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Theoretical Characterization of the Ground State of the Alkaline-Earth Monocarbides: Ordering of the Two Lower-Lying States of the BeC, MgC, and CaC Molecules

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ABSTRACT

The two lower-lying electronic states ($^3\Sigma^-$ and $^5\Sigma^-$) of the BeC, MgC, and CaC molecules were investigated using restricted Hartree–Fock (RHF), generalized valence bond (GVB), and configuration interaction (CI) calculations to establish the relative ordering of those states as a function of the size of the alkaline-earth element. It is shown that as a result of the competition between bonding effects, which predominate for the $^3\Sigma^-$ states, and exchange effects, which stabilize the $^5\Sigma^-$ states, the ordering of these states can be reversed as we move from the Be to the Ca atom. For both the BeC and MgC molecules, the ground state was found to be a triplet $X^3\Sigma^-$ state, but for the CaC molecule, the high-spin $X^5\Sigma^-$ becomes more stable. © 1996 John Wiley & Sons, Inc.

Introduction

The identification of the SiC [1] molecule in space [1] has prompted the search for other monocarbide molecules. Since the experimental characterization and identification of these molecules is based mostly on spectroscopic measurements, the determination of their ground states and the calculation of their spectroscopic constants became an important theoretical problem.

Besides the astrophysical interest, the theoretical investigation of the ground state of these

molecules reveals another interesting aspect of the problem, namely, the competition between a $^3\Sigma^-$ state and a $^5\Sigma^-$ state, originated from different electronic configurations and stabilized by different effects [2].

Previous calculations for BeC [3, 4] and MgC [5–7], using different methodologies, indicated a triplet ground state with a quintet $^5\Sigma^-$ state lying very close above. For the CaC molecule, only the $^3\Sigma^-$ state and higher-energy states have been calculated [8]. In none of these calculations was a comparative analysis attempted to try to understand which effects stabilize each one of the states and how their magnitude would vary with the nature of the alkaline-earth atom.

In a recent publication [2], we discussed the main stabilization effects for the two lower-lying valence states ($^3\Sigma^-$ and $^5\Sigma^-$) of the MgC molecule. It was shown that the $^3\Sigma^-$ state is stabilized mostly by bonding effects while the $^5\Sigma^-$ state is stabilized mostly by exchange effects. It was also pointed out [2] that those effects are sensitive to variations in the interatomic distance, and as the van der Waals radius of the alkaline-earth atom increases, one could observe an inversion in the ordering of the states.

A semiquantitative analysis, based either on the molecular orbital (MO) or valence-bond (VB) models, can be very helpful in understanding the role played by the bonding and exchange effects as the size of the alkaline-earth atom is increased. As we move down in the periodic table, from the Be to the Ca atom, the energies of the outermost atomic orbitals become closer. Therefore, when combining those orbitals with the atomic orbitals of the carbon atom, it is reasonable to expect that the resulting valence molecular orbitals will be much closer in energy for the CaC molecule than for the BeC molecule. In fact, this is exactly what has been

found from a simple HF calculation. Therefore, one should expect orbital single occupation to be favored by the closeness of the MO energies. Thus, exchange effects should increase as we move down the periodic table (Be → Ba). On the other hand, as the alkaline-earth van der Waals radius increases, the bond distances will tend to be larger and the bonding effects less operative. Therefore, one should expect bonding effects to become less important as we move from Be → Ba in the periodic table.

Figure 1 shows the GVB diagrams for the triplet and quintet states of the three molecules. In Figure 1, ∞ represents a p orbital in the plane of the page; $\bigcirc$, a p orbital pointing out the plane of the page; $\bigodot$, a lobe (hybrid s–p) orbital, and only the valence electrons are represented. The dots indicate the number of electrons in each orbital and a straight line connecting them indicates that the electrons are singlet-paired.

