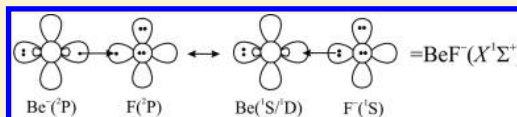


The Nature of the Chemical Bond in BeF^- and Related Species

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ABSTRACT: The beryllium atom represents a curiosity. Its ground state valency is zero, so it should not form chemical bonds. Nevertheless Be is a metal and can form stable chemical species largely due to the participation of its excited ^3P ($2s^12p^1$) state as shown in the cases of Be_2 and Be_3 . BeF^- is a stable ($D_0 \geq 81.4$ kcal/mol) closed shell molecule that has been studied experimentally quite recently. Although it dissociates adiabatically to two closed shell atoms, Be (^1S) and F^- (^1S), the bonding is due to the excited ^3P ($2s^12p^1$) and ^1D ($2p^2$) Be states.



I. INTRODUCTION

One of the most exciting and weird atoms is beryllium whose ground state features a closed shell Hartree–Fock $1s^22s^2$ (^1S) configuration. On the basis of the traditional Lewis–Langmuir theory the valency of its ground state is strictly zero, so it should not form any 2 electron–2 center bond(s) but curiously enough beryllium forms chemical bonds in a variety of compounds. As we have recently shown¹ the ground states of both Be_2 and Be_3 owe their existence to the first excited Be ($2s^12p^1$; ^3P) state lying 2.725 eV² above its ground. The species it can form are considered as a curiosity that defy traditional thinking.^{3–5} One of these exotic molecules is BeF^- whose photodetachment spectroscopy was recently reported by the Heaven group.⁶ They have employed the slow electron velocity map imaging technique and have extracted the electron affinity (EA) of $\text{BeF}(\text{X}^2\Sigma^+)$, $\text{EA} = 8697 \pm 6$ cm⁻¹ and the vibrational constants of $\text{BeF}^-(\text{X}^1\Sigma^+)$, $\omega_e = 1059 \pm 6$ cm⁻¹, $\omega_e x_e = 9.5 \pm 1.8$ cm⁻¹, and $\Delta G_{1/2} = 1040 \pm 7$ cm⁻¹. On the basis of previous BeF results^{7,8} they have also provided a lower bound for the binding energy of $\text{BeF}^-(\text{X}^1\Sigma^+)$, $D_0 \geq 28\,460$ cm⁻¹. In order to probe the nature of the bond in $\text{BeF}^-(\text{X}^1\Sigma^+)$ they have employed quantum mechanical *ab initio* techniques and concluded that the stabilization is due to a dative bonding between two closed shell atoms, F^- (^1S) and Be (^1S), through the donation of electronic density from a F^- $2s2p_z$ hybrid orbital into a Be $2s2p_z$ hybrid orbital that is 87% of $2p_z$ character.

In the present work we report a detailed theoretical analysis of the bonding on both BeF and its anionic species that reveals the *in situ* nature of their constituent fragments. To this end we have employed the multireference (MRCI) and coupled cluster singles and doubles and perturbative triples (CCSD(T)) computational methods coupled with the aug-cc-p(C)V5Z basis sets^{9,10} as implemented in the MOLPRO code.¹¹

II. RESULTS AND DISCUSSION

The neutral BeF species will be our guide and reference point for the deciphering of the chemical bond in BeF^- . In Figure

1, we display the BeF MRCI potential energy curves (PEC) of $^2\Sigma^+$ and $^2\Pi$ symmetry dissociating adiabatically to Be (^1S ,

