

# Energetics and bonding in beryllium metallized carbon clusters

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## Abstract

Small carbon clusters C, C<sub>2</sub> and C<sub>3</sub> metallized with beryllium were studied by first principles within the hybrid density functional approach with generalized gradient correction. Cluster isomer structures for the ground state and several excited states were systematically calculated for C<sub>x</sub>Be<sub>y</sub>, with  $x = 1-3$  and  $y = 1-4$  including the vibrational analysis of all states. Ionization potentials and electron affinities are calculated for the ground state cluster isomers. The thermal stability of the ground state isomers was verified within the harmonic approximation of the Helmholtz free energy up to temperatures of about 1000 K. Within the family of clusters studied, C<sub>2</sub>Be<sub>3</sub> undergoes a solid-like structural transition at about 260 K changing from a planar structure at low temperatures to a linear isomer at high temperatures.

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## 1. Introduction

Beryllium carbide compounds are less well known than compounds of the heavier alkaline earths. The importance of metallized carbon clusters is highlighted by the synthesis applications and characterization of a variety of functionalized fullerenes [1]. The early metallization of small carbon clusters has an intrinsic interest for several nuclear and plasma applications where binary metal carbides form composite materials in thin films and fibers. For example, beryllium carbide thin films are used as confinement target coatings in magnetic fusion reactors. From the perspective of organic compounds, it is important to understand unusual geometries that macromolecules containing Be and other electropositive elements acquire along their synthetic growth. It is recognized that small molecular units are the building blocks of complex molecular assemblies and that the characteristics of those building blocks are fundamental in determining the structure of the assembly. For example, binary tetratomic C<sub>3</sub>Be clusters have isomers with

characteristic electron charge distribution in the bonding region [2]. Similarly, several metal carbide crystals are ceramic materials displaying the antifluorite structure, in which the metal atoms lie in tetrahedral coordination and the C atoms in octahedral sites. On the other hand, studies of boron molecular compounds show the preference for bridged or planar structures [3]. Several polyolithium-carbon compounds are predicted to exhibit planar rather than tetrahedral carbon atoms [4,5], while other compounds have electron deficient bridging lithium sites [6,7]. Recently it was demonstrated that lithium carbide clusters [8] tend to be planar and allow for hyperlithiation. Additionally, calculations of CBe<sub>2</sub>, C<sub>2</sub>Be and C<sub>2</sub>Be<sub>2</sub> demonstrated that several planar structures develop as the size of the cluster grows larger [9].

In this work, we perform an exhaustive all-electron study within the density functional theory (DFT) framework and the generalized gradient approximation (GGA) of C<sub>x</sub>Be<sub>y</sub> clusters containing up to three carbon atoms and four beryllium atoms. Section 2 provides a description of the methodology used, includes results for the CBe molecule and gives a thorough comparison between various calculation methods. The energetics and vibrational frequencies for the family of four CBe<sub>x</sub> ( $x = 1, 2, 3, 4$ ) clusters

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are described in Section 3. Sections 4 and 5 contain the results for seven binary clusters  $C_2Be_x$  ( $x = 1, 2, 3, 4$ ) and  $C_3Be_x$  ( $x = 1, 2, 3$ ), respectively. Concluding remarks are the subject of Section 6.

## 2. Methods and the CBe molecule

Throughout this work the Kohn–Sham equations [10] were solved self-consistently using the GGA representation of the correlation functional and Becke's 3-parameter hybrid functional [11] with Purdue and Wang local and non-local correlation functionals [12,13]. The B3PW91 method, a triple valence basis set containing 8s, 7p and 1d Gaussians contracted as (62111111,3311111,3) and augmented with one d polarization function, and the Gaussian 03 package [14] were used. The basis set was found to be sufficiently large to give good results at a reasonable computational effort. Adding one or two diffuse functions produced insignificant changes in both the energy and bond length of the diatomics. The basis set superposition error (BSSE) [15] gave corrections on the order of 0.025 eV for calculations including one or two polarization functions. Therefore the BSSE was not carried out for the larger clusters. Worth noting is that BSSE is important when the basis set is small, and the basis set used in this work is large.

The DFT hybrid method was validated by a thorough comparison of the ground and first excited states of CBe with full CI, CASSCF with an active space of five orbitals and six electrons. The B3PW91 reproduced these states well, as is shown in Fig. 1. Our calculations for CBe are in excellent agreement with previous CI results [16,17] of the ground and first excited state differing by 2% at most. The ground

state is confirmed to be  $^3\Sigma^-$ , with binding energy of  $-2.566$  eV and constants  $R_e = 1.666$  Å,  $\omega_e = 926$   $\text{cm}^{-1}$ ,  $\omega_e x_e = 10.4$   $\text{cm}^{-1}$ ,  $B_e = 1.179$   $\text{cm}^{-1}$ ,  $\alpha_e = 7.22$  Å<sup>3</sup>,  $\mu_e = 1.41$  D. The fitted Morse parameters for this state are  $D_e = 2.566$  eV,  $R_e$  same as above, and  $\beta = 1.7798$  Å<sup>-1</sup>. The Mulliken charges are  $-0.15$  e on the carbon atom and  $0.15$  e on the Be atom. Our calculated ionization potential (IP) and electron affinity (EA) are  $8.69$  eV and  $1.24$  eV, respectively. The ground state of the cation and anion for the IP and EA are  $^4\Sigma^-$ . The anion ground state is in agreement with that reported in Ref. [18].

The first excited state of different multiplicity is a low-lying  $^5\Sigma^-$  at  $0.1911$  eV above the ground state. The diatomics in this excited state dissociates into  $^3P$  states for both Be and C with  $D_e = 4.67$  eV and has constants  $R_e = 1.630$  Å,  $\omega_e = 995$   $\text{cm}^{-1}$ ,  $\omega_e x_e = 6.4$   $\text{cm}^{-1}$ ,  $B_e = 1.232$   $\text{cm}^{-1}$ ,  $\alpha_e = 5.33$  Å<sup>3</sup> and  $\mu_e = 0.08$  D, and the Morse  $\beta = 1.4$  Å<sup>-1</sup>. The second excited state is a  $^3\Sigma^-$  at  $0.4653$  eV above the ground state that dissociates into the  $^3P$  and  $^1S$  of C and Be, respectively. Constants for this excited state are  $D_e = 2.113$  eV,  $R_e = 1.667$  Å,  $\omega_e = 915$   $\text{cm}^{-1}$ ,  $\omega_e x_e = B_e = 1.178$ ,  $\alpha_e = 8.41$  Å<sup>3</sup>,  $\mu_e = 3.56$  D and the Morse  $\beta = 1.92$  Å<sup>-1</sup>. This state was not reported in previous works [16,17].

