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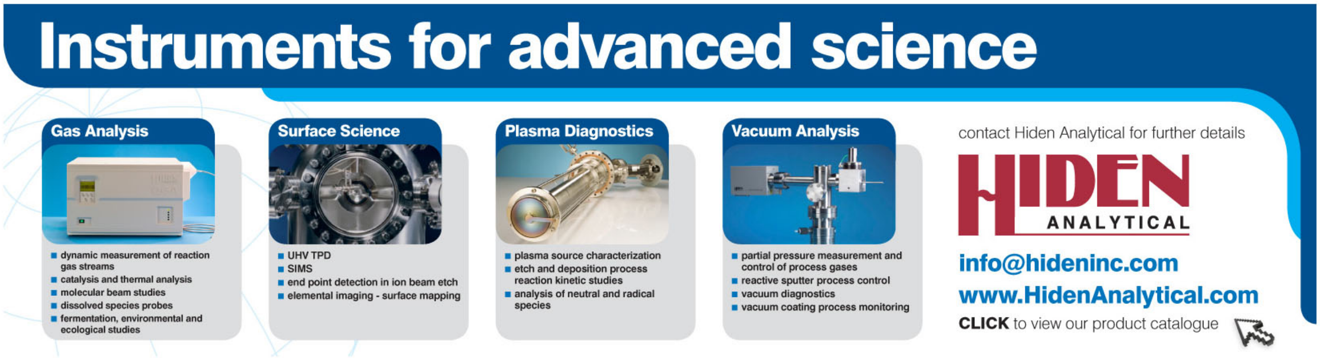

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An *ab initio* study of the electronic structure of BF and BF^+

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The BF and BF^+ molecular systems have been thoroughly studied by multireference variational and single reference coupled-cluster methods employing basis sets of sextuple cardinality. Potential energy curves have been constructed for 33 (BF) and 8 (BF^+) states and the usual molecular parameters have been extracted most of which are in excellent agreement with the available experimental data. A characteristic feature of the BF system is the intense valence-Rydberg interaction in most of the studied states. Its X-state is of $^1\Sigma^+$ symmetry featuring a triple bond of roughly 182 kcal/mol at $r_e = 1.2631$ Å. It is interesting indeed that for the last 50 years it was believed that the charge polarity of BF is B^-F^+. This is the first time that according to the present high level calculations, it is shown that the polarity of BF is the "normal" one B^+F^-, with a total charge transfer from B to F of about 0.2 electrons. Removing a rather inactive σ electron we get the $X^2\Sigma^+$ BF^+ state sharing similar bonding features as the $X^1\Sigma^+$ one of the parental molecule. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4793738]

I. INTRODUCTION

Boron fluoride (BF), a simple 14 electron diatomic molecule isoelectronic to both CO and N_2, has attracted attention since the beginning of the 20th century. The first recorded attempt to investigate experimentally this system seems to be that of Johnson and Jenkins[1] who as early as 1927 tried to photograph it but failed due to intruder SiF bands. A few years later, Johnson and Tawde[2] successfully recorded BF bands in the range 6400–4440 Å, but failed to find the expected resemblance between its bands and those of CO or N_2. In addition to these recorded bands, three new bands all in the UV region were found by Dull[3] in 1935. These newly detected bands were attributed to either a $^3\Sigma \rightarrow {}^3\Pi$ or $^3\Pi \rightarrow {}^3\Sigma$ transition.