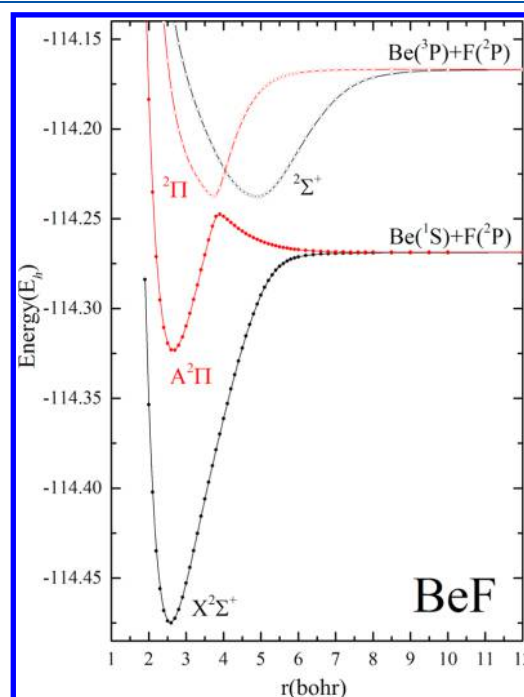


Figure 1. MRCI potential energy curves of $^2\Sigma^+$ and $^2\Pi$ symmetry of the neutral BeF states resulting from Be (^1S , ^3P) + F (^2P).

^3P) + F (^2P). On the basis of the traditional Lewis–Langmuir theory a F (^2P) cannot bind to a closed shell Be atom but this is not the case with an excited Be ($2s^12p^1$; ^3P) atom. Moreover the shape of the displayed PECs is characteristic of the avoided crossing between the same symmetry states and that points to the participation of Be ($2s^12p^1$; ^3P) in both the

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$X^2\Sigma^+$ and $A^2\Pi$ BeF states. Their CASSCF equilibrium details support the above statement:

$$|X^2\Sigma^+\rangle \cong 0.97|1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\pi_x^2 1\pi_y^2\rangle$$

$$2s^{0.93} 2p_z^{0.18} 2p_x^{0.16} 2p_y^{0.16} /_{\text{Be}} 2s^{2.0} 2p_z^{1.85} 2p_x^{1.82} 2p_y^{1.82} /_{\text{F}}$$

$$(q_{\text{Be}} = +0.53)$$

and

$$|A^2\Pi\rangle \cong 0.96|1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi_x^2 2\pi_x^1 1\pi_y^2\rangle$$

$$2s^{0.09} 2p_z^{0.08} 2p_x^{1.08} 2p_y^{0.17} /_{\text{Be}} 2s^{2.0} 2p_z^{1.81} 2p_x^{1.85} 2p_y^{1.82} /_{\text{F}}$$

$$(q_{\text{Be}} = +0.54)$$

with

$$1\sigma \sim 1s(\text{F}), 2\sigma \sim 1s(\text{Be}), 3\sigma \sim 2s(\text{F}),$$

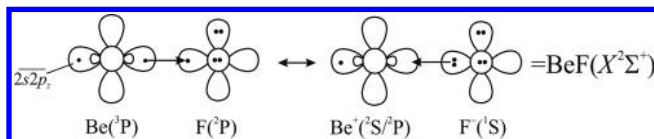
$$4\sigma \sim 0.49 \times 2s(\text{Be}) + 0.44 \times 2p_z(\text{Be}) - 0.93 \times 2p_z(\text{F}),$$

$$5\sigma \sim 0.79 \times 2s(\text{Be}) - 0.46 \times 2p_z(\text{Be}),$$

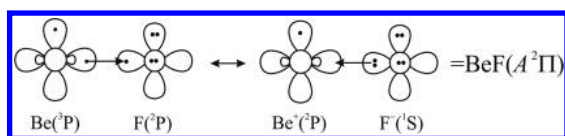
$$1\pi_{x,y} \sim 2p_{x,y}(\text{F}), \text{ and } 2\pi_x \sim 2p_x(\text{Be})$$

On the basis of both the orbitals' composition and the Mulliken atomic populations we can visualize the binding mode with the help of the valence bond Lewis (vbL) diagrams depicted in Schemes 1 and 2:

