



Research paper

 Be_3^- , an *ab initio* study

Apostolos Kalamos

National and Kapodistrian University of Athens, Department of Chemistry, Laboratory of Physical Chemistry, Panepistimiopolis, Athens 157 71, Greece

HIGHLIGHTS

- Chemical elucidation of Be_3^- .
- Bonding mechanism of ground and excited Be_3^- states.
- Excited states of Be_3^- .

ABSTRACT

We present high quality *ab initio* results (MRCI/aug-cc-pV5Z) on eleven Be_3^- states of $\tilde{X}^2\text{B}_1$, 1^2A_1 , 2^4B_1 , 3^4A_2 , $4^2\Pi_u$, $5^4\Pi_g$, 6^2B_2 , $7^4\Sigma_g^-$, 8^2B_1 , 9^2A_2 , and 10^2A_1 symmetry spanning an energy range of about 30 kcal/mol. The ground anionic state is bound by 31.8 kcal/mol with respect to the ground $\tilde{X}^1\text{A}_1$ neutral Be_3 state. The ground ($\tilde{X}^2\text{B}_1$) and first excited (1^2A_1) anionic states result naturally from the ground neutral state by grafting an additional electron to the π and σ frame, respectively.

1. Introduction

Beryllium (Be) is a very strange atom of the periodic table. Although its ground state features the electronic configuration of a rare gas element, *i.e.*, $1s^2 2s^2$ (^1S), it is nevertheless a metal with a melting point of ~ 1300 °C. The Be_2 ground $X^1\Sigma_g^+$ state has been a real headache for quantum chemists concerning the nature of its chemical bond since the early sixties. We have recently shown that the ground dimer state results from the interaction of two excited ^3P ($2s^1 2p^1$) Be atoms held together by two sigma bonds [1]. As strange as it may appear its anion Be_2^- exists in two electronic states of $X^2\Pi_u$ (EA = 0.499 eV) and $1^2\Sigma_g^+$ [$\Delta E(1^2\Sigma_g^+ \leftarrow X^2\Pi_u) = 0.137$ eV] symmetry at the MRCI/aug-cc-pVQZ computational level [1]. The existence of two anionic states is indeed strange if one considers the small binding energy of the neutral molecule of just $D_e(\text{exp}) = 934.9 \pm 0.4$ cm^{-1} [2].

The ground state of the beryllium trimer, Be_3 , may be considered as a singularity since it is overall a strongly bound system stabilized by at least 25 kcal/mol with respect to three Be (^1S) atoms [1]. But what about Be_3^- ? Does it exist, and if yes in how many states? The only experimental study reports that "... Be_3^- is either stable or has a lifetime of > 500 μs ." [3]. The theoretical literature is limited to a handful of papers discussing several anionic states of a linear and triangular structure [4–7] at a rather low computational level. The purpose of the present paper is to study Be_3^- in all of its possible electronic states at the highest possible computational level available today. To this end we

have employed multi reference (MRCI) computational methods coupled with the aug-cc-pV5Z (A5Z) basis set [8] as implemented in the MOLPRO code [9].

2. Results and discussion

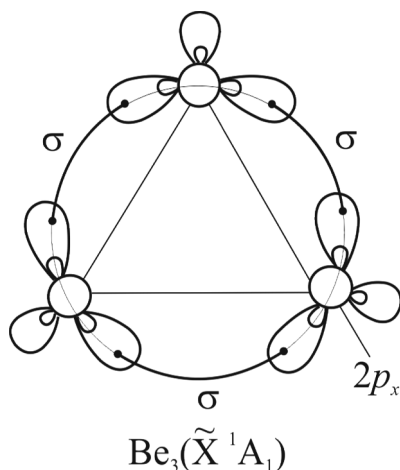
As we have recently shown [1] the valence bond Lewis (vbL) diagram picturing the wavefunction of the ground Be_3 state is displayed in Scheme 1. Its equilibrium equilateral distance is 2.203 Å at the MRCI/A5Z level, see Table 1. It seems plausible to consider that an additional electron can be hosted either by the π or the σ molecular frame. And indeed the drafting of an electron to its π frame gives rise to the $\tilde{X}^2\text{B}_1$ anionic state (under C_{2v} notation) bound by EA = 1.379 eV with respect to Be_3 ($\tilde{X}^1\text{A}_1$). The charged species features a considerable shorter bond length, $r_e(\text{Be}_3^-; \tilde{X}^2\text{B}_1) = 2.106$ Å versus $r_e(\text{Be}_3; \tilde{X}^1\text{A}_1) = 2.203$ Å and that means that there is a new bond present, the delocalized one electron π bond. Similarly, the extra electron can be put along the molecular plane giving rise to a 1^2A_1 state just $\Delta E_e(\tilde{X}^2\text{B}_1 \leftarrow 1^2\text{A}_1) = 0.359$ eV higher. Its bond distance $r_e(\text{Be}_3^-; 1^2\text{A}_1) = 2.177$ Å is certainly longer than that of the ground anionic state but still shorter than the equilibrium distance of the neutral ground state. That means once again that the sigma bonds of the Be_3^- triangular structure appear stronger due to the enhanced polarization of the hybrid orbitals due to the presence of the additional minus charge. Needless to say that both $\tilde{X}^2\text{B}_1$ and 1^2A_1 Be_3^- states retain the perfect D_{3h} nuclear framework of