## 3. Family of $CBe_x$ , $x = 2, 3, 4, 5$ clusters

In this section we describe the energetics for the cluster family  $CBe_x$ , with  $x = 2-5$ . Across the family there is a recurring substructure of an isosceles triangle with the C atom at the apex that occurs in all isomers of the ground state, except for  $CBe_2$ . The CBe bond lengths do not change much along this family of clusters, being close to  $1.6 \pm 0.05$  Å. The addition of one extra Be to the clusters stabilizes the binding energy of the ground state by a gain of  $2.64$  eV on the average. However, the gain in the case of  $CBe_3$  is about  $1$  eV larger indicating a very favorable pyramidal structure. An analysis of the overlap weighted natural atomic orbital bond order shows that the energetically preferred structures have beryllium atoms mutually bonded. However,  $CBe_4$  is an exception where there is no apparent bonding between the Be atoms. As a comparison, in the case of carbon–lithium clusters the metal–metal bonding begins with five metal atoms. This suggests that in the  $CBe_x$  family of clusters, sub-clustering of pure metal atoms may occur in larger structures. In this family of clusters, ground state structures and excited isomers are depicted in Fig. 2, with details reported in Table 1. Worth noticing is the high multiplicity of the ground state. Indeed, the diatomic molecule is a triplet, and all others are quintets with the exception of  $CBe_3$ , which is a singlet.

The normal mode frequencies of vibration were calculated for all the states of each cluster size and are reported in Table 2. Additionally, these frequencies were used in the harmonic calculation of the Helmholtz free energy as a function of temperature. This thermodynamics calculation helps to determine if the ground state isomer at zero temperature continues to be the most stable isomer at finite

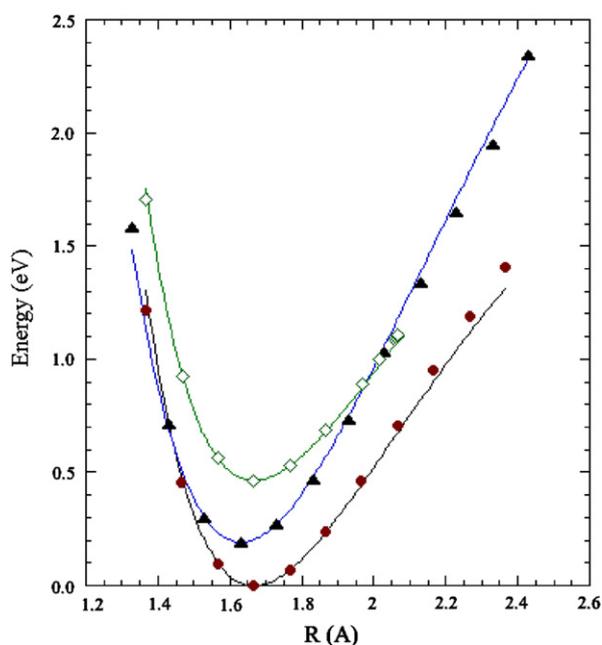


Fig. 1. Potential energy curves of CBe ground state  $^3\Sigma^-$  (circles) and two excited electronic states  $^5\Sigma^-$  (open diamonds) and  $^3\Sigma^-$  (triangles).

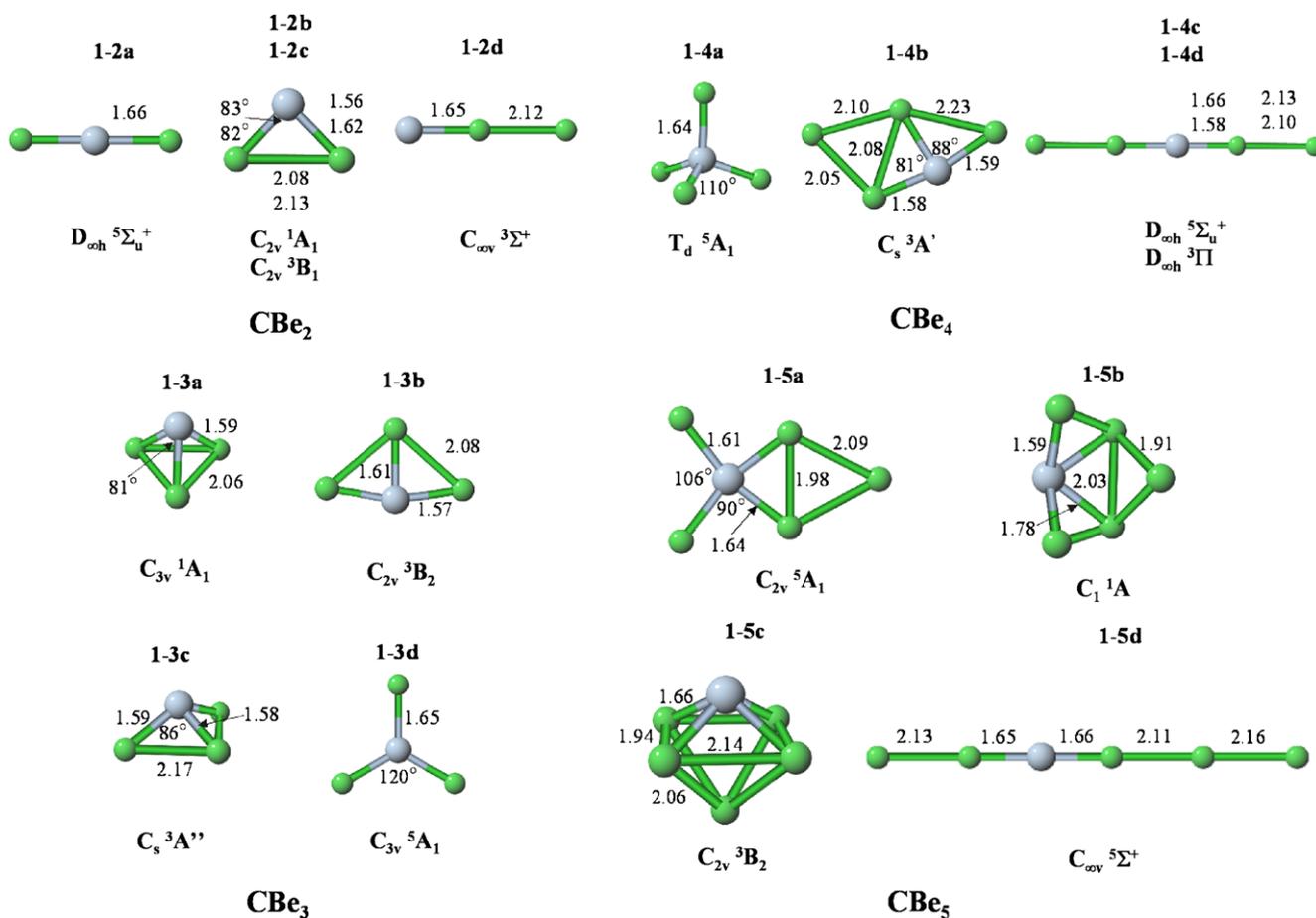


Fig. 2. The  $\text{CBe}_x$  ( $x = 1-5$ ) structural characteristics of the ground state and various excited electronic states. Bond lengths are expressed in Å.