From Figure 1, one sees that the triplet states are stabilized by a σ ($^3\Sigma^-$) bond between the $2p$ (C) and the nsp (Be, Mg, Ca) atomic orbitals and by the delocalization of the np_y (Be, Mg, Ca) orbital toward the carbon atom (long arrow). On the other hand, the quintet states are stabilized by a σ ($^5\Sigma^-$) bond involving the $2sp$ (C) and nsp (Be, Mg, Ca) atomic orbitals and by the exchange effects. Even though the σ ($^5\Sigma^-$) bond is stronger than is the σ ($^3\Sigma^-$) [2], the ground state of the BeC and MgC molecules is a $^3\Sigma^-$ state, what led us to the conclusion that the main stabilization effect for the $^3\Sigma^-$ states is the delocalization (half-bond) of the np_y orbital toward the carbon atom. This effect overcomes the exchange effects stabilizing the $^5\Sigma^-$ states and sets the $^3\Sigma^-$ as the ground state for both molecules. As the van der Waals radius of the alkaline-earth element increases, one should expect a decrease in the overlap between the orbitals
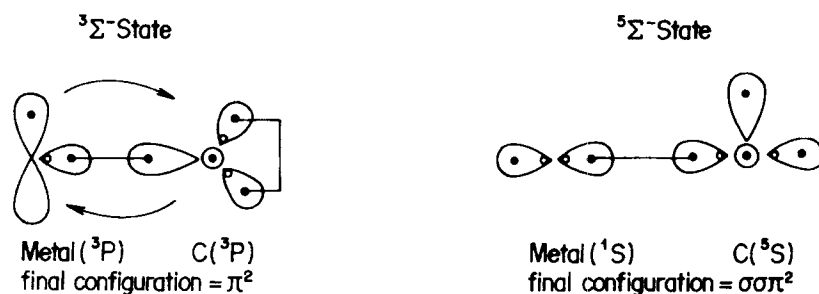

$^3\Sigma^-$ State

Metal (^{3}P)   C(^{3}P)
final configuration = π^2

$^5\Sigma^-$ State

Metal (^{1}S)   C(^{5}S)
final configuration = $\sigma\sigma\pi^2$

FIGURE 1. GVB diagrams for the $^3\Sigma^-$ and the $^5\Sigma^-$ states.
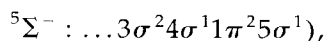
involved in the σ bonds and also in the delocalization (half-bond) of the p_y orbital of the element toward the carbon atom. Thus, as we move down the periodic table (Be → Ba), the bonding effects should become less important and that should affect both the $^3\Sigma^-$ and the $^5\Sigma^-$ states. However, as the interatomic distances increase, one should expect a decrease in the overlap between the two singly occupied σ orbitals of the $^5\Sigma^-$ states and, consequently, an increase in the stabilization by exchange effects.

Therefore, no matter which model (MO or GVB) we use to analyze the relative importance of the two effects, the final conclusion is that somewhere along the column of the alkaline-earth elements one could find an inversion in the ordering of those two states and, consequently, a drastic change in the nature of the ground state.
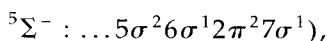
To verify this hypothesis, calculations similar to the ones performed for the MgC molecule [2] were performed for the $^3\Sigma^-$ and $^5\Sigma^-$ states arising from the following electronic configuration:
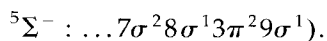
$$BeC\ (^3\Sigma^-\ :\ \ldots 3\sigma^2 1\pi^2 4\sigma^2$$

