVQZ [22b]. This augmentation was deemed necessary, because carbon was observed to acquire significant negative charge as in the isovalent CaC and ZnC molecules [7–9].

In order to assess the adequacy of the basis set and to eliminate any relevant superposition errors, we have also performed calculations with the aforementioned methods near the equilibrium bond distance in both $X^3\Sigma^-$ and $^5\Sigma^-$ states of BeC and MgC, employing the cc-pVnZ_(Be, Mg)/aug-cc-pVnZ_(C) series, with $n = T(3)$, $Q(4)$, and 5, and then extrapolating the binding energies D_e and bond lengths r_e

to the complete basis set (CBS) limit, using the simple exponential formula [23]:

$$P_n = P_\infty + A e^{-Bn}. \quad (5)$$

To improve the D_e , r_e and $T_e(^5\Sigma^- \leftarrow X^3\Sigma^-)$ values, the effect of the $1s^2$ core electrons of Be and C, as well as the “semicore” $2s^2 2p^6$ electron shell of Mg was taken into account by using the cc-pCVQZ_(Be, Mg)/aug-cc-pCVQZ_(C) basis sets [24, 25]. The most extensive basis set used in this work is the cc-pV5Z_(Mg)/aug-cc-pV5Z_(C) basis on MgC containing 222 spherical Gaussian functions. Relativistic effects were assumed to be of minor importance and were not taken into account in the current study.

The zeroth-order space for the multireference calculations was optimized by distributing four electrons (the 2 valence e^- of M + the 2 $p_\pi e^-$ of C) in four orbitals ($2\sigma, 3\sigma, 1\pi_x, 1\pi_y$) using the CAS-SCF methodology and denoted as CAS-SCF(4,4). A fv-CAS-SCF calculation, where all six valence electrons are distributed in the eight valence orbitals corresponding asymptotically to the $ns + np$ and $2s + 2p$ valence orbital spaces of M [= Be ($n = 2$), Mg ($n = 3$)] and C, respectively, was also performed and is denoted as fvCAS-SCF.

Due to implementation limitations, we have used Cartesian Gaussians in all MRBW-CCSD calculations. Furthermore, and in order to reduce computational demands, the potential energy curves in the MRBW-CCSD level were performed with the first four reference Slater determinants of Eq. (3), that is, keeping the two π electrons triplet coupled while utilizing the CAS-SCF(4,4) optimized active space. Thus, the model (projected) reference MRBW-CCSD wavefunction for the $X^3\Sigma^-$ state, Ψ_0^P , is a linear combination of the first four determinants of Eq. (3),

$$\Psi_0^P = \sum_{i=0}^3 C_i \Phi_i. \quad (6)$$

This wavefunction is related to the “exact” ground-state wavefunction Ψ_0 by means of the wave operator $\hat{\Omega}_0$

$$\Psi_0 = \hat{\Omega}_0 \Psi_0^P \quad (7)$$

and to the exact ground-state energy E_0 by means of the effective Hamiltonian, \hat{H}^{eff}

TABLE I

Atomic energies E (hartree) for the ground states of Be($1S$), Mg($1S$), and C(3P) and singlet-triplet ($^3P \leftarrow 1S$) separations (eV) for Be and Mg at different levels of theory, employing the cc-pVQZ_(Be, Mg) and aug-cc-pVQZ_(C) basis.

Method	E			$^3P \leftarrow 1S$	
	Be($1S$)	Mg($1S$)	C(3P)	Be	Mg
NHF ^a	-14.573023	-199.614636	-37.688619		
saSCF ^b	-14.572971	-199.614242	-37.688330	1.620	1.848
CISD	-14.619023	-199.648230	-37.784099	2.741	2.600
CISD+Q ^c			-37.7893		
RCCSD ^d	-14.619023	-199.648230	-37.784586	2.741	2.600
RCCSD(T) ^e			-37.787154		
BW-CCSD ^f			-37.784770		
CAS-SCF(2,2) ^g	-14.591105	-199.626964		2.113	2.140
MR-CI ^h	-14.619132	-199.648232		2.745	2.603
MRBW-CCSD ⁱ	-14.618218	-199.647183		2.720	2.572
fvCAS-SCF ^j	-14.616784	-199.645679	-37.705690	2.867	2.703
fvMR-CI	-14.619137	-199.648235	-37.785706	2.745	2.603
fvMR-CI+Q			-37.788700		
C-RCCSD ^k	-14.665045	-199.950547	-37.836874	2.721	2.662
C-RCCSD(T) ^k	-14.665638	-199.955016	-37.839809	2.735	2.697
C-MRCI ^k	-14.665525	-199.946813	-37.836224	2.744	2.730
C-MRCI+Q ^k	-14.665721	-199.953269	-37.840956	2.735	2.712
Expt. ^l				2.725	2.714

^a Numerical HF (Ref. [31]).

^b Spherically averaged SCF.

^c CISD+Davidson correction.

^d Restricted coupled cluster singles and doubles.

^e RCCSD + perturbative triples.

^f Single-reference BW-CCSD.

^g Active space: $2s + 2p_z$ for Be and $3s + 3p_z$ for Mg.

^h CAS-SCF+1+2.

ⁱ Four-reference BW-CCSD.

^j Full-valence CAS-SCF; active space: $ns + np_{x,y,z}$ for Be ($n = 2$) and Mg ($n = 3$), and $2s + 2p_{x,y,z}$ for C.