In a rather simultaneous attempt, Strong and Knauss[4] photographed 16 new bands in the region 3712–2380 Å during an electrodeless discharge experiment. Their successful analysis of the vibrational structure of the band systems at 32 020.5 (A system) and 37 991 cm^{-1} (B system), provided ω_e and $\omega_e x_e$ values for both of them. Two years later, Paul and Knauss[5] reported on the rotational analysis of the (0,0), (0,1), (0,2), and (1,0) bands of the previously studied A system interpreted by assuming a $^3\Sigma \rightarrow {}^3\Pi$ transition. An upper limit of 0.2 cm^{-1} could be deduced for the Λ-doubling of the $^3\Pi$ state. The triplet band system was revisited by Dodsworth and Barrow[6] and Barrow *et al.*[7] in 1955 and 1958, respectively, who questioned the magnitude of the Λ-doubling previously reported. They concluded that the $^3\Pi$ state is regular and deduced molecular constants for the $b^3\Sigma^+$, $e^3\Sigma^+$, and $a^3\Pi$ states.

In 1949, Chrétien and Miescher[8] found the main singlet band assigned to a $A^1\Pi \rightarrow X^1\Sigma^+$ emission, that was also rotationally and vibrationally analyzed.[9] Almost ten years later, Onaka[10] reported on the same singlet emission system that was studied with the aid of a higher dispersion spectrograph, resulting in more accurate molecular constants. The next study on singlet BF states appears in 1963 by Robinson[11] who discovered seven new band systems involving overall eight states in the region 9500–28 000 cm^{-1} through emission spectroscopy. Molecular constants are reported and tentative assignments have been given. An estimated value of 88 500 cm^{-1}(=10.97 eV) for the first ionization energy is also reported. With the exception of $A^1\Pi$, all upper states seem to have equal and shorter bond distances than the ground state, a feature suggestive of Rydberg character with the same charged core (BF^+). A band system whose origin lies at 14 900 cm^{-1} and interpreted as a $J^1\Sigma \rightarrow H^1\Sigma$ transition,[11] was re-examined by Czarny and Felenbok[12] who attributed it to a $e^3\Sigma \rightarrow b^3\Sigma$ transition based on a previous suggestion by Lefebvre-Brion and Moser.[13] Actually the $H^1\Sigma$ state was the $b^3\Sigma$ one observed by Barrow *et al.*[7] Another triplet band system, the $c^3\Sigma^+ \rightarrow a^3\Pi$, was studied by Krishnamachari and Singh[14] resulting only to an ω_e value due to insufficient data.

In a 1970 *tour de force* study, Caton and Douglas[15] recorded both the emission and absorption spectrum from 900 to 11 000 Å. They have found new band systems, including Rydberg series, identified new electronic states, and corrected previous assignments. All the electronic states except the ground state and the lowest excited singlet and triplet states are of Rydberg character, interacting strongly among them but also with valence states. An ionization energy of IE = 11.115 ± 0.004 eV is also reported based on a series limit of 0-0 bands near 1100 Å. Unfortunately, they could not deduce any information on the dissociation energy (D) of the X-state, although a value of 7.81 ± 0.13 eV had already been given based on previous thermochemical data.[16] It is worth noticing at this point that a D_0 value larger by 5 kcal/mol based on a Birge–Sponer extrapolation of the vibrational levels of the $A^1\Pi$ state had been already reported.[17] This 5 kcal/mol difference was attributed to a

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maximum in the potential curve of that $A^1\Pi$ state, considering the systematic and uniform discrepancies found in a series of group IIIA monofluorides.[16]