and

$$^5\Sigma^-\ :\ \ldots 3\sigma^2 4\sigma^1 1\pi^2 5\sigma^1),$$

$$MgC\ (^3\Sigma^-\ :\ \ldots 5\sigma^2 2\pi^2 6\sigma^2$$

and

$$^5\Sigma^-\ :\ \ldots 5\sigma^2 6\sigma^1 2\pi^2 7\sigma^1),$$

and

$$CaC\ (^3\Sigma^-\ :\ \ldots 7\sigma^2 3\pi^2 8\sigma^2$$

and

$$^5\Sigma^-\ :\ \ldots 7\sigma^2 8\sigma^1 3\pi^2 9\sigma^1).$$

Computational Details

For the BeC calculations, we used a $(11s6p2d/6s4p2d)$ basis set originated from Dunning's [9, 10] basis augmented with diffuse and polarization functions [3] for the berilium atom. For the carbon atom, we used a $(11s7p2d/6s5p2d)$ basis, also originated from Dunning's [9] $(10s6p/5s4p)$ basis set, augmented with diffuse s and p functions [10] and d polarization functions [11].

For the MgC molecule, we used Dunning's $(9s5p/5s3p)$ basis for the carbon atom [12] and McLean and Chandler's $(12s8p/6s4p)$ Gaussian basis set [13] for the magnesium atom. Both sets were augmented with d-type polarization functions as suggested by Castro et al. [5]. The basis set for the carbon atom was further augmented with one s-type and one p-type basis function, as described in [5].

For the CaC molecule, we used Wachters' [14] basis set for the calcium atom and Dunning's [12] basis for the carbon atom, both augmented with one diffuse s and p function and one d-type polarization function as suggested in [8]. The final bases are for C: $(14s11p2d/8s6p2d)$, and for Ca: $(10s6p2d/6s4p2d)$. The sizes of our final basis sets, although limited by our computational capabilities, should not affect the main conclusions of our calculations.

Wave functions were computed at the HF and GVB [15–17] levels of calculation, for the states shown in Figure 1. A detailed description of the GVB wave function for the MgC molecule can be found in [2] and similar expressions can be written for the BeC and CaC molecules.

TABLE I

Energies (Hartree) for each state at different levels of calculation; the nos. in parentheses are their equilibrium internuclear distance (Å).

	BeC		MgC		CaC	
	$^3\Sigma^-$	$^5\Sigma^-$	$^3\Sigma^-$	$^5\Sigma^-$	$^3\Sigma^-$	$^5\Sigma^-$
SDCI–HF	−52.4392	−52.4528	−237.4380	−237.4394	−714.5713	−714.5946
	(1.825)	(1.632)	(2.150)	(2.080)	(2.399)	(2.357)
SDCI–HF + Q	−52.4571	−52.4576	−237.4524	−237.4438	−714.5891	−714.5988
	(1.735)	(1.624)	(2.100)	(2.080)	(2.338)	(2.360)
SDCI–GVB	−52.4536	−52.4534	−237.4513	−237.4401	−714.5899	−714.5950
	(1.695)	(1.640)	(2.110)	(2.080)	(2.384)	(2.357)
SDCI–GVB + Q	−52.4599	−52.4573	−237.4572	−237.4439	−714.5949	−714.5990
	(1.700)	(1.641)	(2.120)	(2.080)	(2.389)	(2.359)

In addition, CI wave functions were computed using the basis of molecular orbitals obtained from the HF and GVB calculations. For the CI calculations, we considered variational spaces formed by the HF and/or GVB plus the virtual orbitals, from the self-consistent calculations performed on each of the states shown in Figure 1, for the three molecules. The variational spaces comprise 57 orbitals (23σ, 26π, and 8δ) for the BeC molecule, 50 orbitals (20σ, 22π, and 8δ) for the MgC molecule, and 54 orbitals (22σ, 24π and 8δ) for the CaC molecule. The core orbitals of each molecule were kept frozen in all calculations.

For each molecule, two sets of CI calculations were performed considering all single and double (SD) excitations from the occupied valence orbitals to the respective virtual spaces. In the first set of calculations, we used the HF basis and the HF configuration as a reference to generate the CI wave functions (SDCI–HF). In the other set of calculations, the GVB basis was used. In this set of calculations, all the GVB configurations needed to describe the couplings shown in Figure 1 were used as reference configurations [2]. We denote this set of wave functions as (SDCI–GVB). These two sets of wave functions were corrected for quadruple excitations using either Langhoff and Davidson's [18] expression (SDCI–HF + Q) or Jankowski's expression [19] (SDCI–GVB + Q).