^k The $1s^2$ and $2s^2 2p^6$ electrons of Be and Mg, respectively, were included in the correlation treatment.

^l Experimental data (Ref. [32]).

$$\hat{H}^{eff}\Psi_0^P = \mathbf{E}_0\Psi_0^P. \quad (8)$$

The wave operator $\hat{\Omega}_0$ is subject to the state-specific (single-root) Brillouin–Wigner analogue of the Bloch equation

$$\hat{\Omega}_0 = 1 + \hat{B}_0\hat{V}\hat{\Omega}_0, \quad (9)$$

where \hat{V} is the perturbation operator within the Møller–Plesset ansatz, and \hat{B}_0 the Brillouin–Wigner resolvent

$$\hat{B}_0 = \sum_{q>3} \frac{|\Phi_q\rangle\langle\Phi_q|}{\mathbf{E}_0 - E_q}. \quad (10)$$

The matrix elements of \hat{H}^{eff} in a basis of four references $\{\Phi\}_{i=0}^3$, $i = 0 \cdots 3$, have been given previously (Ref. [6(a, c)]). The MRBW-CCSD energy \mathbf{E}_0 is obtained by diagonalization of the $4 \times 4 H^{eff}$ matrix. This energy is then used for upgrading the resolvent (10) and constructing new CC amplitudes and H^{eff} matrix elements, and the whole process is iterated as with the usual single-reference CC methods. The resulting size nonextensivity error is practically eliminated by applying the recently developed a posteriori size-extensivity correction (Refs. [6(b), 26]).

The spectroscopic constants ω_e , $\omega_e x_e$ were calculated by solving the one-dimensional nuclear Schrödinger equation employing a Numerov technique [27].

TABLE II

Total energies E (hartree), binding energies D_e (kcal/mol), bond lengths r_e (Å), frequencies ω_e , $\omega_e X_e$ (cm^{-1}) and energy gaps T_e (${}^5\Sigma^- \leftarrow X^3\Sigma^-$, kcal/mol) of the BeC $X^3\Sigma^-$ and ${}^5\Sigma^-$ states at different levels of theory, employing the cc-pVQZ_{Be}/aug-cc-pVQZ_C basis.^a

Method ^b	$X^3\Sigma^-$					${}^5\Sigma^-$					T_e
	E	D_e	r_e	ω_e	$\omega_e X_e$	E	D_e	r_e	ω_e	$\omega_e X_e$	
ROHF	-52.272605	7.1	1.726	586.7	30.0	-52.350935	93.6	1.624	1035.0	7.0	-49.2
CISD	-52.452186	36.5	1.698	894.6	13.1	-52.467165	104.0	1.628	1008.0	7.2	-9.4
CISD+Q	-52.482712	45.9	1.727	899.5	8.7	-52.474364	104.8	1.633	995.5	6.9	5.2
RCCSD	-52.463855	37.8	1.700	877.3	10.2	-52.469330	104.5	1.630	1004.5	7.1	-3.4
RCCSD(T)	-52.480912	46.9	1.677	901.0	7.8	-52.474232	105.9	1.634	995.0	6.9	4.2
CAS-SCF(4,4)	-52.351200	45.0	1.666	947.4	7.9						0.2 ^c
MR-CI	-52.473155	47.7	1.680	906.7	8.5						3.8 ^c
MR-CI+Q	-52.482277	46.5	1.633	894.7	8.8						5.0 ^c
MRBW-CCSD(4-ref)	-52.474911	45.3	1.677	905.2	9.0	-52.469692 ^d	104.6	1.630	1003.9	6.9	3.3 ^c
MRBW-CCSD(6-ref)	-52.476831	46.5	1.669								4.5 ^{c,e}
fvCAS-SCF	-52.392202	42.5	1.692	900.4	7.7	-52.389041	105.4	1.647	982.3	7.6	2.0
fvMR-CI	-52.481986	48.5	1.684	909.4	8.0	-52.472601	106.2	1.635	991.9	5.9	5.9
fvMR-CI+Q	-52.486183	49.2	1.684	906.2	8.3	-52.475917	106.1	1.635	990.1	6.4	6.4
MR-CI ^f	-52.469248	55.1	1.667	951	8.42	-52.461149	118.1	1.621	1035	7.15	5.1
MR-DCI+Q ^g	-52.478118	47.0	1.693	905		-52.46783	103.1	1.640	978		6.5
GVB-CI ^h	-52.4536		1.695			-52.4534		1.640			0.1
GVB-CI+Q ^{h,i}	-52.4599		1.700	648.65		-52.4573		1.641	318.38		1.6
MRACPF ^j			1.684	908	8.5			1.633	999	7.1	5.0
MR-CI ^k		49.3	1.683	925	11.25						

^a Unless otherwise noted, results are from the current work.

^b See Table I for explanation of the acronyms. All correlated calculations correlate the six-valence electrons, unless otherwise noted.

^c The CAS-SCF(4,4)-based results of the ${}^5\Sigma^-$ state are identical to the ROHF-based results.

^d Single-reference BW-CCSD.

^e Value obtained by subtracting the single-reference BW-CCSD energy of the ${}^5\Sigma^-$ state from the 6-reference BW-CCSD energy of the $X^3\Sigma^-$ state.