E-mail address: kalamos@chem.uoa.gr.<https://doi.org/10.1016/j.cplett.2019.136964>

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Scheme 1. vbL diagram of the $\text{Be}_3(\tilde{X}^1A_1)$ state.

their neutral ancestor. It is also worth saying that both these states are the Renner–Teller components of the linear $4^2\Pi_u$ Be_3^- state (see Fig. 1) lower than the \tilde{X}^1A_1 Be_3 state by 0.479 eV. This linear configuration is a stationary point on the doublet spin surface separated by the minima of the \tilde{X}^2B_1 and 1^2A_1 Be_3^- states by a potential barrier of 1.19 (at 135°) and 1.85 (at 120°) kcal/mol, respectively. The above two anionic states are pretty much straightforward to conceive. We simply add an electron to the ground neutral species either along its molecular π or σ frames. But are there other anionic states? In order to find out we should first study the low-lying neutral states that can act as potential precursors for the anion. Those studied are, in ascending energy order, of \tilde{X}^1A_1 , $1^1\Sigma_g^+$, $2^3\Sigma_u^+$, 3^3B_1 , 4^3A_2 , and $5^3\Pi_u$ symmetry, see Table 1 and Fig. 2. The D_{3h} ground state has an equilibrium wavefunction (under C_{2v} notation, counting only valence electrons while linear configurations lie on the y axis) $|\tilde{X}^1A_1\rangle \cong 0.87 |1a_1^2 2a_1^2 1b_2^2\rangle$ and has been already discussed. At linearity it becomes the $1^1\Sigma_g^+$ state ($T_e = 10.1$ kcal/mol) with a potential barrier of 2.68 kcal/mol (at 115°) (see Fig. 1) with the following

equilibrium wavefunction $|1^1\Sigma_g^+\rangle \cong |1a_1^2(0.77 \times 2a_1^2 - 0.53 \times 2b_2^2)1b_2^2\rangle$. Its triplet analog, $2^3\Sigma_u^+$ ($\cong 0.94 |1a_1^2 2a_1^2 1b_2^2 2b_2^2\rangle$), is situated slightly higher, $T_e = 15.0$ kcal/mol, and it is practically degenerate with two triangular configurations (C_{2v}) of 3^3B_1 ($T_e = 16.4$ kcal/mol, $\theta_e = 68.7^\circ$) and 4^3A_2 ($T_e = 16.8$ kcal/mol, $\theta_e = 53.9^\circ$) symmetry. Their equilibrium wavefunctions are $|3^3B_1\rangle \cong |1a_1^2 2a_1^2 1b_1^2(0.90 \times 1b_2^2 - 0.20 \times 3a_1^2)\rangle$ and $|4^3A_2\rangle \cong |1a_1^2(0.89 \times 2a_1^2 - 0.22 \times 3a_1^2)1b_1^2 1b_2^2\rangle$ while at linearity they become of $3^3\Pi_u$ and $3^3\Pi_g$ symmetry, respectively. Under C_s symmetry these two minima ($3^3B_1, 4^3A_2$) are on the same adiabatic potential surface. The linear ancestor, $5^3\Pi_u$, of the 3^3B_1 Jahn–Teller component lies at $T_e = 22.6$ kcal/mol and has the following equilibrium wavefunction $|5^3\Pi_u\rangle_{3B_1} \cong 0.88 |1a_1^2 2a_1^2 1b_1^2 1b_2^2\rangle - 0.22 |1a_1^2 1b_2^2 2b_2^2 1a_1^2\rangle$, $|5^3\Pi_u\rangle_{3A_1}$. It results from the $2^3\Sigma_u^+$ state through the $2b_2^2 \rightarrow 1b_1^2$ electron transition.