Results and Discussion

For all molecules, the results obtained at the HF and GVB levels of calculation indicate the $^5\Sigma^-$ state as the ground state. This was expected from our previous analysis. It is well known that the HF wave function does not take into account the correlation needed to properly compute the bonding effects but does describe reasonably well the exchange effects which stabilize high-spin states of unpaired electrons. In the GVB description, that part of the correlation energy, called nondynamic correlation, is recovered and the difference in energy between the two states drops substantially. However, the consideration of the nondynamic correlation is not enough to overcome the stabilization of the $^5\Sigma^-$ by the exchange effects.

Table I shows the results obtained with the different CI wave functions for the three molecules. From Table I, we can clearly see how dependent is the ordering of the states on our ability to properly

describe the bonding effects. At the lowest level of calculation (SDCI–HF), only part of the dynamic correlation effects are recovered, and as a result, the $^5\Sigma^-$ states are lower in energy than are the respective $^3\Sigma^-$ states. After higher-order correlation effects are considered (SDCI–HF + Q), the $^3\Sigma^-$ and $^5\Sigma^-$ states of the BeC molecule become
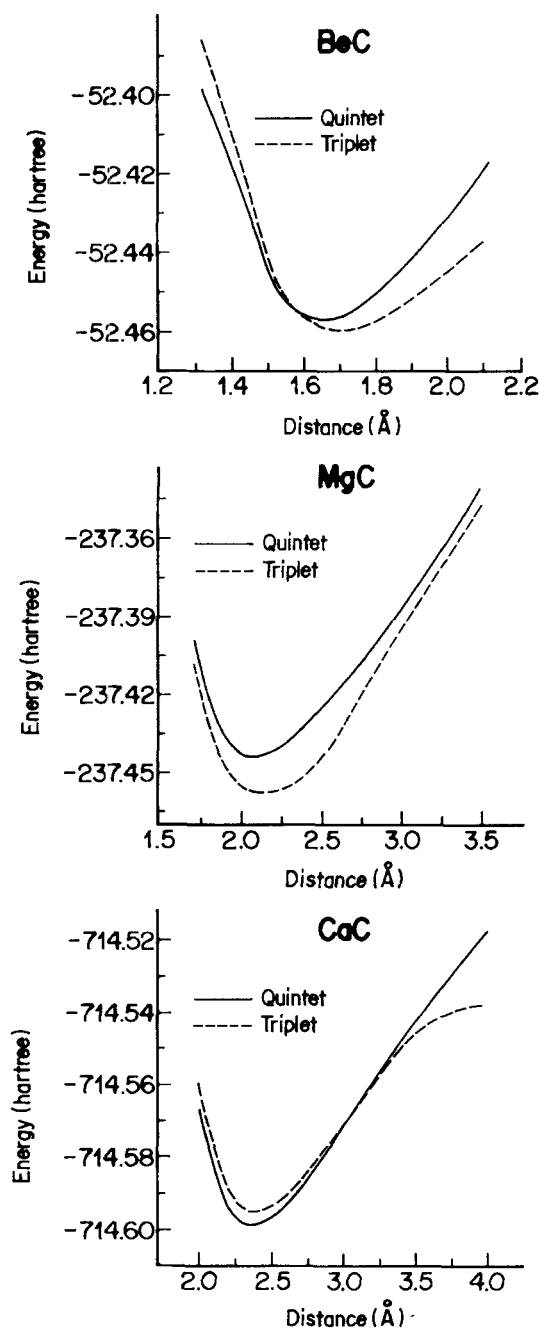

FIGURE 2. Potential curves at SDCI–GVB + Q level for the $^3\Sigma^-$ and $^5\Sigma$ states of BeC, MgC, and CaC molecules.

