The Nature of the Chemical Bond in BeF\textsuperscript{−} and Related Species

Apostolos Kalemos\textsuperscript{*}

Department of Chemistry, Laboratory of Physical Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis, Athens 15771, Greece

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\textsuperscript{3P} (2s\textsuperscript{1}2p\textsuperscript{1}) state as shown in the cases of Be\textsubscript{2} and Be\textsubscript{3}. BeF\textsuperscript{−} 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\textsuperscript{−} (1S), the bonding is due to the excited\textsuperscript{3P} (2s\textsuperscript{2}p\textsuperscript{1}) and 1D (2p\textsuperscript{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\textsuperscript{2}2s\textsuperscript{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 shown\textsuperscript{1} the ground states of both Be\textsubscript{2} and Be\textsubscript{3} owe their existence to the first excited Be (2s\textsuperscript{2}p\textsuperscript{1}; 3P) state lying 2.725 eV\textsuperscript{2} above its ground. The species it can form are considered as a curiosity that defy traditional thinking.\textsuperscript{3–5} One of these exotic molecules is BeF\textsuperscript{−} whose photodetachment spectroscopy was recently reported by the Heaven group.\textsuperscript{6} They have employed the slow electron velocity map imaging technique and have extracted the electron affinity (EA) of BeF(X\textsubscript{2}\Sigma\textsuperscript{+}), \(EA = 8697 \pm 6\) cm\textsuperscript{−1} and the vibrational constants of BeF\textsuperscript{−}(X\textsubscript{1}\Sigma\textsuperscript{+}), \(\omega_e = 1059 \pm 6\) cm\textsuperscript{−1}, \(\omega_{ex} = 9.5 \pm 1.8\) cm\textsuperscript{−1}, and \(\Delta G_{1/2} = 1040 \pm 7\) cm\textsuperscript{−1}. On the basis of previous BeF results\textsuperscript{7,8} they have also provided a lower bound for the binding energy of BeF\textsuperscript{−}(X\textsubscript{1}\Sigma\textsuperscript{+}), \(D_0 \geq 28460\) cm\textsuperscript{−1}. In order to probe the nature of the bond in BeF\textsuperscript{−}(X\textsubscript{1}\Sigma\textsuperscript{+}) they have employed quantum mechanical \textit{ab initio} techniques and concluded that the stabilization is due to a dative bonding between two closed shell atoms, F\textsuperscript{−} (1S) and Be (1S), through the donation of electronic density from a F\textsuperscript{2s2p\textsubscript{z}} hybrid orbital into a Be 2s2p\textsubscript{z} hybrid orbital that is 87% of 2p\textsubscript{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\textsuperscript{9,10} as implemented in the MOLPRO code.\textsuperscript{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\textsuperscript{−}. In Figure 1, we display the BeF MRCI potential energy curves (PEC) of \(^2\Sigma^+\) and \(^3\Pi\) symmetry dissociating adiabatically to Be (\(^1\text{S}, ^3\text{P}\)) + F (\(^2\text{P}\)).

\(1^3\text{P}) + F (^2\text{P})\). On the basis of the traditional Lewis–Langmuir theory a F (\(^2\text{P}\)) cannot bind to a closed shell Be atom but this is not the case with an excited Be (2s\textsuperscript{2}p\textsuperscript{1}; \(^3\text{P}\)) 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\textsuperscript{2}p\textsuperscript{1}; \(^3\text{P}\)) in both the
X^2Σ^+ and A^2Π Be states. Their CASSCF equilibrium details support the above statement:

\[ |X^2Σ^+ \rangle \cong 0.971|σ^22σ^22σ^24σ^25σ^11π^21\pi^2\rangle \]

\[ 2σ^{0.93}_x 2p^{0.18}_x 2p^{0.16}_x 2p^{0.16}_x / \text{Be} 2s^{2.03}_x 2p^{1.86}_x 2p^{1.82}_y / \text{Be} \]

\[ (q_{\text{Be}} = +0.53) \]