As already mentioned the \tilde{X}^2B_1 and 1^2A_1 Be_3^- states result from the \tilde{X}^1A_1 Be_3 state by adding an extra electron to its π or σ frame, and are the Renner–Teller components of the $4^2\Pi_u$ anionic state. The latter results from the $5^3\Pi_u$ neutral state by placing an electron to its $2a_1$ molecular orbital. We should remind at this point [1] that both Be atoms in Be_2^- ($X^2\Pi_u$) are found *in situ* in their excited $3P$ state. The Mulliken population analysis shows an extremely low $2s^{0.80}$ density for the middle Be atom and a rather low $2s^{1.60}$ density for the terminal ones, both indicative of the excited state character of the constituent Be atoms. The next excited state is of 2^4B_1 symmetry, practically degenerate to the 3^4A_2 one. Interestingly enough the 2^4B_1 state becomes the $7^4\Sigma_g^-$ state at linearity with a small potential barrier of 0.7 kcal/mol (see Fig. 1). The quartet spin symmetry dictates its constituents fragments, *i.e.*, $\text{Be}(^3P) + \text{Be}_2^-$ ($X^2\Pi_u$). It results from the 3^3B_1 neutral state by adding an electron to the $3a_1$ molecular orbital. On the contrary the 3^4A_2 state results as the Jahn–Teller component of the $5^4\Pi_g$ state after passing a potential barrier of 7.6 kcal/mol at an angle of $\sim 95^\circ$. Its companion 4^4B_2 Jahn–Teller component is clearly repulsive (see Fig. 1). The $5^4\Pi_g$ state is the high spin analog of the $4^2\Pi_u$ state resulting from an $2a_1^2 \rightarrow 2b_2^2$ excitation. It correlates also to the 4^3A_2 neutral state through the addition of an $3a_1$ electron.

There are four more states practically degenerate of doublet spin

Table 1

Energies E (hartree), bond distances r_e (Å), bond angles $\theta_{\text{Be}_2\text{Be}_1\text{Be}_3}$ (degrees), energy gaps ΔE (kcal/mol) with respect to $\text{Be}_3(\tilde{X}^1A_1)$, and main configurations of the Be_3 and Be_3^- states presently studied at the MRCI/A5Z computational level. The states presented are tagged under C_{2v} notation, r_e refers to the bond length between the middle (Be_1) and the terminal ($\text{Be}_{2,3}$) atoms while linear configurations lie on the y axis.