TABLE II

Spectroscopic constants for the two lower-lying states of the BeC, MgC, and CaC molecules.

	BeC		MgC		CaC	
	$^3\Sigma^-$	$^5\Sigma^-$	$^3\Sigma^-$	$^5\Sigma^-$	$^3\Sigma^-$	$^5\Sigma^-$
r_e (Å)	1.700	1.641	2.103	2.096	2.389	2.359
B_e (cm^{-1})	1.481	-1.263	0.469	0.488	0.319	0.328
ϖ_e (cm^{-1})	648.65	318.38	492.51	559.10	424.87	474.06
$\Delta G_{v+1/2}$ (cm^{-1})	828.16($\nu_{0\to1}$)	1261.14($\nu_{0\to1}$)	482.69($\nu_{0\to1}$)	567.32($\nu_{0\to1}$)	433.43($\nu_{0\to1}$)	463.56($\nu_{0\to1}$)
	973.83($\nu_{1\to2}$)	1358.55($\nu_{1\to2}$)	483.86($\nu_{1\to2}$)	561.29($\nu_{1\to2}$)	446.93($\nu_{1\to2}$)	464.75($\nu_{1\to2}$)

practically degenerated, but for the MgC and CaC molecules, the difference in energy is large enough to characterize their ground states as $^3\Sigma^-$ (MgC) and $^5\Sigma^-$ (CaC). These results are again consistent with our previous discussion about the relative importance of bonding and exchange effects in the ordering of the states. Because the bonding effects are larger for the BeC molecule, they may not be fully recovered at the SDCI–HF + Q level of calculation inasmuch as this is an approximation to the total contribution of the quadruple excitations. On the other hand, since bond effects should become less important as one increases the size of the alkaline-earth atom, it is reasonable to expect that most of the correlation needed to properly describe the bonding effects for the MgC and CaC molecules can be recovered at the SDCI–HF + Q level of calculation.

The SDCI–GVB results should be similar to the SDCI–HF + Q ones because some of the reference configurations used in the GVB–CI calculations are already double excited relative to the HF reference configuration. This is confirmed by the results in Table I. For the BeC molecule, the states are practically degenerated and the ordering of the states for the other two molecules is the same one resulting from the SDCI–HF + Q calculations.

After correcting the SDCI–GVB wave functions for quadruples excitation, the results indicate a $^3\Sigma^-$ for the ground state of the BeC and MgC molecules but a $^5\Sigma^-$ for the ground state of the CaC molecule. The results for the BeC and MgC molecules are in good agreement with more extensive calculations [3–7]. Therefore, we believe that our calculations correctly predict the ordering of the states of the CaC molecule. The potential curves for these molecules, obtained at SDCI–GVB + Q level of calculation, are shown in Figure 2. From those curves, the spectroscopic constants shown in Table II were calculated using the MOLCAS [20]

code. The similarity of the spectroscopic constants, mainly for the MgC and CaC molecules, must be carefully considered in any attempt to experimentally characterize the ground state of these molecules.

Conclusions

From the calculations described in the previous sections, the following conclusions can be drawn: The ground state of the BeC and MgC molecules is the triplet $^3\Sigma^-$ state with a quintet $^5\Sigma^-$ state lying very close above. For the CaC molecule, the ordering of these states is reversed. The correct ordering of these states is achieved only after allowing SD excitations from GVB configurations (SDCI–GVB). The $^5\Sigma^-$ states are stabilized mostly by exchange effects, whereas bonding effects predominate in the $X^3\Sigma^-$. The bonding effects become less important as we move down in the periodic table (Be → Ba), while the exchange effects become more important. As a consequence, one observes an inversion in the ordering of the $^3\Sigma^-$ and $^5\Sigma^-$ states as the van der Waals radius of the alkaline-earth atom increases.

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