Scheme 1. vbL Diagram Depicting the Bonding in the $X^2\Sigma^+$ State of BeF



Scheme 2. vbL Diagram Depicting the Bonding in the $A^2\Pi$ State of BeF



In both the X and A states there is a σ bond (4σ) between a $2s2p_z$ Be (3P) electron and the one in $2p_z$ F (2P) with an enhanced polarity of Be^+F^- ($q_{\text{Be}} = +0.5$) while the symmetry defining electron sits either in a $2s2p_z (=5\sigma)$ Be hybrid ($X^2\Sigma^+$) or in a $\sim 2p_\pi (=2\pi)$ Be orbital ($A^2\Pi$). In a resonant way and due to the polarity of the molecule the σ bond in both of these states can be considered as arising from the charged Be^+ (2S and 2P) and F^- (1S) fragments. There is a σ -type penetration of the $2p_z^2$ F^- (1S) electrons to the $2s2p_z$ Be^+ hybrid with the spin defining electron either in a sigma (5σ) orbital of a Be^+ ion found in a mixture of its 2S ($2s^1$) and 2P ($2p^1$) states or in a $2p_x$ orbital of the quasi pure Be^+ (2P). Actually the $T_e(A^2\Pi) = 4.12$ eV (see Table 1) reflects the excitation energy of Be^+ $\Delta E(^2P \leftarrow ^2S) = 3.959$ eV.² From the Mulliken charges of Be, we can say that both resonant situations, "covalent" and "ionic" contribute practically equally ($\sim 50\%$) to the bonding.

The vbL diagrams of the above states can be thought provoking. What can we do with a single electron ($X^2\Sigma^+$) (see Scheme 1) or with a "hole" ($A^2\Pi$) (see Scheme 2) in the rear side of Be? In the first case we can approach an H (2S) atom and form the H–BeF ($^1\Sigma^+$) ($r_e(\text{HBe}) = 1.3271$ Å and $r_e(\text{BeF}) = 1.3713$ Å) species bound by as large as 94.0 kcal/mol with respect to its adiabatic fragments at the CCSD(T) computational level while in the second case, i.e., BeF ($A^2\Pi$), we can approach linearly a He (1S) atom and form $\text{He} \rightarrow \text{BeF} (^2\Pi)$ ($r_e(\text{HeBe}) = 1.4047$ Å and $r_e(\text{BeF}) = 1.3973$ Å). This interaction amounts to 15.3 kcal/mol with respect to He (1S) + BeF ($A^2\Pi$) at the CCSD(T) level of theory. Graphically the interaction is captured by the vbL diagram of Scheme 3.

The equilibrium Mulliken distributions $1s^{1.86}/_{\text{He}} 2s^{0.14} 2p_z^{0.16} 2p_x^{1.09} 2p_y^{0.09} /_{\text{Be}} 2s^{2.0} 2p_z^{1.79} 2p_x^{1.83} 2p_y^{1.87} /_{\text{F}}$ ($q_{\text{He}} = +0.12$, $q_{\text{Be}} = +0.37$, $q_{\text{F}} = -0.50$) are in agreement with the vbL diagram of Scheme 3. The He atom penetrates into the "hole" of the BeF ($A^2\Pi$) molecule and transfers some density ($+0.12 e^-$) into the $2s2p_z$ Be orbital. In both HBeF ($^1\Sigma^+$) and HeBeF ($^2\Pi$) the r_e of the BeF subunit remains very similar to the r_e of the free BeF ($X^2\Sigma^+$) and BeF ($A^2\Pi$) molecules, respectively, (see Table 1). Exactly the same binding mechanism applies to the HeBeO system.^{3,5} The upshot of the above discussion is the fact that the excited 3P Be state plays a significant role in the bonding of the X and A BeF molecular states.

Having studied the neutral $X^2\Sigma^+$ and $A^2\Pi$ states and having understood the details of their electronic character we are now ready to decipher the bonding intricacies of the BeF^- species. The additional electron can be placed into the available empty orbitals either along the σ or π frames localized more or less on Be. Considering the BeF ($X^2\Sigma^+$) state one can generate a $\text{BeF}^- (^1\Sigma^+)$ species by singlet coupling the extra e^- to the one already present in the $2s2p_z$ Be hybrid orbital. And this is indeed the ground anionic species as found experimentally.⁶ Placing the additional e^- into a $\sim 2p_\pi(\text{Be})$ orbital we will get a $^1,^3\Pi$ BeF^- state that should be higher in energy than the $^1\Sigma^+$ one due to the repulsion of the $\sim 2p_\pi(\text{F})$ electronic density with the minus charge. And this is indeed true. The $^1,^3\Pi$ BeF^- states are only a few mE_h above the BeF ($X^2\Sigma^+$) energy minimum at the MRCI+Q level of theory.