Table 1  
Calculated binding energies and dipole moments of  $\text{CBe}_x$  ( $x = 1-5$ ) for the ground state and various excited states (structure given in Fig. 2)

Species	Cluster	Group	State	$E_b^a$ (eV)	$\ D\ ^d$
CBe	1-1a	$C_{\infty v}$	$^3\Sigma^-$	-2.5936	1.4095
	1-1b	$C_{\infty v}$	$^5\Sigma^-$	-2.4024	0.0765
	1-1c	$C_{\infty v}$	$^3\Sigma^-$	-2.1283	3.556
CBe <sub>2</sub>	1-2a	$D_{\infty h}$	$^5\Sigma_u^+$	-5.5665	0
	1-2b	$C_{2v}$	$^1A_1$	-5.4537	3.6434
	1-2c	$C_{2v}$	$^3B_1$	-5.4372	2.3713
	1-2d	$C_{\infty v}$	$^3\Sigma^-$	-4.0199	0.9535
CBe <sub>3</sub>	1-3a	$C_{3v}$	$^1A_1$	-9.2844	1.96
	1-3b	$C_{2v}$	$^3B_2$	-8.9338	1.1544
	1-3c	$C_s$	$^3A''$	-8.9147	1.5991
	1-3d	$C_{3v}$	$^5A_1$	-8.1582	0.0002
CBe <sub>4</sub>	1-4a	$T_d$	$^5A_1$	-11.2225	0
	1-4b	$C_s$	$^3A'$	-10.8196	3.3506
	1-4c	$D_{\infty h}$	$^5\Sigma_u^+$	-8.46191	0
	1-4d	$D_{\infty h}$	$^3\Pi$	-8.04918	0
CBe <sub>5</sub>	1-5a	$C_{2v}$	$^5A_1$	-13.1449	1.073
	1-5b	$C_1$	$^1A$	-13.0324	1.7484
	1-5c	$C_{2v}$	$^3B_2$	-12.9936	0.9521
	1-5d	$C_{\infty v}$	$^5\Sigma^-$	-9.80623	0.1753

Table 2  
Calculated normal mode vibrational frequencies of  $\text{CBe}_x$  ( $x = 1-5$ ) corresponding to the states reported in Table 1

Species	Cluster	Frequencies ( $\text{cm}^{-1}$ )
CBe	1-1a	927
	1-1b	995
	1-1c	913
CBe <sub>2</sub>	1-2a	218, 218, 756, 1138
	1-2b	497, 1081, 1152
	1-2c	371, 963, 971
	1-2d	184, 184, 475, 1031
CBe <sub>3</sub>	1-3a	404(2), 477, 995(2), 1059
	1-3b	96, 304, 401, 798, 979, 1274
	1-3c	88, 230, 290, 865, 1025, 1114
	1-3d	180(2), 262, 727, 1022(2)
CBe <sub>4</sub>	1-4a	168(2), 219(3), 724, 984(3)
	1-4b	113, 172, 229, 401, 447, 613, 829, 937, 1267
	1-4c	58(2), 165(2), 309(2), 362, 523, 904, 1193
	1-4d	48, 52, 143, 166, 223, 290, 369, 489, 958, 1309
CBe <sub>5</sub>	1-5a	98, 151, 196, 262, 267, 412, 424, 651, 745, 809, 1111, 1152
	1-5b	179, 195, 350, 452, 467, 597, 618, 690, 749, 808, 996, 1068
	1-5c	281, 373, 378, 381, 498, 585, 614, 646, 650, 916, 933, 959
	1-5d	44, 45, 115, 116, 212(2), 282, 336(2), 464, 669, 921, 1197

temperatures up to about 1000 K or if a solid-like structural transition to one of the excited isomers is apparent. In this family of clusters, the ground state isomer continues to be the most stable (lowest free energy) up to temperatures of about 1000 K.

***CBe<sub>2</sub>***: There are four states studied for this cluster size, two of them belonging to isomers of similar geometry. The symmetry and state identification are shown in Fig. 2, isomers 1-2a through 2d, and in Table 1. The ground state is a linear  ${}^5\Sigma_g^-$  with a binding energy of  $-5.57$  eV, ionization potential of  $7.50$  eV, and electron affinity of  $1.68$  eV. The ionization potential (IP) and electron affinity (EA) were calculated with respect to the ground states of the cation and anion clusters, which are relaxed linear structures:  $\text{CBe}_2^+$  in the  ${}^4\Sigma_g^+$  state and  $\text{CBe}_2^-$  in the  ${}^4\Pi$  state, respectively. Our findings for the ground state are in disagreement with results by Koch et al. [9], who report the ground state being a non-linear  $C_{2v}$   ${}^1A_1$  isomer. Their results are based on CASSCF and MP2 with a smaller basis set than the one used in this study. The ground state of Koch et al. [9] is comparable to the first excited state found in our work. The energy difference between our ground state and first excited state is  $0.11$  eV, but is questionable in reference [9]. The C–Be bond lengths in the  $D_{\infty h}$  structure are  $1.66$  Å, which are comparable to Koch et al. [9] linear isomer triplet state, which was a saddle point in our study.

Normal mode vibrational frequencies for these four states are given in Table 2. The most intense IR active mode of the ground state at  $1138$   $\text{cm}^{-1}$  corresponds to an oscillation of the carbon atom back and forth between the two beryllium atoms.

***CBe<sub>3</sub>***: There are four states studied for this cluster size, all of them belonging to isomers with different geometries as shown in Fig. 2, 1-3a through 1-3d. The ground state structure is non-planar  $C_{3v}$   ${}^1A_1$  state with binding energy of  $-9.28$  eV and a total dipole of  $1.96$  Debye as shown in Table 1. It is worth noting that in this family of clusters, this cluster size is the only one having a singlet ground state and the largest dipole moment. The ground state of the relaxed cation  $\text{CBe}_3^+$  is a  ${}^2A'$  with  $C_s$  geometry and the relaxed anion  $\text{CBe}_3^-$  is a  ${}^4A_1$  with  $C_{3v}$  geometry. The ionization potential is  $7.09$  eV and the electron affinity is  $1.53$  eV. The strongest normal mode vibrations are  $404$  and  $1059$   $\text{cm}^{-1}$ . The C–Be bond lengths are  $1.59$  Å, the shortest in this family of clusters.