^f Configuration-selected MR-CI with $[8s5p2d1f]_{\text{Be}}/[7s6p3d1f]_{\text{C}}$ basis. Dipole moments: $\langle \mu \rangle = 1.573 D$ ($X^3\Sigma^-$) and $0.221 D$ (${}^5\Sigma^-$) (Ref. [11]).

^g Configuration-selected MR-CI with $[6s4p2d1f]_{\text{Be}}/[6s5p2d1f]_{\text{C}}$ basis. Dipole moments: $\langle \mu \rangle = 1.43 D$ ($X^3\Sigma^-$) and $0.40 D$ (${}^5\Sigma^-$) (Ref. [13]).

^h Generalized valence bond + configuration interaction, $[6s4p2d]_{\text{Be}}/[6s5p2d]_{\text{C}}$ basis (Ref. [14]).

ⁱ GVB-CI + Davidson correction (Ref. [14]).

^j Multireference averaged coupled pair functional, cc-pVQZ + $[3s3p2d1f]$ diffuse basis. Dipole moments: $\langle \mu \rangle = 1.70 D$ ($X^3\Sigma^-$) and $0.24 D$ (${}^5\Sigma^-$) (Ref. [15]).

^k Configuration-selected MR-CI with $6-311+G(3d1f)$ basis (Ref. [16]).

For the MRBW-CCSD calculations we have employed a version of the Aces II program [28] extended for MRBW-CCSD calculations [6(a)]; all other calculations have been performed with the Gaussian 98 [29] and Molpro 2002 [30] suite of codes.

Results and Discussion

Table I lists total energies of Be, Mg, and C atoms at various levels of theory, as well as the ${}^3P(ns^1np^1) \leftarrow$

${}^1S(ns^2)$ splittings of Be and Mg. Because the two MC molecular states under current examination, namely, ${}^3\Sigma^-$ and ${}^5\Sigma^-$, correlate to $M({}^1S) + C({}^3P)$ and $M({}^3P) + C({}^3P)$, respectively, it is obvious that the proper description of the ${}^3P \leftarrow {}^1S$ atomic energy differences is crucial for an accurate determination of the energy separation $T_e({}^5\Sigma^- \leftarrow {}^3\Sigma^-)$. From Table I it can be seen that at the highest levels of theory, that is, C-RCCSD(T) and C-MRCI+Q, the ${}^3P \leftarrow {}^1S$ atomic splittings for both metals are in excellent agreement with the experimental values, 2.725 (Be) and 2.714 (Mg) eV [32].

TABLE III

Basis set convergence of binding energies D_e (kcal/mol) and bond lengths r_e (Å) of the BeC $X^3\Sigma^-$ and $5\Sigma^-$ states and the energy gap T_e ($5\Sigma^- \leftarrow X^3\Sigma^-$, kcal/mol) between them at different levels of theory.

Method ^a	$X^3\Sigma^-$							$5\Sigma^-$					
	AVTZ	AVQZ	AV5Z	CBS ^b	Δ_{Core}^c	Best value ^d	AVTZ	AVQZ	AV5Z	CBS ^b	Δ_{Core}^c	Best value ^d	
RCCSD	D_e	36.7	37.8	38.0	38.0	+0.3	38.3	103.4	104.5	104.6	104.6	+0.8	105.4
	r_e	1.708	1.700	1.698	1.697	-0.007	1.690	1.637	1.630	1.630	1.630	-0.006	1.624
	T_e							-3.37	-3.44	-3.41		-0.93	-4.3
MRBW-CCSD (4-ref)	D_e	44.1	45.3				103.6	104.6					
	r_e	1.685	1.677				1.637	1.630					
	T_e						3.26	3.28					
RCCSD(T)	D_e	45.6	46.9	47.2	47.3	+0.5	47.8	104.8	105.9	106.1	106.1	+0.9	107.0
	r_e	1.684	1.677	1.677	1.677	-0.006	1.671	1.641	1.634	1.633	1.633	-0.006	1.627
	T_e							4.09	4.19	4.23	4.26	-0.45	3.8
fvMR-CI	D_e	47.4	48.5	48.8	48.9	0.0	48.9	104.6	106.2	106.3	106.3	+0.9	107.2
	r_e	1.692	1.684	1.684	1.684	-0.005	1.679	1.642	1.635	1.635	1.635	-0.007	1.628
	T_e							5.93	5.89	5.89	5.89	-0.91	5.0
fvMR-CI+Q	D_e	48.0	49.2	49.5	49.6	+0.1	49.7	105.2	106.1	106.2	106.2	+0.7	106.9
	r_e	1.692	1.684	1.684	1.684	-0.004	1.680	1.642	1.635	1.635	1.635	-0.007	1.628
	T_e							6.46	6.44	6.45	6.45	-0.86	5.6

^a See Table I for explanation of the acronyms: AVnZ stands for the (cc-pVnZ)_{Be}/(aug-cc-pVnZ)_C basis set, with $n = T(3), Q(4),$ and 5. All correlated calculations correlate the six-valence electrons, unless otherwise noted.

^b Complete basis set limit.

^c Defined as the difference between the values obtained using the AVQZ and the (cc-pCVQZ)_{Be}/(aug-cc-pCVQZ)_C basis sets.

^d Defined as CBS limit value + Δ_{core} value.