In a microwave study, Lovas and Johnson[18] observed direct rotational transitions in the ground vibrational state of ^{10,11}BF leading to improved ground state constants. A dipole moment value of 0.5 ± 0.2 D was also reported for the first (and last) time. The relative large error bars are due to the small Stark shift. Improved molecular constants of the $A^1\Pi \rightarrow X^1\Sigma^+$ system based on a re-analysis of nine bands were provided by Le Floch *et al.*[19] in 1980. Accurate molecular constants for the X-state of ^{11}BF were derived by an analysis of its rovibrational bands through the pulse discharge modulation method.[20] Three years later in a high-resolution spectra in the near IR (6000–12 000 cm^{-1}) Bredohl *et al.*[21] observed three singlet bands from $H^1\Sigma^+$ to $A^1\Pi$ through the $D^1\Pi$ and the $B^1\Sigma^+$ states and two triplet bands involving the $d^3\Pi$–$b^3\Sigma^+$ and $g^3\Sigma^+$–$d^3\Pi$ transitions. Accurate rotational constants are reported for the states entailed which are of Rydberg character with the exception of the $A^1\Pi$ state. In a milli- and sub-millimeter wave spectrum of BF observed in the lowest vibrational states, Cazzoli *et al.*[22] extracted the most accurate rotational constants corrected also for Born–Oppenheimer (BO) breakdown effects. The last experimental study seems to be that of Zhang *et al.*,[23] who in 1995 obtained accurate molecular constants by the high resolution IR emission spectrum of the fundamental and several hot bands of ^{10,11}BF. Through the combination of existing microwave data, they determined improved Dunham parameters for the $X^1\Sigma^+$ state that incorporate also non-adiabatic effects.

The first theoretical report on the X-state of BF seems to be a Hartree–Fock (HF) study by Ransil,[24] the first of a series of papers under the general title "Studies in Molecular Structure," a project initiated in the Laboratory of Molecular Structure and Spectra at the University of Chicago in the 1960s. Ransil[24] reports results on simple diatomics such as total energies, dissociation energies, and dipole moments. Based on a Slater LCAO calculation, the dipole moment of BF is found to be 2.16 D with the "remarkable" polarity B^-F^+. Similar work at the HF level reporting also several molecular properties has been considered by Fraga and Ransil,[25] Nesbet,[26] Huo,[27] Yoshimine and McLean,[28] Sadlej,[29] Laaksonen *et al.*,[30] da Costa *et al.*,[31] and Huzinaga *et al.*[32] In all these studies, the reported dipole moment has the polarity B^-F^+ initially found by Ransil.[24] Even limited MCSCF wavefunctions predict the same chemically counterintuitive charge distribution.[32] Surprisingly enough, this is still believed nowadays based on MP2 and QCISD/6-311++G(2d, 2p/3df, 3pd) calculations.[33] Quite interestingly Lefebvre-Brion and Moser[13] calculated successfully a number of Rydberg states of both singlet and triplet spin multiplicity at the HF level as early as 1965.

The first post-HF study appeared in 1981 by Kurtz and Jordan[34] with the main goal to investigate the effect of electron correlation on the dipole moment of the $X^1\Sigma^+$ state, that seemed to have an opposite polarity as expected based on electronegativity arguments. Through second order perturbation theory calculations coupled mainly with a $[5s3p1d/_B6s3p1d/_F]$ basis set, they found a dipole moment of $\mu = 0.89$ D (B^-F^+). Based on a 0.02 Å overestimation of the BF bond length, they were also led to the conclusion that a partial triple bond character is possible resulting from a charge donation from the F $2p_\pi$ orbitals to the vacant B $2p_\pi$ orbitals. Just a year later and with the same incentives, Rosmus *et al.*[35] studied the correlation effect on the dipole moment through the MCSCF and CEPA (coupled electron pair approximation) methodology. Both methods predict a B^-F^+ polarity with dipole moment values of 1.12 and 0.88 D, respectively. The vibrationally averaged MCSCF dipole moments decrease with increasing vibrational quantum number and change sign at v = 13. This behavior is rationalized on the basis of a strong charge transfer from F($2p_\pi$) to B($2p_\pi$) at short distances, diminishing gradually as the two atoms are pulled apart. Similar results were also obtained by Botschwina[36] based on the CEPA methodology.