Species	-E	r_e	$\theta_{\text{Be}_2\text{Be}_1\text{Be}_3}$	ΔE	Main configurations
$\text{Be}_3(\tilde{X}^1A_1)$	43.898 160	2.203	60.0	0.0	$ \tilde{X}^1A_1\rangle \cong 0.87 1a_1^2 2a_1^2 1b_2^2\rangle$
$\text{Be}_3(1^1\Sigma_g^+)$	43.882 018	2.207	180.0	10.1	$ 1^1\Sigma_g^+\rangle \cong 1a_1^2(0.77 \times 2a_1^2 - 0.53 \times 2b_2^2)1b_2^2\rangle$
$\text{Be}_3(2^3\Sigma_u^+)$	43.874 237	2.145	180.0	15.0	$ 2^3\Sigma_u^+\rangle \cong 0.94 1a_1^2 2a_1^2 1b_2^2 2b_2^2\rangle$
$\text{Be}_3(3^3B_1)$	43.872 020	1.991	68.7	16.4	$ 3^3B_1\rangle \cong 1a_1^2 2a_1^2 1b_1^2(0.90 \times 1b_2^2 - 0.20 \times 3a_1^2)\rangle$
$\text{Be}_3(4^3A_2)$	43.871 463	2.134	53.9	16.8	$ 4^3A_2\rangle \cong 1a_1^2(0.89 \times 2a_1^2 - 0.22 \times 3a_1^2)1b_1^2 1b_2^2\rangle$
$\text{Be}_3(5^3\Pi_u)$	43.862 156	2.071	180.0	22.6	$ 5^3\Pi_u\rangle_{3B_1} \cong 0.88 1a_1^2 2a_1^2 1b_1^2 1b_2^2\rangle - 0.22 1a_1^2 1b_2^2 2b_2^2 1a_1^2\rangle$, $ 5^3\Pi_u\rangle_{3A_1} \cong 0.88 1a_1^2 2a_1^2 3a_1^2 1b_2^2\rangle - 0.22 1a_1^2 1b_2^2 2b_2^2 3b_2^2\rangle$
$\text{Be}_3^-(\tilde{X}^2B_1)$	43.948 849	2.106	60.0	-31.8	$ \tilde{X}^2B_1\rangle \cong 0.86 1a_1^2 2a_1^2 1b_1^2 1b_2^2\rangle$
$\text{Be}_3^-(1^2A_1)$	43.935 643	2.177	60.0	-23.5	$ 1^2A_1\rangle \cong 0.87 1a_1^2 2a_1^2 3a_1^2 1b_2^2\rangle$
$\text{Be}_3^-(2^4B_1)$	43.923 337	2.011	65.6	-15.8	$ 2^4B_1\rangle \cong 0.88 1a_1^2 2a_1^2 3a_1^2 1b_1^2 1b_2^2\rangle$
$\text{Be}_3^-(3^4A_2)$	43.923 088	2.107	55.9	-15.6	$ 3^4A_2\rangle \cong 0.89 1a_1^2 2a_1^2 3a_1^2 1b_1^2 1b_2^2\rangle$
$\text{Be}_3^-(4^2\Pi_u)$	43.916 155	2.148	180.0	-11.3	$ 4^2\Pi_u\rangle_{2B_1} \cong 0.81 1a_1^2 2a_1^2 1b_1^2 1b_2^2\rangle - 0.44 1a_1^2 1b_1^2 1b_2^2 2b_2^2\rangle$, $ 4^2\Pi_u\rangle_{2A_1} \cong 0.81 1a_1^2 2a_1^2 3a_1^2 1b_2^2\rangle - 0.44 1a_1^2 3a_1^2 1b_2^2 2b_2^2\rangle$
$\text{Be}_3^-(5^4\Pi_g)$	43.909 228	2.084	180.0	-6.9	$ 5^4\Pi_g\rangle_{4B_2} \cong 0.95 1a_1^2 2a_1^2 3a_1^2 1b_2^2 2b_2^2\rangle$, $ 5^4\Pi_g\rangle_{4A_2} \cong 0.95 1a_1^2 2a_1^2 1b_1^2 1b_2^2 2b_2^2\rangle$
$\text{Be}_3^-(6^2B_2)$	43.906 703	2.086	54.8	-5.4	$ 6^2B_2\rangle \cong 1a_1^2(0.87 \times 2a_1^2 - 0.21 \times 3a_1^2)1b_1^2 2b_2^2\rangle$
$\text{Be}_3^-(7^4\Sigma_g^-)$	43.906 322	2.030	180.0	-5.1	$ 7^4\Sigma_g^-\rangle \cong 0.88 1a_1^2 2a_1^2 3a_1^2 1b_1^2 1b_2^2\rangle$
$\text{Be}_3^-(8^2B_1)$	43.903 714	2.021	66.6	-3.5	$ 8^2B_1\rangle \cong 0.85 1a_1^2 2a_1^2 3a_1^2 1b_1^2 2b_2^2\rangle$
$\text{Be}_3^-(9^2A_2)$	43.903 302	2.128	55.5	-3.2	$ 9^2A_2\rangle \cong 0.82 1a_1^2 2a_1^2 3a_1^2 1b_1^2 1b_2^2\rangle$
$\text{Be}_3^-(10^2A_1)$	43.902 245	2.304	56.3	-2.6	$ 10^2A_1\rangle \cong 1a_1^2(0.76 \times 2a_1^2 4a_1^2 + 0.39 \times 2a_1^2 3a_1^2)1b_2^2\rangle$