BeC

Tables II and III present numerical results for the $X^3\Sigma^-$ and $5\Sigma^-$ states of the BeC molecule in a sequence of methods of increasing sophistication. Complete potential energy curves (PEC) at the RCCSD, RCCSD(T), MRBW-CCSD, and fvMR-CI/[cc-pVQZ_(Mg)/aug-cc-pVQZ_(C)] levels are given in Figure 1.

Following the results of Table II, we see that the ROHF, CISD, and CCSD methods fail in predicting the correct ordering of the $3\Sigma^-$, $5\Sigma^-$ states, in contrast to CISD+Q and RCCSD(T), which give the correct ordering and reasonable binding energies. On the other hand, the MRBW-CCSD approach based either on four or six references gives the correct ordering, as opposed to the RCCSD method, and a fairly good binding energy as contrasted to our best value of 50 kcal/mol (see below). The significance of multireference character of the wavefunction for the $3\Sigma^-$ state is obvious at the fvCAS-SCF level, showing dramatic improvement in comparison even with the CISD and RCCSD methods.

The $5\Sigma^-$ state, due to its strictly single-reference character, is described equally well in all methods, even at the ROHF level; see Table II.

In Table III we report the effect of basis set size and the $1s^2$ core electrons of both Be and C to the properties of the $3\Sigma^-$ and $5\Sigma^-$ states of BeC, as we move from AVTZ to AVQZ to AV5Z size bases. For technical reasons we were unable to carry out MRBW-CCSD/AV5Z calculations.

The inclusion of the core electrons decreases the bond distances in both states by less than 0.01 Å, whereas it increases the D_e values by no more than 1 kcal/mol. Interestingly, at the RCCSD/A5Z+core level, the $5\Sigma^- - 3\Sigma^-$ separation increases by about 1 kcal/mol as compared with the RCCSD/AQZ, predicting erroneously the $5\Sigma^-$ state to be the ground state.

Our best extrapolated fvMR-CI+core+Q r_e and D_e values for the $X^3\Sigma^-$ and $5\Sigma^-$ states are 1.680 and 1.628 Å, and 49.7 and 106.9 kcal/mol, respectively, with a $5\Sigma^- \leftarrow X^3\Sigma^-$ energy separation of 5.6 kcal/mol.

MgC

Tables IV and V list our findings on the $X^3\Sigma^-$ and $5\Sigma^-$ states of MgC, whereas full PECs at all methods employed in this study coupled with the AVQZ basis sets are presented in Figure 2.