In what follows, we shall present the most important features of the ground $X^1\Sigma^+$ BeF^- state. The CASSCF equilibrium details point to its quasi valence character:

$$|X^1\Sigma^+\rangle \cong 0.95|1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi_x^2 1\pi_y^2\rangle$$

$$2s^{1.63} 2p_z^{0.40} 2p_x^{0.12} 2p_y^{0.12} /_{\text{Be}} 2s^{2.0} 2p_z^{1.82} 2p_x^{1.91} 2p_y^{1.91} /_{\text{F}}$$

$$(q_{\text{Be}} = -0.37 \text{ and } q_{\text{F}} = -0.63)$$

with

$$1\sigma \sim 1s(\text{F}), 2\sigma \sim 1s(\text{Be}), 3\sigma \sim 2s(\text{F}),$$

$$4\sigma \sim 0.41 \times 2s(\text{Be}) + 0.47 \times 2p_z(\text{Be}) - 0.91 \times 2p_z(\text{F}),$$

$$5\sigma \sim 0.65 \times 2s(\text{Be}) + 0.17 \times s'(\text{Be}) - 0.37 \times 2p_z(\text{Be}),$$

$$1\pi_{x,y} \sim 2p_{x,y}(\text{F})$$

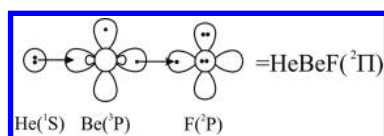
The extra electron ($0.90 = +0.53(q_{\text{Be}} \text{ of } X^2\Sigma^+) - (-0.37)(q_{\text{Be}} \text{ of } X^1\Sigma^+)$) is practically localized on the valence $2s2p_z$ Be

Table 1. Energies E (E_h), Bond Distances r_e (Å), Harmonic Frequencies ω_e (cm^{-1}), Anharmonic Corrections $\omega_e x_e$ (cm^{-1}), Adiabatic Dissociation Energies D_e (kcal/mol), and Separation Energies/Electron Affinities T_e/EA (cm^{-1}) of the Studied Species at Various Computational Levels, with Experimental Results in Square Brackets

species	method	$-E$	r_e	ω_e	$\omega_e x_e$	D_e	T_e/EA
BeF($X^2\Sigma^+$)	MRCI	114.481399	1.3722	1235.87	9.01	133.0	
	MRCI+Q	114.487823	1.3730	1232.03	9.09	131.2	
	CCSD(T)	114.497207	1.3678	1258.72	11.41	136.0	
	C-CCSD(T) ^a	114.547242	1.3623	1265.59	10.62	136.9	
			[1.3610] ^b	[1247.36] ^b	[9.12] ^b	[134.91] ^{b,c}	
BeF($A^2\Pi$)	MRCI	114.331075	1.3961	1176.46	8.36	38.69	32992.3
	MRCI+Q	114.344654	1.3994	1165.29	8.05	41.39	31421.9
	CCSD(T)	114.245752	1.3991	1168.76	9.72	40.91	33240.5
	C-CCSD(T) ^a	114.395641	1.3945	1174.39	10.01	41.77	33272.6
			[1.3935] ^b	[1154.67] ^b	[8.78] ^b	[40.02] ^{b,d}	[33233.7] ^b
BeF ⁻ ($X^1\Sigma^+$)	MRCI	114.527947	1.4165	1058.64	13.10	85.0	10216.1
	MRCI+Q	114.535290	1.4154	1061.30	13.09	85.4	10417.8
	CCSD(T)	114.536445	1.4142	1063.30	11.65	82.1	8611.7
	C-CCSD(T) ^a	114.586305	1.4080	1072.93	11.70	82.9	8573.3
				[1059 ± 6] ^e	[9.5 ± 1.8] ^e	[≥81.4] ^{e,f}	[8697 ± 6] ^e