In a comparative study of nine closed shell diatomics including first and second row atoms, Peterson and Woods[37] report MP4SDQ/[8*s*5*p*2*d*] total energies and the usual molecular parameters, and a CISD dipole moment value for the $X^1\Sigma^+$ state of BF. They report a value of 1.02 D (B^-F^+) in line with the previously calculated values. In a MRDCI/[6*s*4*p*1*d*] study, Honigmann *et al.*[38] reported for the first time potential energy curves (PECs), and the associated molecular constants for seven states of $^{1,3}\Sigma^+$ and $^{1,3}\Pi$ symmetry as well as dipole transition matrix elements. The calculated dipole moment of the $X^1\Sigma^+$ is still found with the B^-F^+ polarity, an "interesting feature" as it is stated. In a dynamic polarizability and hyperpolarizability study of CO and BF and with the aim to study the effect of the first low-lying states on the convergence of the above properties, Mérawa *et al.*[39] obtained transition energies for four $^1\Pi$ and five $^1\Sigma^+$states through a time-dependent gauge invariant method.

In an exhaustive basis set convergence study on the BF_3 molecule based on the coupled-cluster CCSD(T) method, Martin and Taylor[40] obtained as a byproduct an accurate value of the binding energy of the $X^1\Sigma^+$ BF state including core-valence (CV) and spin-orbit effects, D_e (D_0) = 182.13 (180.13) kcal/mol. In the same spirit is also the work by Bauschlicher and Ricca,[41] who based on B3LYP geometries, obtained CCSD(T) energies for the valence electrons while core-valence and scalar relativistic effects were considered through the modified coupled pair functional (MCPF) method coupled with the appropriate basis sets. Their best atomization energy value amounts to $D_0 = 179.85$ kcal/mol. Also, Feller and Sordo[42] studied the convergence of the CCSDT method for diatomic dissociation energies. They reported a $D_e = 180.1$ kcal/mol at the CCSD(T)/cc-pVQZ level of theory. In a combined experimental/theoretical work of the BCl molecule, Irikura *et al.*[43] report equation of motion (EOM)-CCSD results on 14 excited states of BF, predominantly of Rydberg character and in very good agreement with the existing experimental data.

The last theoretical work on BF that we are aware of, is a study of several Rydberg states based on the R-matrix method by Chakrabarti *et al.*[44] Twenty-two Rydberg states are reported covering an energy range of ~10.5 eV, in excellent agreement with the experimental transition energy values.

It is rather evident from the above detailed exposition that research on BF has been active for nearly 90 years. It is also clear that theoretical work is pretty much limited and unsystematic either because of the inadequacy of the methods and techniques or due to the number of states examined. We believe that a systematic and extensive theoretical description of the BF system is needed. To this end, we have performed multireference variational (MRCI) calculations for 13 and 8 bound states of BF and BF^+, respectively, using extended basis sets. PECs arising from B $[^2P(2s^22p^1)$, $^4P(2s^12p^2)$, $^2S(2s^23s^1)$, $^2P(2s^23p^1)]$ + $F(2s^22p^5;\ ^2P)$ and $B^+(2s^2;\ ^1S)$ + $F^-(2s^22p^6;\ ^1S)$ channels of singlet, triplet, and quintet spin multiplicity and of $\Lambda = 0^{\pm}$, 1, and 2 spatial symmetry, have been constructed and the usual molecular parameters were extracted. For the BF^+ molecular system, PECs for 8 states of $^2\Sigma^+[3]$, $^2\Sigma^-$, $^2\Pi[3]$, and $^2\Delta$ symmetry originating to $B^+(^1S,\ ^3P) + F(^2P)$ asymptotic limits have been considered.

II. METHODOLOGY

For both B and F atoms, the augmented correlation consistent basis sets of quintuple (aug-cc-pV5Z = A5ζ)[45] and sextuple (aug-cc-pV6Z = A6ζ)[46] zeta quality have been employed, generally contracted to $[7s6p5d4f3g2h]_{B,F}$ and $[8s7p6d5f4g3h2i]_{B,F}$, respectively. For CV correlation and scalar relativistic effects, the appropriately optimized aug-cc-pCV5Z (=AC5ζ)[45] and aug-cc-pV5Z-DK (=A5ζ-DK)[45] basis sets have been used, while the combined effects were considered through the aug-cc-pCV5Z-DK (AC5ζ-DK) basis set.