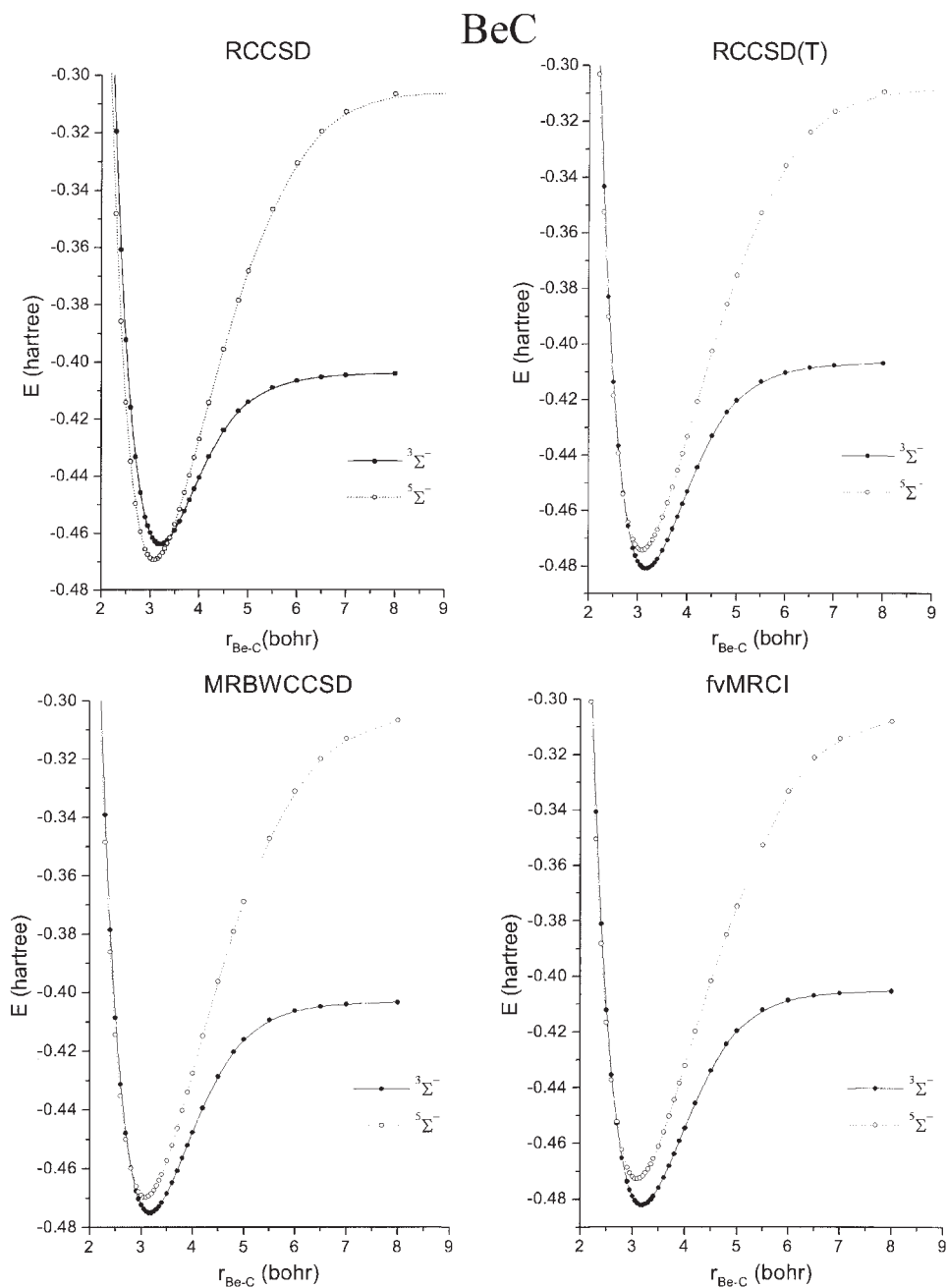


FIGURE 1. The PECs of the $X^3\Sigma^-$ and $5\Sigma^-$ states of the BeC molecule at selected levels of theory. Energies have been shifted by +52 hartree.

With the necessary changes made, the results on MgC follow closely the corresponding values on BeC. At the ROHF level, the $X^3\Sigma^-$ state is repulsive and the CISD method predicts erroneously the $5\Sigma^-$ as the ground state. Although RCCSD predicts correctly the ground-state symmetry, the $5\Sigma^- \leftarrow X^3\Sigma^-$

energy separation is far from being satisfactory, 2.9 versus 11.3 kcal/mol, considered to be our best value (see below). Certainly, as in the case of BeC, the CISD+Q and RCCSD(T) properties of the $X^3\Sigma^-$ state are in very good agreement with our best fvMR-CI+Q+core CBS values.

TABLE IV

Total energies E (hartree), binding energies D_e (kcal/mol), bond lengths r_e (Å), frequencies ω_e , $\omega_e X_e$ (cm^{-1}), and energy gaps T_e (${}^5\Sigma^- \leftarrow X^3\Sigma^-$, kcal/mol) of the MgC $X^3\Sigma^-$ and ${}^5\Sigma^-$ states at different levels of theory, employing the cc-pVQZ_{Mg}/aug-cc-pVQZ_C basis.^a

Method ^b	$X^3\Sigma^-$					${}^5\Sigma^-$					T_e
	E	D_e	r_e	ω_e	$\omega_e X_e$	E	D_e	r_e	ω_e	$\omega_e X_e$	
ROHF	Repulsive					-237.352577	72.7	2.042	619.3	3.4	-35.5
CISD	-237.462852	23.5	2.105	505.0	6.7	-237.468087	83.1	2.052	599.7	3.7	-3.3
CISD+Q	-237.493582	35.0	2.074	578.1	4.7	-237.475341	83.9	2.057	593.2	3.6	11.4
RCCSD	-237.474871	26.4	2.097	526.5	6.0	-237.470208	83.4	2.053	597.7	3.5	2.9
RCCSD(T)	-237.489220	33.8	2.085	554.7	4.4	-237.475184	85.0	2.058	591.9	3.5	8.8
CAS-SCF(4,4)	-237.362770	29.7	2.069	578.5	4.3						6.4 ^c
MR-CI	-237.483792	35.3	2.083	556.0	4.5						9.9 ^c
MR-CI+Q	-237.492306	34.7	2.090	546.5	4.4						10.6 ^c
MRBW-CCSD(4-ref)	-237.483888	32.7	2.086	546.2	4.1	-237.470584 ^d	83.6	2.054	594.6	1.8	8.3 ^c
MRBW-CCSD(6-ref)	-237.484394	33.0	2.077								8.7 ^{c,e}
fvCAS-SCF	-237.401404	30.1	2.101	549.1	4.1	-237.388329	83.0	2.072	589.0	3.3	8.2
fvMR-CI	-237.490411	35.6	2.089	550.0	4.4	-237.473300	85.1	2.059	589.9	3.4	10.7
fvMR-CI+Q	-237.494795	36.4	2.090	547.3	4.5	-237.477063	85.3	2.059	588.7	3.5	11.1
UHF-MBPT(4) ^f			2.093	527.1	5.6						
MR-CI+Q ^g		35.7 ^h	2.071 ⁱ				84.9 ^j	2.078 ^j			10.1 ^j
MBPT(2) ^k	-237.54866		2.087	507		-237.56361		2.064	593		-9.4
QCISD(T) ^l	-237.47358		2.083			-237.45680		2.062			10.5
MR-CI ^m	-237.48796		2.094	543		-237.47211		2.065	573		9.9
MR-CI+Q ^m	-237.49350		2.099	536		-237.47539		2.066	572		11.4
GVB-CI ⁿ	-237.4513		2.110			-237.4401		2.080			7.0
GVB-CI+Q ^{n,o}	-237.4572	89.2 ^p	2.103	492.51	8.016 ^p	-237.4439	112.0 ^p	2.096	559.10	8.137 ^p	8.3
MRACPF ^q			2.089	558	7.4						
MR-CI ^r		35.5	2.089	555	5.55						

^a Unless otherwise noted, results are from the current work.

^b See Table I for explanation of the acronyms. All correlated calculations correlate the six-valence electrons, unless otherwise noted.

^c The CAS-SCF(4,4)-based results of the ${}^5\Sigma^-$ state are identical to the ROHF-based results.

^d Single-reference BW-CCSD.