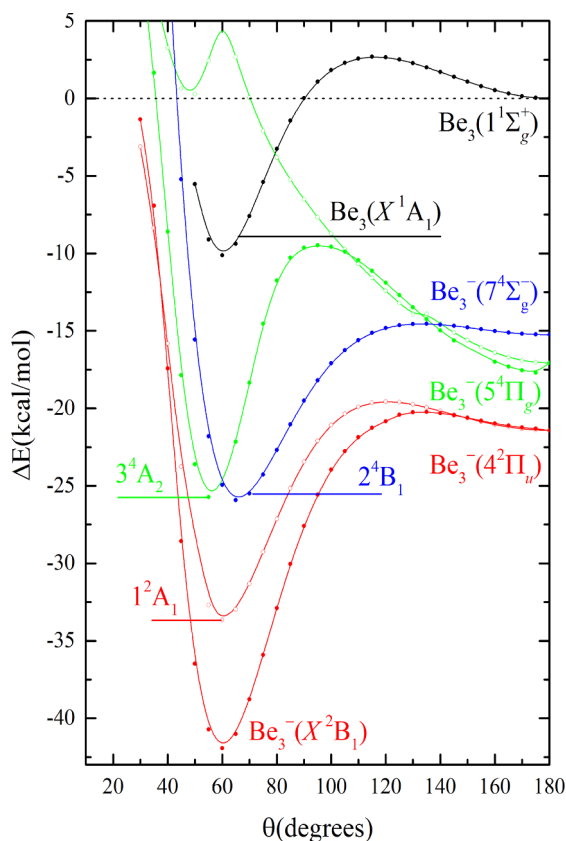


Fig. 1. Evolution along the bending coordinate of several Be₃⁻ and one Be₃ linear states at the MRCI/A5Z computational level. The bond distances are optimized at every bond angle.

symmetry spanning all four irreducible representations of the C_{2v} point group, namely ²A_{1,2} and ²B_{1,2}, see Table 1 and Fig. 2.

From all the above we understand that Be₃⁻ is a rich system existing into many electronic states, perhaps unexpectedly from a chemical intuition point of view.

We have also studied the rather exotic Be₃²⁻ system that has attracted some attention the last years. In particular they have studied its stability, reactivity, aromaticity and bond stretch isomerism, see e.g. [10–14]. Our MRCI/A5Z calculations predict that all states studied, i.e., ^{1,3}A_{1,2} and ^{1,3}B_{1,2}, are practically degenerate (E = -43.876 hartree) and above the ground neutral Be₃ state by ~14 kcal/mol (see Fig. 2).

3. Conclusions

We have studied at the highest possible level (MRCI/A5Z) the Be₃⁻ species. We report data on eleven states of both linear and bent configuration spanning an energy range of around 30 kcal/mol from -31.8 kcal/mol (Be₃⁻(X²B₁); EA = 1.379 eV) to -2.6 kcal/mol (Be₃⁻(10²A₁)) with respect to Be₃(X¹A₁). In all of the calculated anionic states the bond distance is found shorter by around 0.1 Å with respect to the bond distance of the ground neutral molecule. The ground and first excited anionic states result naturally from the ground neutral state by grafting an additional electron to the π and σ frame, respectively. This electron addition boosts the binding ability of the neutral Be₃ (X¹A₁) framework by 31.8 (Be₃⁻(X²B₁)) and 23.5 (Be₃⁻(1²A₁)) kcal/mol.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

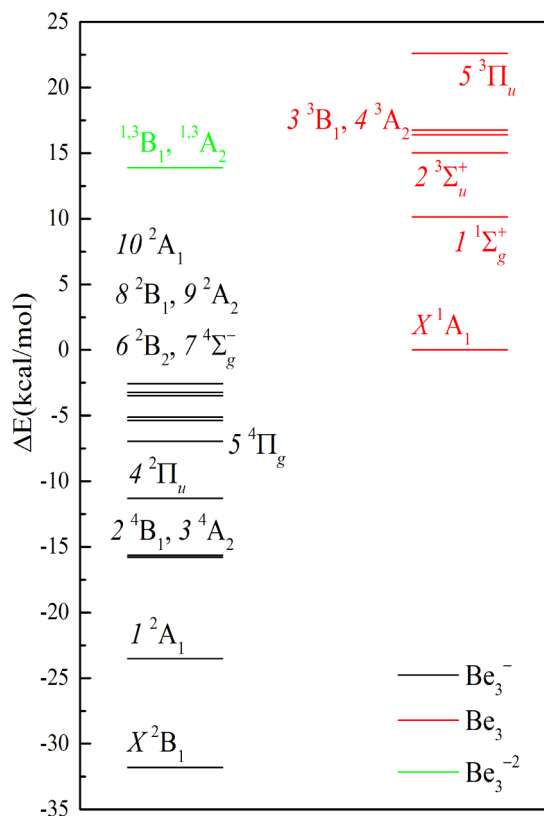


Fig. 2. Energy diagram of all Be₃ (red colour), Be₃⁻ (black colour) and Be₃²⁻ (green colour) states presently studied at the MRCI/A5Z computational level. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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