and

\[ |A^2Π \rangle \cong 0.961|σ^22σ^22σ^24σ^21\pi^21\pi^2\rangle \]

\[ 2σ^{0.09}_x 2p^{0.08}_x 2p^{0.18}_x 2p^{0.17}_y / \text{Be} 2s^{2.03}_x 2p^{1.81}_x 2p^{1.83}_y / \text{Be} \]

\[ (q_{\text{Be}} = +0.54) \]

with

1σ ~ 1s(\text{F}), 2σ ~ 1s(\text{Be}), 3σ ~ 2s(\text{F}),

4σ ~ 0.49 \times 2n(\text{Be}) + 0.44 \times 2p_x (\text{Be}) - 0.93 \times 2p_y (\text{Be}),

5σ ~ 0.79 \times 2s(\text{Be}) - 0.46 \times 2p_x (\text{Be}),

1π_x^y ~ 2p_x(F), \text{and} 2π_x ~ 2p_y (\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^2Σ^+ State of BeF

Scheme 2. vbL Diagram Depicting the Bonding in the A^2Π State of BeF

In both the X and A states there is a σ bond (4σ) between a 2s2p_x Be (1P) electron and the one in 2p_y F (1P) with an enhanced polarity of BeF^- (q_{Be} = -0.5) while the symmetry defining electron site either in a 2s2p_x (\approx 5σ) Be hybrid (X^2Σ^+) or in a ~2p_x (\approx 2σ) Be orbital (A^2Π). 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 1P) and F^- (1S) fragments. There is a σ-type penetration of the 2s_x F^- (1S) electrons to the 2s2p_x 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_x) and 1P (2p_x) states or in a 2p_x orbital of the quasi pure Be^+ (1P). Actually the T_{A^2Π} \cong 4.12 eV (see Table 1) reflects the excitation energy of Be^+ (ΔE(1P - 2S) \cong 3.959 eV). From the Mulliken charges of Be, we can say that both resonant situations, “covalent” and “ionic” contribute practically equally (~50%) to the bonding.

The vbL diagrams of the above states can be thought provoking. What can we do with a single electron (X^2Σ^+) (see Scheme 1) or with a “hole” (A^2Π) (see Scheme 2) in the rear side of Be? In the first case we can approach an H (1S) atom and form the H-BeF (X^2Σ^+) (r_{HBe}) = 1.327 Å and r_{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^2Π), we can approach linearly a He (1S) atom and form He \rightarrow BeF (Π) (r_{HeBe} = 1.4047 Å) and r_{BeF} = 1.3973 Å). This interaction amounts to 15.3 kcal/mol with respect to He (1S) + BeF (A^2Π) 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}/He 2s^{0.14}2p_x^{0.63}2p_y^{0.09}/Be 2s^{2.02}2p_x^{1.72}2p_y^{1.82}/F (q_{Be} = +0.12, q_{Be} = +0.37, q_{F} = -0.50) are in agreement with the vbL diagram of Scheme 3. The He atom penetrates into the “hole” of the BeF (A^2Π) molecule and transfers some density (+0.12 e^-) into the 2s_x Be orbital. In both HBeF (Σ^+) and HeBeF (Π) the r_x of the BeF subunit remains very similar to the r_z of the free BeF (X^2Σ^+) and BeF (A^2Π) 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 1P Be state plays a significant role in the bonding of the X and A BeF molecular states.

Having studied the neutral X^2Σ^+ and A^2Π 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^2Σ^+) state one can generate a BeF^- (Σ^-) species by singlet coupling the extra e^- into the one already present in the 2s_x Be hybrid orbital. And this is indeed the ground anionic species as found experimentally.6 Placing the additional e^- into a 2p_x(\text{Be}) orbital we will get a 3^2Π BeF state that should be higher in energy than the 1Σ^- one due to the repulsion of the ~2p_x(\text{F}) electronic density with the minus charge. And this is indeed true. The 3^2Π BeF^- states are only a few mE\text{h} above the BeF (X^2Σ^+) energy minimum at the MRCI+Q level of theory.