^e Value obtained by subtracting the single-reference BW-CCSD energy of the ${}^5\Sigma^-$ state from the 6-reference BW-CCSD energy of the $X^3\Sigma^-$ state.

^f Fourth-order many-body perturbation theory based on an unrestricted HF reference with $[6s4p2d]_{\text{Mg}}/[6s4p2d]_{\text{C}}$ basis. Dipole moment at the UHF level: $\langle \mu \rangle = 3.17 D$ ($X^3\Sigma^-$) (Ref. [18]).

^g MR-CI + Davidson correction with $[9s9p7d4f1g]_{\text{Mg}}/[6s5p4d3f2g]_{\text{C}}$ basis (Ref. [17]).

^h D_0 value.

ⁱ Value obtained with the use of a CPP.

^j Values obtained with the $[9s9p7d4f1g]_{\text{Mg}}/[5s4p3d2f]_{\text{C}}$ basis.

^k Second order many-body perturbation theory with 6-311+G* basis (Ref. [20]).

^l Quadratic CI + perturbative triple excitations with 6-311+G(2df) basis (Ref. [20]).

^m MR-CI and MR-CI+Q with $[7s5p3d2f]_{\text{Mg}}/[7s5p3d2f]_{\text{C}}$ basis (Ref. [20]).

ⁿ Generalized valence bond + configuration interaction, $[6s4p2d]_{\text{Mg}}/[6s4p2d]_{\text{C}}$ basis (Ref. [14]).

^o GVB-CI + Davidson correction (Ref. [14]).

^p Reference [21].

^q Multireference averaged coupled pair functional, cc-pVQZ + $[3s3p2d1f]$ diffuse basis. Dipole moment: $\langle \mu \rangle = 3.51 D$ ($X^3\Sigma^-$) (Ref. [15]).

^r Configuration selected MR-CI with 6-311+G(3d1f) basis (Ref. [16]).

Comparing the RCCSD properties of the $X^3\Sigma^-$ state as well as the ${}^5\Sigma^- \leftarrow X^3\Sigma^-$ splitting with the corresponding MRBW-CCSD(4-ref or 6-ref) numbers, the superiority of the latter method is clear: the binding energies and ${}^5\Sigma^- \leftarrow X^3\Sigma^-$

separation are in reasonable agreement with our best findings, showing again the pitfalls of single-reference methods in cases where near-degeneracy effects are prominent; see also Refs. [7–9].

TABLE V

Basis set convergence of binding energies D_e (kcal/mol) and bond lengths r_e (Å) of the MgC $X^3\Sigma^-$ and $^5\Sigma^-$ states and the energy gap T_e ($^5\Sigma^- \leftarrow X^3\Sigma^-$, kcal/mol) between them at different levels of theory.

Method ^a		$X^3\Sigma^-$						$^5\Sigma^-$					
		AVTZ	AVQZ	AV5Z	CBS ^b	Δ_{Core}^c	Best value ^d	AVTZ	AVQZ	AV5Z	CBS ^b	Δ_{Core}^c	Best value ^d
RCCSD	D_e	25.7	26.4	26.7	26.9	-0.5	26.4	83.0	83.4	83.8	84.6	+1.2	85.8
	r_e	2.103	2.097	2.094	2.091	-0.013	2.078	2.059	2.053	2.052	2.052	-0.014	2.038
	T_e							2.94	2.93	2.93	2.93	-0.25	2.7
MRBW-CCSD (4-ref)	D_e	31.9	32.7					83.1	83.6				
	r_e	2.091	2.086					2.059	2.054				
	T_e							8.31	8.35				
RCCSD(T)	D_e	32.9	33.8	34.1	34.3	-0.4	33.9	84.4	85.0	85.4	86.2	+1.2	87.4
	r_e	2.091	2.085	2.083	2.082	-0.014	2.068	2.063	2.058	2.056	2.055	-0.016	2.039
	T_e							8.69	8.81	8.84	8.85	+0.44	9.3
fvMR-CI	D_e	34.8	35.6	35.9	36.1	-1.4	34.7	84.6	85.1	85.5	87.1	+0.8	87.9
	r_e	2.095	2.089	2.087	2.086	-0.016	2.070	2.064	2.059	2.057	2.056	-0.016	2.040
	T_e							10.7	10.7	10.7	10.7	-0.1	10.6
fvMR-CI+Q	D_e	35.6	36.4	36.7	36.9	-1.4	35.5	84.7	85.3	85.7	86.5	+0.9	87.4
	r_e	2.095	2.090	2.087	2.083	-0.017	2.066	2.065	2.059	2.057	2.056	-0.018	2.038
	T_e							11.1	11.1	11.1	11.1	+0.2	11.3

^a See Table I for explanation of the acronyms; AVnZ stands for the (cc-pVnZ)_{Mg}/(aug-cc-pVnZ)_C basis set, with $n = T(3), Q(4),$ and 5. All correlated calculations correlate the six-valence electrons, unless otherwise noted.

^b Complete basis set limit.

^c The difference between the values obtained using the AVQZ and the (cc-pCVQZ)_{Mg}/(aug-cc-pCVQZ)_C basis sets.

^d The CBS limit value + Δ_{core} value.

No comments are needed for the $^5\Sigma^-$ state, where its strictly single-reference character renders its treatment much easier.