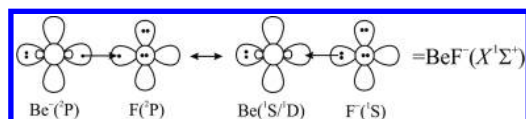
^aCore–valence CCSD(T) calculations with the aug-cc-pCV5Z basis set. ^bReference 12. ^c D_0^0 value; ^d $D_0^0(A^2\Pi) = D_0^0(X^2\Sigma^+) - \nu_{00}$ ($A \leftarrow X$); ^eReference 6. ^f D_0 value.

Scheme 3. vbL Diagram Depicting the Bonding in the $^2\Pi$ State of HeBeF



orbital. On the basis of the bonding characteristics of the neutral BeF ($X^2\Sigma^+$) state visualized in Scheme 1 we can explain the bonding interaction in the anionic species by the vbL diagram shown in Scheme 4.

Scheme 4. vbL Diagram Depicting the Bonding in the $X^1\Sigma^+$ State of BeF⁻



As before, we have the resonance of two bonding “situations”. In the “covalent” one we have a σ bond (4σ) between a $2s2p_z$ Be⁻ (2P) electron and the one in $2p_z$ F (2P) with a charge transfer toward the F center while a pair of electrons is in the $2s2p_z$ Be hybrid pointing away from the Be–F bond. The Be⁻/F situation is also reflected in the Mulliken atomic charge of Be, $q_{\text{Be}} = -0.37$. A minus charge on Be can only be explained through the participation of its excited 3P state with respect to which Be⁻ is stable with an experimentally measured EA of 290.99 ± 0.10 meV.¹³ In the “ionic” picture we have a bonding interaction that arises from a σ -type penetration of the $2p_z^2$ F⁻ (1S) electrons into a $2s2p_z$ hybrid orbital of a Be atom found in a mixture of its ground 1S and its doubly excited 1D ($2p^2$) state ($2s^{1.63}2p_z^{0.40}2p_x^{0.12}p_y^{0.12}$), 7.053 eV higher.² The latter bonding component is qualitatively similar to the one proposed in ref 6 (see also section I) although the authors did not explicitly reveal the *in situ* nature of the constituent fragments. The equilibrium distance is now found longer by ~ 0.05 Å (see

Table 1) due to the electronic congestion along the sigma frame while its binding energy ($D_e \approx 83$ kcal/mol; see Table 1) drops by ~ 55 kcal/mol with respect to the binding energy of its neutral ancestor due to the participation of the high lying 1D beryllium state.

III. CONCLUSIONS

In the present work, we have thoroughly examined the neutral BeF $X^2\Sigma^+$ and $A^2\Pi$ and the only anionic BeF⁻ $X^1\Sigma^+$ states through the MRCI and CCSD(T) computational methods coupled with large basis sets. The chemical bonding in the BeF ($X^2\Sigma^+$) state can be viewed as a hybrid of two equally contributing resonant forms, a “covalent” one with the Be atom excited in its 3P ($2s^12p^1$) state and an “ionic” one between Be⁺ ($^2S/2P$) and F⁻ (1S). The binding mechanism of the BeF⁻ $X^1\Sigma^+$ molecule traces its characteristics to the neutral $X^2\Sigma^+$ case. The substantial bonding ($D_e \approx 83$ kcal/mol) arises from the resonance of a Be⁻ (2P) – F (2P) “covalent” and a Be ($^1S/1D$) – F⁻ (1S) “ionic” forms. In both cases the Be atom is found excited in its 3P ($2s^12p^1$) and 1D ($2p^2$) states. Otherwise it would not be possible to have such a strong interaction between two closed shell species, Be (1S) and F⁻ (1S), through a dative bond since Be (1S) cannot accept electronic density, its EA is negative. The celebrated Lewis acidity of Be is an ample manifestation of the open shell excited states contributing quantum mechanically in the bonding.

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Notes

The author declares no competing financial interest.

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