In what follows, we shall present the most important features of the ground X^2Σ^+ BeF^- state. The CASSCF equilibrium details point to its quasi valence character:

\[ |X^2Σ^+ \rangle \cong 0.951 |σ^22σ^22σ^24σ^25σ^11π^21\pi^2\rangle \]

\[ 2\Delta^{0.64}p_x^{0.40}p_x^{0.12}p_y^{0.12}/\text{Be} 2s^{2.03}_x 2p^{1.82}_x 2p^{1.91}_y / \text{F} \]

\[ (q_{Be} = -0.37 \text{ and } q_F = -0.63) \]

with

1σ ~ 1s(\text{F}), 2σ ~ 1s(\text{Be}), 3σ ~ 2s(\text{F}),

4σ ~ 0.41 \times 2s(\text{Be}) + 0.47 \times 2p_x (\text{Be}) - 0.91 \times 2p_y (\text{Be}),

5σ ~ 0.65 \times 2s(\text{Be}) + 0.17 \times s(\text{Be}) - 0.37 \times 2p_x (\text{Be}),

1π_x^y ~ 2p_x (\text{F})

The extra electron (0.90 = +0.53(q_{Be} of X^2Σ^+) - (-0.37) (q_{Be} of X^2Σ^+)) is practically localized on the valence 2s_x Be
Table 1. Energies $E^a$, Bond Distances $r_a$ (Å), Harmonic Frequencies $\omega_a$ (cm$^{-1}$), Anharmonic Corrections $\omega_a \chi_a$ (cm$^{-1}$), Adiabatic Dissociation Energies $D_i$ (kcal/mol), and Separation/Electron Affinities $T_r/EA$ (cm$^{-1}$) of the Studied Species at Various Computational Levels, with Experimental Results in Square Brackets

<table>
<thead>
<tr>
<th>Species</th>
<th>Method</th>
<th>$-E$</th>
<th>$r_a$</th>
<th>$\omega_a$</th>
<th>$\omega_a \chi_a$</th>
<th>$D_i$</th>
<th>$T_r/EA$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeF($X^\Sigma^+$)</td>
<td>MRCI</td>
<td>114.481399</td>
<td>1.3722</td>
<td>1235.87</td>
<td>9.01</td>
<td>133.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MRCI-Q</td>
<td>114.481399</td>
<td>1.3730</td>
<td>1232.03</td>
<td>9.09</td>
<td>131.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>114.497207</td>
<td>1.3678</td>
<td>1258.72</td>
<td>11.41</td>
<td>136.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CCSD(T)+</td>
<td>114.547242</td>
<td>1.3623</td>
<td>1265.59</td>
<td>10.62</td>
<td>136.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CCSD(T)+$^{\text{a}}$</td>
<td>114.547242</td>
<td>1.3623</td>
<td>1265.59</td>
<td>10.62</td>
<td>136.9</td>
<td></td>
</tr>
<tr>
<td>BeF($A^\Pi$)</td>
<td>MRCI</td>
<td>114.331075</td>
<td>1.3961</td>
<td>1176.46</td>
<td>8.36</td>
<td>38.69</td>
<td>32992.3</td>
</tr>
<tr>
<td></td>
<td>MRCI+Q</td>
<td>114.346654</td>
<td>1.3994</td>
<td>1165.29</td>
<td>8.05</td>
<td>314.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>114.245752</td>
<td>1.3991</td>
<td>1168.76</td>
<td>9.72</td>
<td>40.91</td>
<td>3240.5</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)+</td>
<td>114.395641</td>
<td>1.3945</td>
<td>1174.39</td>
<td>10.01</td>
<td>41.77</td>
<td>3272.6</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)+$^{\text{a}}$</td>
<td>114.395641</td>
<td>1.3945</td>
<td>1174.39</td>
<td>10.01</td>
<td>41.77</td>
<td>3272.6</td>
</tr>
<tr>
<td>BeF($X^\Sigma^+$)</td>
<td>MRCI</td>
<td>114.527947</td>
<td>1.4165</td>
<td>1058.64</td>
<td>13.10</td>
<td>80.5</td>
<td>10216.1</td>
</tr>
<tr>
<td></td>
<td>MRCI+Q</td>
<td>114.535290</td>
<td>1.4154</td>
<td>1061.30</td>
<td>13.09</td>
<td>85.4</td>
<td>10417.8</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)</td>
<td>114.536445</td>
<td>1.4142</td>
<td>1063.30</td>
<td>11.65</td>
<td>82.1</td>
<td>8611.7</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)+</td>
<td>114.586305</td>
<td>1.4080</td>
<td>1072.93</td>
<td>11.70</td>
<td>82.9</td>
<td>8573.3</td>
</tr>
<tr>
<td></td>
<td>CCSD(T)+$^{\text{a}}$</td>
<td>114.586305</td>
<td>1.4080</td>
<td>1072.93</td>
<td>11.70</td>
<td>82.9</td>
<td>8573.3</td>
</tr>
</tbody>
</table>