The first excited state has a planar  $C_{2v}$  geometry in the  ${}^3B_2$  state. This isomer has a binding energy that differs from the ground state by  $0.3506$  eV. The strongest normal mode vibrations are  $366$  and  $1274$   $\text{cm}^{-1}$ . The energies and normal mode frequencies for the second and third excited states are found in Tables 1 and 2.

***CBe<sub>4</sub>***: Four states of this cluster size were studied, two of them belonging to linear isomers of similar geometry. The ground state isomer is tetrahedral  $T_d$  in the  ${}^5A_1$  state consisting of a metallic cage around the carbon atom as shown in Fig. 2. Bond lengths and angles are depicted in

the same figure. The ground state binding energy is  $-11.22$  eV and this highly symmetric isomer has zero dipole moment as summarized in Table 1. The ground states of the cation  $\text{CBe}_4^+$  and anion  $\text{CBe}_4^-$  are relaxed  $T_d$  structures: the  $D_{2d}$   ${}^2B_2$  and the  $T_d$   ${}^4A_1$ , respectively. The ionization potential is  $6.72$  eV and electron affinity is  $1.56$  eV. The strongest IR mode of vibration is  $984$   $\text{cm}^{-1}$  which is threefold degenerate.

The first excited state has a planar geometry  $C_s$   ${}^3A'$  state. The excited state binding energy differs by  $0.403$  eV from the ground state. The second and third excited states are both linear  $D_{\infty h}$  with the second being a quintet ( ${}^5\Sigma_g^-$ ) and the third being a triplet ( ${}^3\Pi$ ). The frequencies of normal mode vibrations are reported in Table 2.

***CBe<sub>5</sub>***: There are four states studied for this cluster size, all of them belonging to isomers with different geometries. The ground state isomer is a planar  $C_{2v}$  structure having a state  ${}^5A_1$  and a binding energy of  $-13.1449$  eV. The dipole moment is  $1.099$  Debye in the direction of the carbon and the most distant beryllium atom. The ionization potential is  $6.45$  eV and electron affinity is  $1.96$  eV. The ground states of the cation and anion are relaxed  $C_{2v}$  geometries in the  ${}^2B_2$  state and  ${}^4B_2$  state, respectively. The strongest normal modes of vibration are  $267$ ,  $410$  and  $1112$   $\text{cm}^{-1}$ .

The first excited state is a non-planar  $C_1$  structure in the  ${}^1A$  state with a binding energy  $0.113$  eV below the ground state. The dipole is  $1.75$  Debye which points perpendicular to the plane created by the three bonded beryllium atoms in the direction of the other two beryllium atoms that are out of the plane. The second excited state has a  $C_{2v}$  geometry with the carbon on the top and a beryllium rectangular pyramid on the bottom as depicted in Fig. 2 1-5c. The third excited state has a linear  $C_{\infty v}$  geometry.

#### 4. The $C_2\text{Be}_x$ , $x = 1, 2, 3, 4$ clusters

The energetics and electronic properties for the family of clusters  $C_2\text{Be}_x$  are described in this section. Across this family the ground state contains a sub-cluster  $C_2$  with about constant bond length of  $1.26$  Å, which is characteristic of the C–C triple bond. The binding energy as a function of the number of metal atoms in the cluster indicates that the linear  $C_2\text{Be}_2$  is relatively more stable than other clusters in the family and is the only non-polar cluster. Contrary to the cluster family containing one C atom, the ground states in this group are singlets, with the exception of  $C_2\text{Be}_2$  which is a triplet. Geometries are reported in Fig. 3, while symmetry and energy values are summarized in Table 3.

The normal mode frequencies of vibration were calculated for all the isomers of each cluster size in this family as reported in Table 4. When these frequencies were used in the harmonic calculation of the Helmholtz free energy as a function of temperature, a solid-like structural transition was detected for  $C_2\text{Be}_3$ . On the other hand, the ground state of  $C_2\text{Be}$ ,  $C_2\text{Be}_2$  and  $C_2\text{Be}_4$  continue to be the most stable up to temperatures of about 1000 K.