Our MR-CI or MR-CI+Q results (Table IV) are the best so far published, judging from the absolute energies of previously published works and also in comparison with the results of Table V (see below). The GVB-CI+Q dissociation energies of $X^3\Sigma^-$ and $^5\Sigma^-$ states, 89.2 and 112.0 kcal/mol, listed in Table IV [21] are clearly wrong, possibly because the end products were considered to be Mg($3s^13p^1; ^3P$) + C(3P) and Mg($3s^2; ^1S$) + C($2s^12p^3; ^5S$), respectively.

The effects of basis set size (AVTZ to AV5Z)+core on the two states of MgC are reported in Table V. The inclusion of core electrons ($2s^22p^6$ on Mg and $1s^2$ on C) decreases the bond distances in both states by about 0.015 Å, whereas D_e values decrease (increase) by 0.5–1.5 (1.0) kcal/mol in the $X^3\Sigma^-$ ($^5\Sigma^-$) state; T_e ($^5\Sigma^- \leftarrow X^3\Sigma^-$) values remain practically unaffected. Unfortunately, and due to technical reasons, we were unable to extend our calculations to the MRBW-CCSD(4-ref)/AV5Z level of theory.

Our best fvMR-CI+core+Q CBS limit results are: $X^3\Sigma^-$: $r_e = 2.066$ Å, $D_e = 35.5$ kcal/mol; and $^5\Sigma^-$: $r_e = 2.039$ Å, $D_e = 87.4$ kcal/mol, T_e ($^5\Sigma^- \leftarrow X^3\Sigma^-$) = 11.3 kcal/mol.

Synopsis and Scholia

The $^3\Sigma^-$ and $^5\Sigma^-$ states of the diatomic carbides BeC and MgC were examined by various single and multireference methods. The main goal of the current work was the comparison of the RCCSD with the newly developed multireference MRBW-CCSD method. Our results indicate an overall better performance of the MRBW-CCSD method as contrasted to the single-reference RCCSD approach. In particular, the former predicts correctly the ground-state symmetry of BeC, $^3\Sigma^-$, as opposed to RCCSD, which favors the $^5\Sigma^-$ state. The $^5\Sigma^- \leftarrow X^3\Sigma^-$ energy separation is $T_e = 4.5$ kcal/mol at the MRBW-CCSD(6-ref) level, in fair agreement with the fvMR-CI+Q value of 6.4 kcal/mol. Including the $1s^2$ core electrons of both Be and C in the CI procedure, the $^5\Sigma^- \leftarrow X^3\Sigma^-$ splitting reduces to a final value of 5.6 kcal/mol.

Analogous results are obtained in the case of MgC. Here, the T_e ($^5\Sigma^- \leftarrow X^3\Sigma^-$) splitting is 11.1 kcal/mol at the fvMR-CI+Q level but only 2.9 kcal/mol using the RCCSD approach. The MRBW-CCSD(6-ref) method improves significantly the RCCSD T_e value to 8.7 kcal/mol, now in much better agreement with the fvMR-CI+Q number.