$^a$Core–valence CCSD(T) calculations with the aug-cc-pCV5Z basis set. $^b$Reference 12. $^cD_0^a$ value; $^dD_0^a(A^\Pi) = D_0^a(X^\Sigma^+) - \nu_{00} (A \leftrightarrow X)$; $^e$Reference 6. $^fD_0$ value.

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

Scheme 4. vbL Diagram Depicting the Bonding in the $^1\Sigma^+$ State of BeF
(2) Kramida, A.;Ralchenko, Yu.;Reader, J.; NIST ASD Team
NIST Atomic Spectra Database (ver. 5.5.6); National Institute of
Standards and Technology: Gaithersburg, MD, 2018; https://
physics.nist.gov/asd.
(3) Kalemos, A. The Nature of the Chemical Bond in BeO−,
BeOBe+,BeOBeH+,BeOBeH++,and HBeOBeH. J. Chem. Phys. 2017, 146,
104307.
(4) Heaven, M. C.; Merritt, J. M.; Bondybey, V. E. Bonding in
(5) Heaven, M. C.; Bondybey, V. E.; Merritt, J. M.; Kaledin, A. L.
The Unique Bonding Characteristics of Beryllium and the Group
(6) Green, M. L.; Jean, P.; Heaven, M. C. Dative Bonding Between
(7) Farber, M.; Srivastava, R. D. Dissociation Energies of Beryllium
Fluoride (BeF) and Beryllium Chloride (BeCl) and Heat of
Formation of Beryllium Chlorofluoride (BeClF). J. Chem. Soc.,
(8) Hildenbrand, D. L.; Murad, E. Mass–Spectrometric Determina-
tion of the Dissociation Energy of Beryllium Monofluoride. J.
(9) Prascher, B. P.; Woon, D. E.; Peterson, K. A.; Dunning, T. H.,
Jr.;Wilson, A. K. Gaussian Basis Sets for Use in Correlated
Molecular Calculations. VII Valence, Core–Valence, and Scalar
Relativistic Basis Sets for Li, Be, Na, and Mg. Theor. Chem. Acc.
2011, 128, 69–82.
(10) Peterson, K. A.; Dunning, T. H., Jr.Accurate Correlation
Consistent Basis Sets for Molecular Core—Valence Correlation
Effects: The Second Row Atoms Al–Ar and the First Row Atoms
Schütz, M.; Celani, P.; Gyorffy, W.; Kats, D.; Korona, T.; Lindh,
R.; et al. MOLPRO, version 2012.1, a package of ab initio programs;
(12) Huber, K. P.; Herzberg, G. Constants of Diatomic Molecules
(data prepared by J.W. Gallagher and R.D. Johnson, III). NIST
Chemistry WebBook, NIST Standard Reference Database Number 69.
(13) Kristensen, P.; Petrunin, V. V.; Andersen, H. H.; Andersen, T.
Laser Spectroscopy of the Be+ Ion: Binding Energies of Metastable