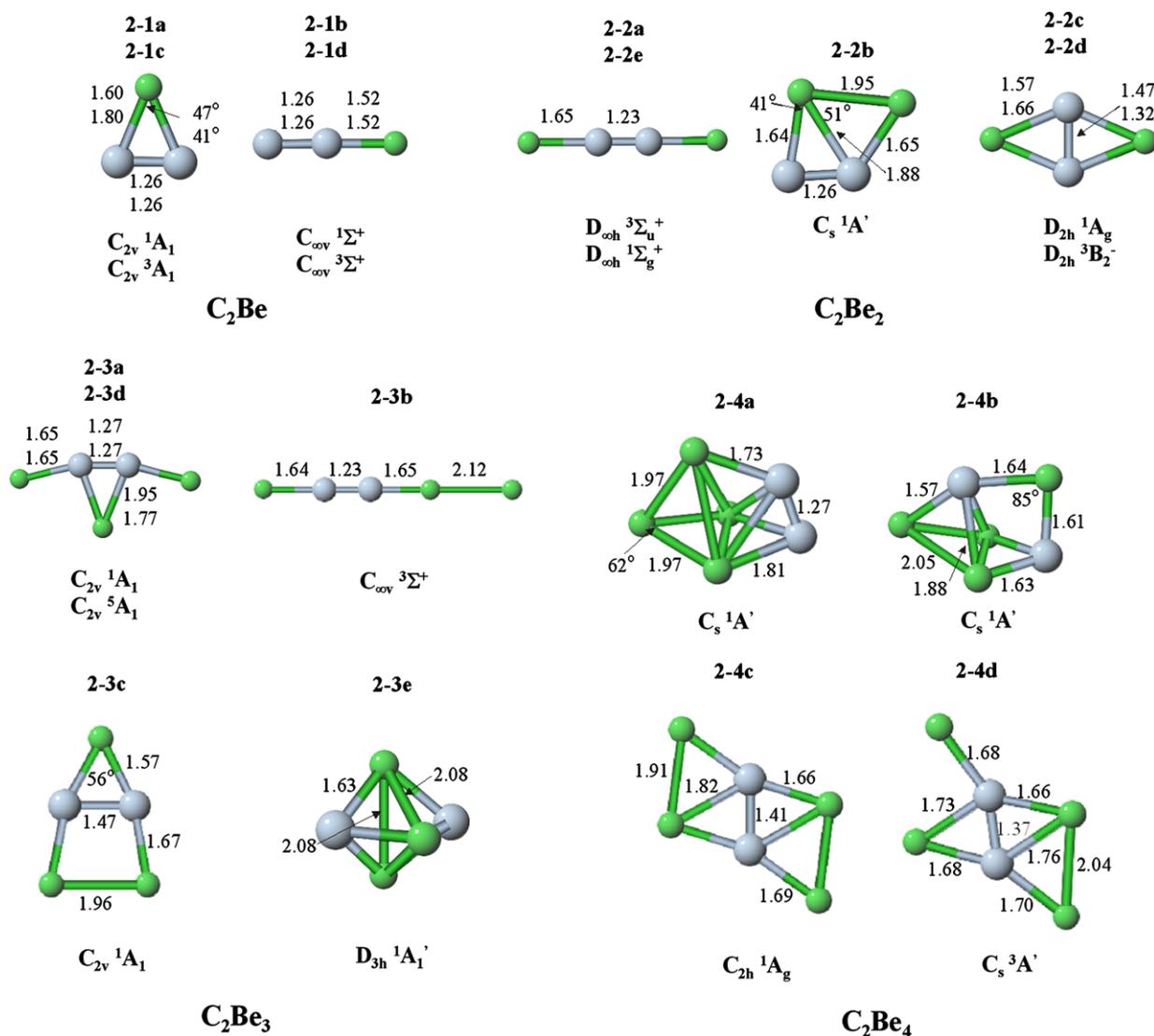


Fig. 3. The  $C_2Be_x$  ( $x = 1-4$ ) structural characteristics of the ground state and various excited electronic states. Bond lengths are expressed in Å.

$C_2Be$ : There are four states studied for this cluster size, all of them having geometries belonging to  $C_{2v}$  or  $C_{\infty v}$ . The ground state depicted in Fig. 3 2-1a is a planar  $C_{2v}$  structure in the  $^1A_1$  state. The binding energy is  $-11.4898$  eV with a total dipole of 4.697 Debye and strongest IR vibrational mode of  $1100\text{ cm}^{-1}$ . The C–Be and C–C bond lengths agree with the reported CASSCF calculations of Koch et al. [9]. The ground states of the cation and anion are relaxed  $C_{2v}$  structures in states  $^2A_1$  and  $^2A_1$ , respectively. The ionization potential is 9.52 eV and electron affinity is 1.99 eV. Worth noting is that the ground state of  $C_2Be^-$  is lower in energy than the linear anion isomer reported by Chen et al. [18]. In fact the linear anion is not stable.

The first excited state, depicted in Fig. 3 2-1b, is a linear  $C_{\infty v}$  structure in the  $^1\Sigma^+$  state located 1.2 eV above the ground state. This is in disagreement with Koch et al. who reported this structure to be 0.2 eV above the ground state. Additionally, these authors report the linear  $^3\Sigma^+$  to

be almost degenerate with the corresponding singlet. We find this state to be the fourth excited state, located 1.38 eV above the ground state. Our second excited state (Fig. 3, 2-1c) has a planar  $C_{2v}$  geometry in  $^3A_1$  state, which is not reported in Koch et al.

$C_2Be_2$ : The most stable geometry for this cluster size is the linear  $D_{\infty h}$   $^3\Sigma_g^-$  as shown in Fig. 3 2-2a. The binding energy for this isomer is  $-14.4786$  eV with zero dipole moment and strongest normal mode vibration at  $985\text{ cm}^{-1}$ . The first excited isomer is a planar structure (Fig. 3, 2-2b) that is 0.4 eV above the ground state. The identification of the ground state and first excited state are both in agreement with Koch et al., although in their study the excited state isomer is 3.5 eV above the ground state.

Both the ground state and the first excited state have C–C bonds that resemble a triple bond, while the second excited state  $D_{2h}$   $^1A_g$  (Fig. 3, 2-2c) has a C–C bond length consistent with the single bond. The ground states of the

Table 3  
Calculated binding energies and dipole moments of  $C_2Be_x$  ( $x = 1-4$ ) for the ground state and various excited states

Species	Cluster	Group	State	$E_b^a$ (eV)	$\ D\ ^d$
$C_2Be$	2-1a	$C_{2v}$	$^1A_1$	-11.4898	4.6974
	2-1b	$C_{\infty v}$	$^1\Sigma^-$	-10.2685	7.982
	2-1c	$C_{2v}$	$^3A_1$	-10.1610	0.0436
	2-1d	$C_{\infty v}$	$^3\Sigma^-$	-10.1011	0.2349
$C_2Be_2$	2-2a	$D_{\infty h}$	$^3\Sigma_u^+$	-14.4786	0
	2-2b	$C_s$	$^1A'$	-14.0761	1.8671
	2-2c	$D_{2h}$	$^1A_g$	-13.3813	0
	2-2d	$D_{2h}$	$^3B_g^-$	-13.1002	0
	2-2e	$D_{\infty h}$	$^1\Sigma_g^+$	-12.9363	0
$C_2Be_3$	2-3a	$C_{2v}$	$^1A_1$	-16.0982	1.5903
	2-3b	$C_{\infty v}$	$^3\Sigma^-$	-16.0021	0.2945
	2-3c	$C_{2v}$	$^1A_1$	-15.6165	2.3735
	2-3d	$C_{2v}$	$^5A_1$	-15.6128	0.1699
	2-3e	$C_{2v}$	$^1A_1$	-15.2087	0.0026
$C_2Be_4$	2-4a	$C_s$	$^1A'$	-18.0239	1.2093
	2-4b	$C_s$	$^1A'$	-18.0036	1.2789
	2-4c	$C_{2h}$	$^1A_g$	-17.7812	0
	2-4d	$C_s$	$^3A'$	-17.7347	0.5131

The structure of the clusters is given in Fig. 3.