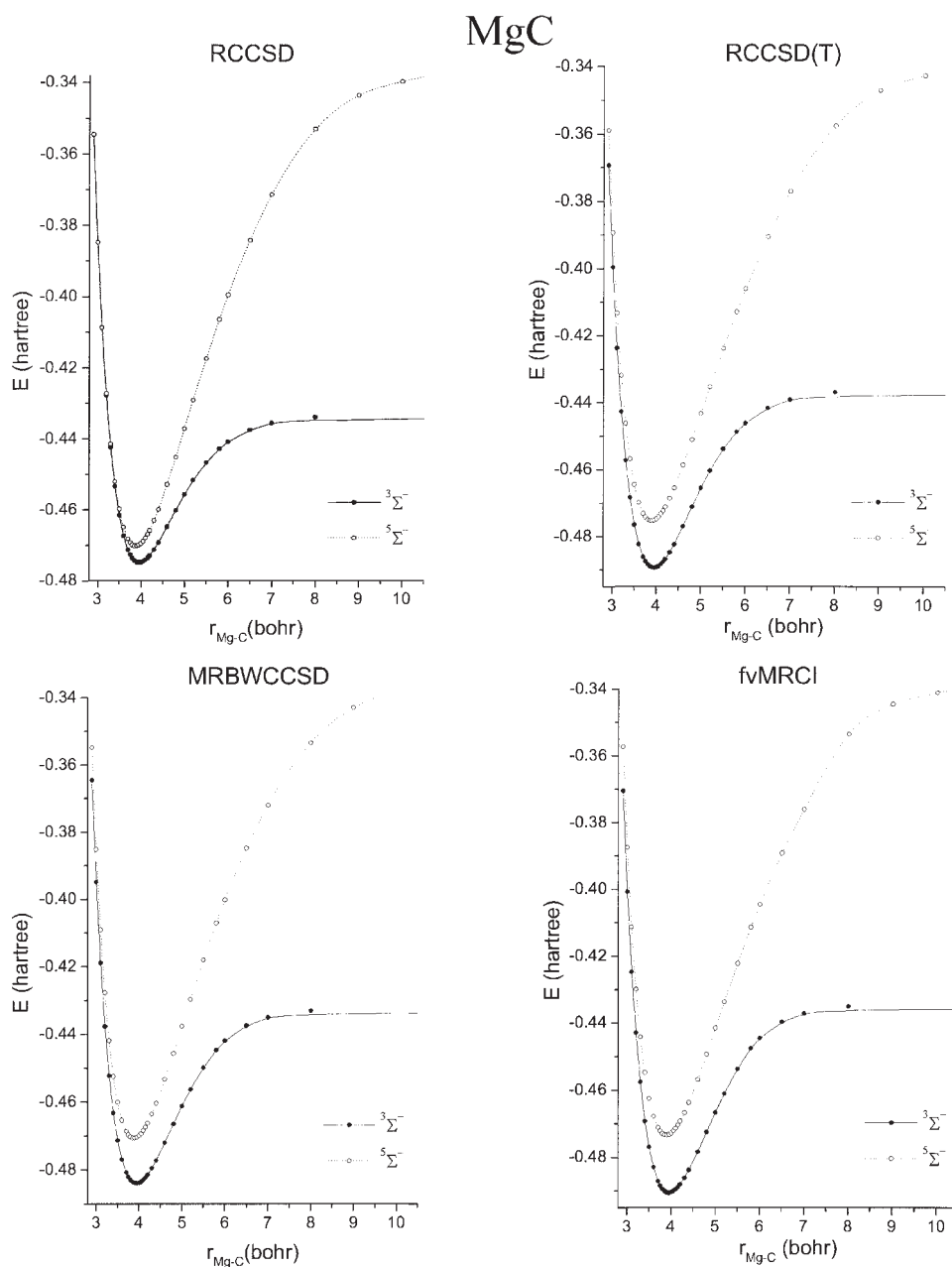


FIGURE 2. The PECs of the $X^3\Sigma^-$ and $5^5\Sigma^-$ states of the MgC molecule at selected levels of theory. Energies have been shifted by +237 hartree.

The bonding, described pictorially in Schemes 4 and 2 of the introduction for the $3^3\Sigma^-$ and $5^5\Sigma^-$ states, respectively, is also corroborated nicely by the Mulliken atomic CAS-SCF population analysis:

$X^3\Sigma^-$ [Scheme 4]:

$$2s^{0.85}2p_z^{0.44}2p_x^{0.09}2p_y^{0.09} / \text{Be}2s^{1.76}2p_z^{0.89}2p_x^{0.89}2p_y^{0.89} / \text{C}$$

$$3s^{1.11}3p_z^{0.28}3p_x^{0.04}3p_y^{0.04} / \text{Mg}2s^{1.86}2p_z^{0.84}2p_x^{0.93}2p_y^{0.93} / \text{C}$$

$5^5\Sigma^-$ [Scheme 2]:

$$2s^{0.71}2p_z^{0.57}2p_x^{0.11}2p_y^{0.11} / \text{Be}2s^{1.76}2p_z^{0.91}2p_x^{0.87}2p_y^{0.87} / \text{C}$$

$$3s^{0.87}3p_z^{0.42}3p_x^{0.06}3p_y^{0.06} / \text{Mg}2s^{1.83}2p_z^{0.93}2p_x^{0.92}2p_y^{0.92} / \text{C}$$

TABLE VI

Summary of best predicted bond lengths r_e (Å), binding energies D_e (kcal/mol), and dipole moments $\mu(D)$ for the $X^3\Sigma^-$ and $^5\Sigma^-$ states of the four metal carbides BeC, MgC, CaC, and ZnC, as well as the $T_e(^5\Sigma^- \leftarrow X^3\Sigma^-)$ separation energies (kcal/mol).

Property		BeC ^a	MgC ^a	CaC ^b	ZnC ^c
r_e	$X^3\Sigma^-$	1.680	2.066	2.330 ^d	1.960
	$^5\Sigma^-$	1.628	2.038	2.305	1.925
D_e	$X^3\Sigma^-$	49.7	35.5	51.0	23.7
	$^5\Sigma^-$	107	87.4	86.2	90.4
μ	$X^3\Sigma^-$	1.70 ^e	3.50 ^e	3.51 ^f	3.17 ^f
	$^5\Sigma^-$	0.21 ^e	2.57 ^e	3.37 ^f	2.07 ^f
T_e		5.6	11.3	4.3–7	26–29

^a Results obtained from current work.

^b Ref. [8].

^c Ref. [9].

^d Experimental r_0 value: 2.3015 Å, Ref. [10].

^e Finite field values at the C-fvMR-CI+Q/[CQZ/ACQZ] level.

^f Expectation values at the fvMR-CI level.

In both symmetries, the bonding is due to the electron transfer from the metal to the empty $2p_z$ orbital of the in situ C atom in the $^3P(M_L = 0)$ state. Overall, 0.47 (BeC) and 0.58 e^- (MgC) are transferred from the metal to the C atom in the $X^3\Sigma^-$ state. The corresponding numbers for the $^5\Sigma^-$ state are 0.43 and 0.61 electrons. The same kind of bonding was observed in the isovalent molecules CaC and ZnC and for the same symmetries [7–9].

Finally, and for reasons of easy comparison, Table VI lists best (based on MR-CI findings) bond distances (r_e), dissociation energies (D_e), dipole moments (μ) and $^5\Sigma^- \leftarrow X^3\Sigma^-$ energy separations (T_e) of all four isovalent carbides, BeC, MgC, CaC, and ZnC. With the exception of the r_e value of the $X^3\Sigma^-$ state of CaC [10], no experimental results are available for those four species; we hope that our findings will help their experimental detection and characterization.

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