Table 4  
Calculated normal mode vibrational frequencies of  $C_2Be_x$  ( $x = 1-4$ ) corresponding to the states reported in Table 3

Species	Cluster	Frequencies ( $cm^{-1}$ )
$C_2Be$	2-1a	663, 1100, 1800
	2-1b	39(2), 1013, 1892
	2-1c	207, 780, 1869
	2-1d	91(2), 868, 2098
$C_2Be_2$	2-2a	133(2), 294(2), 730, 985, 2160
	2-2b	295, 422, 658, 837, 950, 1869
	2-2c	340, 770, 840, 1151, 1225, 1300
	2-2d	192, 482, 544, 787, 839, 1552
	2-2e	101(2), 315(2), 708, 886, 2147
$C_2Be_3$	2-3a	223, 369, 374, 500, 510, 746, 790, 898, 1797
	2-3b	75(2), 198(2), 329(2), 419, 806, 1030, 2158
	2-3c	76, 281, 300, 677, 687, 775, 984, 1190, 1286
	2-3d	146, 172, 266, 312, 602, 686, 799, 959, 1911
	2-3e	517, 518, 550, 793, 796, 989, 998, 1000, 1043
$C_2Be_4$	2-4a	220, 342, 366, 406, 483, 491, 585, 633, 686, 727, 809, 1734
	2-4b	187, 316, 353, 444, 529, 552, 630, 838, 894, 972, 1010, 1196
	2-4c	161, 232, 241, 354, 439, 586, 623, 740, 796, 903, 1045, 1346
	2-4d	142, 184, 219, 304, 321, 501, 591, 752, 786, 851, 1059, 1490

cation and anion are relaxed  $D_{\infty h}$  linear clusters in the  $^2\Sigma_g^-$  and the  $^1A_g$  states, respectively. The ionization potential is 7.78 eV and electron affinity is 0.76 eV.

$C_2Be_3$ : The most stable geometry for this cluster size is the planar  $C_{2v}$  geometry in the  $^1A_1$  state (shown in Fig. 3, 2-3a). The binding energy, as reported in Table 3, is -16.0982 eV with a total dipole moment of 1.6 D. The strongest IR mode of vibration is 1798  $cm^{-1}$ . The ionization potential and electron affinity were calculated from the ground state of  $C_2Be_3^+$  and  $C_2Be_3^-$  and are 7.11 eV and 1.85 eV, respectively. Both cation and anion ground

states are relaxed  $C_s$  structures in the  $^2A'$  states. This first excited state is a linear  $C_{\infty v}$   $^3\Sigma^-$  with binding energy that differs from the ground state by about 0.1 eV. The strongest IR vibrational mode of this excited structure is 1030  $cm^{-1}$  with the total dipole moment of 0.29 D.

The harmonic analysis of the normal mode vibrations shows that at about 260 K this cluster undergoes a structural transition from the ground state to the first excited state becoming linear at higher temperatures. As a matter of fact, the linear isomer is estimated to be about 0.37 eV more stable at 1000 K. The  $\omega_e x_e$  anharmonic corrections to the nine vibrational modes are: 2, 4, 24, 11, 4, 8, 4, 13 and 1  $cm^{-1}$ , from low to high frequencies as shown in Table 4. Based on these values, an estimate of the anharmonic correction to the free energy indicates that the structural transition would be shifted to about 270 K when up to seven anharmonic excitations are taken into account in this temperature range.

$C_2Be_4$ : The  $C_2Be_4$  cluster has four different isomers and states as depicted in Fig. 3, 2-4a through 2-4d. The first two isomers are 3-D structures, whereas the further up excited isomers are planar. The most stable structure has a state of  $^1A'$  and belongs to the  $C_s$  point group. The ground state binding energy of this structure is -18.0239 eV. The most intense active IR modes are 366, 483, 633 and 1734  $cm^{-1}$ . The ionization potential and electron affinity calculated from the relaxed  $C_s$  ground states of the cation and anion are 6.64 eV and 1.65 eV, respectively.

The first excited state is another  $C_s$  geometry,  $^1A'$  state, that differs by only 0.02 eV from the ground state. Despite this energy proximity, the harmonic analysis of the Helmholtz free energy verified that the ground state continues to be the most stable at all temperatures up to 1000 K. A peculiarity of these two isomers is that they are formed around the  $CBe_2$  shown in Fig. 2 1-3a, and therefore the subunit  $C_2$  is not present but rather the metal atoms intercalate between the carbon atoms. The other two higher energy excited isomers are substantially above the ground state by 0.22 and 0.27 eV, are planar, contain the  $C_2$  subunit, and no crossover is apparent at finite temperatures.

## 5. $C_3Be_x$ clusters, $x = 1, 2, 3$

This family of structures has linear, planar, and non-planar geometries in the ground state. The ground state of the smallest cluster in this family has a structure built around a triangular  $C_3$ . However, the ground state of the mid-size cluster is a linear structure built around a linear  $C_3$ . The largest cluster studied in this family is different because the ground state does not have a  $C_3$  sub-cluster within it, but rather is composed by joining two triangular structures  $CBe_2$  and  $C_2Be$  (the smallest sub-groups of the two previous families) to yield a 3-D cluster.

The normal mode frequencies of vibration were calculated for all the isomers of each cluster size. These frequencies were used in the harmonic calculation of the Helmholtz free energy as a function of temperature. In this family of

clusters, the ground state isomer continues to be the most stable with the lowest free energy up to temperatures of about 1000 K. Solid-like structural transitions are not apparent for this family of clusters.

$C_3Be$ : There are six states studied for this cluster size, all of them having geometries belonging to planar  $C_{2v}$  or linear  $C_{\infty v}$  point groups. The most stable geometry depicted in Fig. 4 3-1a is a planar rhombic-like  $C_{2v}$  cluster in a  $^1A_1$  state. This structure and its bond lengths, shown in Fig. 4, are in agreement with previous studies by Sudhakar et al. [2]. The ground state binding energy is  $-16.6380$  eV and the most active IR modes are 654, 1241 and

$1406\text{ cm}^{-1}$ . This cluster has a very high dipole moment, making it the most polar cluster of those studied in this work. The ionization potential and electron affinity calculated from the relaxed  $C_3Be^+$  and  $C_3Be^-$  are 7.99 eV and 2.30 eV, respectively. The ground state of the cation and of the anion are planar  $C_{2v}$   $^2A_1$ . The linear  $C_3Be^-$  is a higher energy ionic isomer. Chen et al. [18] reported this linear anion as the ground state.

The first excited state is a planar isomer,  $C_{2v}$   $^1A_1$ , depicted in Fig. 4 3-1b, which is in agreement with Sudhakar et al. [2] prediction. The binding energy of this isomer is 0.29 eV above the ground state. The C–C bond lengths are

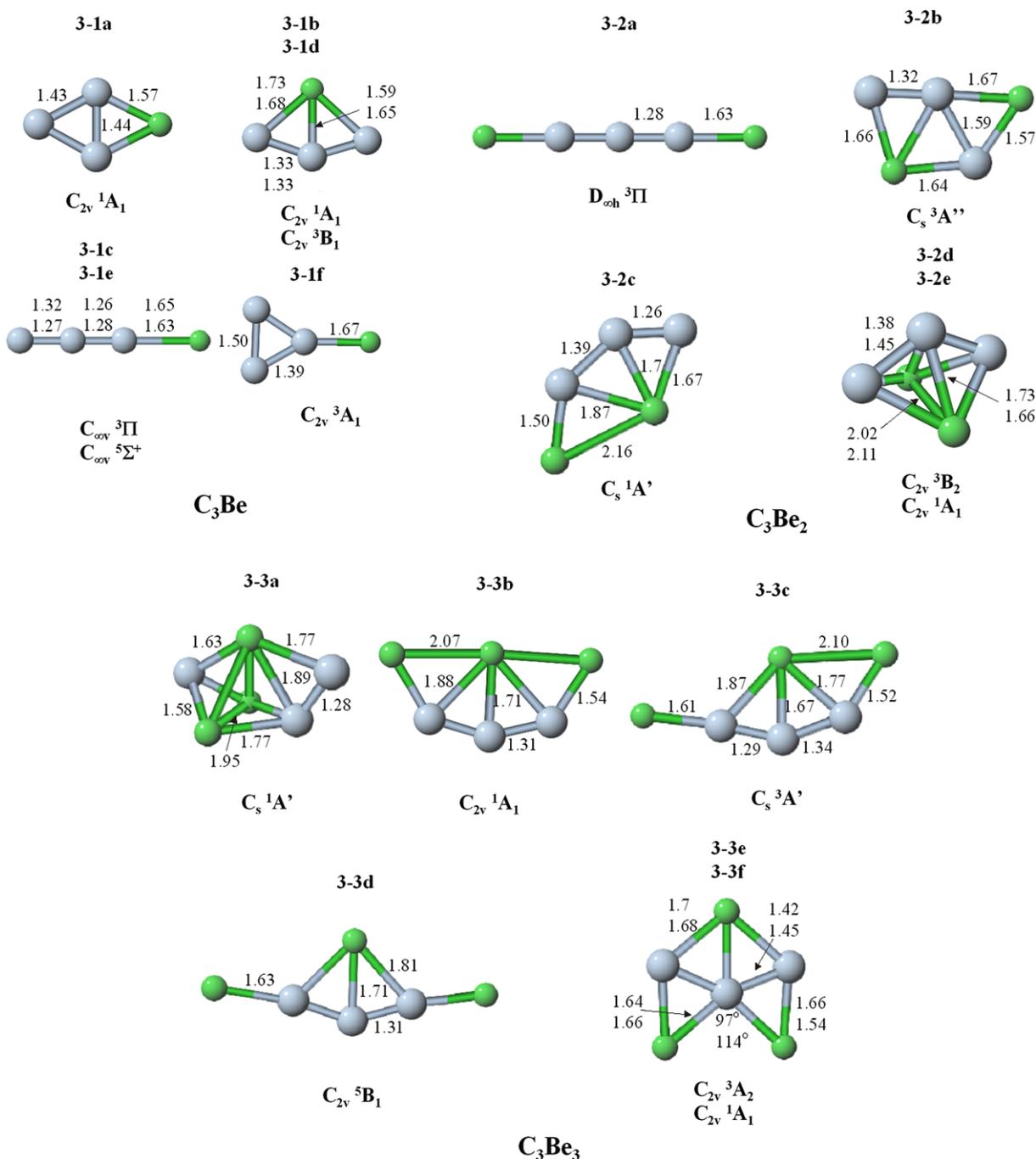


Fig. 4. The  $C_3Be_x$  ( $x = 1-3$ ) structural characteristics of the ground state and various excited electronic states. Bond lengths are expressed in Å.

Table 5  
Calculated binding energies, and dipole moments of  $C_3Be_x$  ( $x = 1-3$ ) for the ground state and various excited states

Species	Cluster	Group	State	$E_b^a$ (eV)	$\ D\ ^d$
$C_3Be$	3-1a	$C_{2v}$	$^1A_1$	-16.6380	6.559
	3-1b	$C_{2v}$	$^1A_1$	-16.3482	4.0368
	3-1c	$C_{\infty v}$	$^3\Pi$	-16.3330	2.8761
	3-1d	$C_{2v}$	$^3B_1$	-16.3007	3.1557
	3-1e	$C_{\infty v}$	$^5\Sigma^+$	-15.3454	0.6593
	3-1f	$C_{2v}$	$^3A_1$	-15.3155	2.9146
$C_3Be_2$	3-2a	$D_{\infty h}$	$^3\Pi$	-19.3745	0
	3-2b	$C_s$	$^3A''$	-19.0996	1.8524
	3-2c	$C_s$	$^1A'$	-18.5819	5.4486
	3-2d	$C_{2v}$	$^3B_2$	-18.4998	1.9962
	3-2e	$C_{2v}$	$^1A_1$	-18.1706	3.1998
$C_3Be_3$	3-3a	$C_s$	$^1A'$	-22.7375	2.1728
	3-3b	$C_{2v}$	$^1A_1$	-22.4110	2.9047
	3-3c	$C_s$	$^3A'$	-22.1828	4.1835
	3-3d	$C_{2v}$	$^5B_1$	-22.0573	0.1966
	3-3e	$C_{2v}$	$^3A_2$	-21.9894	1.2301
	3-3f	$C_{2v}$	$^1A_1$	-21.7351	4.0806

The structure of the clusters is given in Fig. 4.

Table 6  
Calculated normal mode vibrational frequencies of  $C_3Be_x$  ( $x = 1-3$ ) corresponding to the states reported in Table 5

Species	Cluster	Frequencies ( $cm^{-1}$ )
$C_3Be$	3-1a	318,654,959,1156,1241,1406
	3-1b	169, 646, 707, 1088, 1286, 1391
	3-1c	130, 158, 276, 408, 759, 1293, 1960
	3-1d	512, 683, 753, 1001, 1253, 1298
	3-1e	173(2), 454(2), 783, 1418, 1725
	3-1f	189, 266, 685, 895, 1578, 3150
$C_3Be_2$	3-2a	93, 115, 168, 237, 449, 506, 670, 920, 1520, 1779
	3-2b	227, 385, 443, 536, 640, 846, 890, 1189, 1349
	3-2c	299, 364, 521, 677, 727, 831, 995, 1407, 1832
	3-2d	444, 485, 501, 636, 707, 836, 910, 1211, 1290
	3-2e	426, 467,504, 557, 730, 836, 868, 978, 1150
$C_3Be_3$	3-3a	54, 449, 477, 547, 564, 624, 659, 801, 921, 998, 1112, 1684
	3-3b	176, 228, 359, 361, 528, 557, 619, 812, 957, 1084, 1476, 1706
	3-3c	111, 118, 207, 355, 474, 542, 624, 751, 991, 1094, 1503, 1847
	3-3d	67, 84, 105, 239, 508, 510, 530, 655, 915, 936, 1495, 1685
	3-3e	71, 315, 319, 376, 588, 671, 765, 886, 904, 1005, 1171, 1233
	3-3f	210, 241, 339, 465, 623, 719, 759, 842, 1039, 1172, 1259, 1293

close to the bond length in the linear  $C_3$  sub-group. The remaining higher energy isomers and states are reported in Table 5 and Fig. 4.

$C_3Be_2$ : The ground state for this cluster is a linear  $D_{\infty h}$  in the  $^3\Pi$  state. The binding energy is -19.3745 eV with zero dipole moment. The most intense IR active vibrational modes have frequencies at 919 and 1778  $cm^{-1}$ , which correspond to motion of the three carbon atoms oscillating between the Be atoms and to the central carbon oscillating out of phase with other atoms in the chain, respectively. The ionization potential and electron affinity calculated

from the relaxed  $C_3Be_2^+$  and  $C_3Be_2^-$  are 7.65 eV and 2.24 eV, respectively. Both cation and anion ground states are linear  $D_{\infty h} \ ^2\Pi$ .

The first excited isomer has a planar  $C_s$  geometry with  $^3A''$  state constructed from the first excited isomer of  $C_3Be$  with the additional Be decorating one of the C–C bonds. The binding energy for the first excited state differs by 0.27 eV from the ground state. The other two excited isomers are also built from the same sub-unit with the additional Be decorating different places of the sub-structure. Energetics and structural characteristics for these three higher energy isomers are reported in Table 5 and Fig. 4.

$C_3Be_3$ : Five different isomers were found for this cluster size, with the most stable cluster being the only 3-D structure in this family's ground states. This isomer is depicted in Fig. 4 3-3a and has low symmetry  $C_s$  in the  $^1A'$  state. The binding energy of the ground state is -22.7375 eV, which makes this isomer quite stable when adding a Be to its predecessor in the family. The dipole moment of this cluster is 2.17 D. The more intense IR active modes of vibration have frequencies 921 and 1112  $cm^{-1}$ . The ionization potential is 6.98 eV and the electron affinity is 0.64 eV. The cation and anion both have  $C_s$  geometries with states  $^2A'$  and  $^4A''$ , respectively.

Interestingly, all the other isomers of higher energy are planar structures as shown in Fig. 4 3-3b through 3-3f. Details of the energetics and vibration frequencies are provided in Tables 5 and 6.

## 6. Conclusion

In this study, we have presented an analysis of small carbon clusters metallized with beryllium using the DFT approach with non-local functionals provided by Perdew–Wang. This work puts together a complete analysis on the structure, binding energy, and harmonic frequencies of vibration for all isomers in the ground state and in several excited states. The energetically preferred structures of these clusters have metal atoms mutually bonded, suggesting that sub-clusters of pure metal atoms are likely to form in larger carbon–beryllium structures. Within each of the studied families of clusters, the ionization potential decreases as the number of beryllium atoms is increased. However, there is no specific trend for the electron affinities. The high multiplicity of most of the clusters in the  $CBe_x$  family indicates their relevance for magnetic applications. The compound  $C_2Be$  has the highest ionization potential and electron affinity, which is also the case for  $C_2Li$  [8]. A solid-like structural transition is predicted for  $C_2Be_3$  at about 260 K. Interestingly, all other isomers are thermally very stable.

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## References

- [1] A.K. Sandana, F. Liang, B. Brinson, S. Arepalli, S. Farhat, R.H. Hauge, R.E. Smalley, W.E. Billups, *J. Phys. Chem. B* 109 (2005) 4416.
- [2] P.V. Sudhakar, K. Lammertsma, *J. Phys. Chem.* 96 (1992) 4830.
- [3] P.H.M. Budzelaar, P.v.R. Schleyer, K. Krogh-Jespersen, *Angew. Chem. Int. Ed. Engl* 23 (1984) 825.
- [4] J.B. Collins, J.D. Dill, E.D. Jemmis, Y. Apeloig, P.v.R. Schleyer, R. Seeger, J.A. Pople, *J. Am. Chem. Soc.* 98 (1976) 5419.
- [5] W.D. Laidig, H.F. Schaefer, *J. Am. Chem. Soc.* 100 (1978) 5972.
- [6] E.D. Jemmis, D. Poppinger, P.v.R. Schleyer, J.A. Pople, *J. Am. Chem. Soc.* 99 (1977) 5796.
- [7] Y. Apeloig, P.v.R. Schleyer, J.S. Binkley, J.A. Pople, W.A. Jorgensen, *Tetrahedron Lett.* 17 (1976) 3923;  
G. Rauscher, T. Clark, D. Poppinger, P.V.R. Schleyer, *Angew. Chem.* 90 (1978) 306;  
E.D. Jemmis, J. Chandrasekhar, P.V.R. Schleyer, *J. Am. Chem. Soc.* 101 (1979) 2848;
- A.J. Kos, D. Poppinger, P.v.R. Schleyer, W. Thiel, *Tetrahedron Lett.* 21 (1980) 2151.
- [8] A.D. Patrick, A. Skene, E. Blaisten-Barojas, *J. Mol. Struct. Theochem.* 807 (2007) 163.
- [9] W. Koch, G. Frenking, J. Gauss, D. Cremer, A. Sawaryn, P.v.R. Schleyer, *J. Am. Chem. Soc.* 108 (1986) 5732.
- [10] W. Kohn, L.J. Sham, *Phys. Rev. A* 140 (1965) 1133.
- [11] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [12] J.P. Perdue, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, *Phys. Rev. B* 46 (1992) 6671.
- [13] J.P. Perdue, K. Burke, Y. Wang, *Phys. Rev. B* 54 (1996) 16533.
- [14] M.J. Frisch et al., Gaussian Inc., Pittsburg, PA, 1998.
- [15] F. van Duijneveldt, J. van Duijneveldt-van de Rijdt, J. van Lenthe, *Chem. Rev.* 94 (1994) 1873.
- [16] A.I. Boldyrev, J. Simons, *Periodic Table of Diatomic Molecules*, Wiley, New York, 1997.
- [17] J. Kalcher, A.F. Sax, *J. Mol. Struct. Theochem.* 498 (2000) 77.
- [18] M.D. Chen, X.B. Li, J. Yang, Q.E. Zhang, C.T. Au, *J. Mass Spectrom.* 253 (2006) 30.