Our reference wavefunctions are of the complete active space self-consistent field (CASSCF) type. Correlation effects have been extracted through the MRCI = CASSCF + 1 + 2 and RCCSD(T) (restricted coupled-cluster + single + double + perturbative connected triplets)[47] computational methods. For the construction of the potential energy curves that capture correctly the valence, Rydberg, and ion-pair mixing, a reference wavefunction of state average SACASSCF character was designed that resulted by distributing 8 valence electrons to 11 orbitals correlating to $(2s,\ 2p,\ 3s,\ 3p)_B + (2p)_F$. Valence correlation (10 e^- for BF, 9 e^- for BF^+) was considered through single and double excitations out of all configuration functions (CF) of the reference space within the internally contracted icMRCI scheme.[48] The valence MRCI spaces range from 5.8×10^9 $(^3B_1)$ to 3.0×10^9 $(^1A_2)$ CFs internally contracted to 33.5×10^6 and 26.5×10^6 CFs, respectively. Size non-extensivity errors amount to approximately 7 mE_h at the MRCI level and are largely corrected by the Davidson (+Q) correction.[49] Core-valence effects (14 e^- for BF, 13 e^- for BF^+) were evaluated only at the RCCSD(T) level of theory. Scalar relativity was considered through the second order Douglas–Kroll–Hess (DKH2) approximation.[50,51]

All calculations were performed under C_{2v} symmetry restrictions by the MOLPRO 2010.1 program.[52]

III. RESULTS AND DISCUSSION

A. BF

Table I presents the numerical data for 13 states with corresponding PECs at the MRCI/A6ζ level of theory displayed in Figures 1–5. Molecular states dissociating to the ground asymptotic limit $B(2s^22p^1;\ ^2P) + F(2s^22p^5;\ ^2P) \rightarrow BF\ ^{1,3}(\Sigma^+[2],\ \Sigma^-,\ \Pi[2],\ \Delta)$ as well as to the excited $B(2s^12p^2;\ ^4P) + F(2s^22p^5;\ ^2P) \rightarrow BF\ ^{3,5}(\Sigma^+,\ \Sigma^-[2],\ \Pi[2],\ \Delta)$, $B^+(2s^2;\ ^1S) + F^-(2s^22p^6;\ ^1S) \rightarrow BF\ (^1\Sigma^+)$, $B(2s^23s^1;\ ^2S) + F(2s^22p^5;\ ^2P) \rightarrow BF\ ^{1,3}(\Sigma^+,\ \Pi)$ and $B(2s^23p^1;\ ^2P) + F(2s^22p^5;\ ^2P) \rightarrow BF\ ^{1,3}(\Sigma^+[2],\ \Sigma^-,\ \Pi[2],\ \Delta)$ atomic channels, lying experimentally[53] 3.551, 4.90, 4.963, and 6.02 eV higher have been considered, revealing the strong interplay between states of valence and Rydberg nature that is reflected in the interesting topology of the potential curves along the internuclear distance. In what follows, we present the most salient features for 13 out of a total of 33 states considered (*vide infra*) in this study. We tag the molecular states by a number in parenthesis representing the energy order and a letter corresponding to their spectroscopic notation.

1. $X^1\Sigma^+(1)$, $B^1\Sigma^+(5)$, $C^1\Sigma^+(7)$, and $^1\Sigma^+(12)$

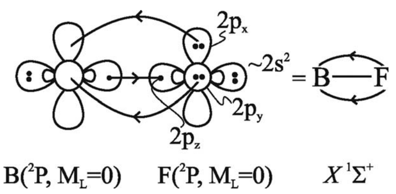
The ground state of the BF molecule is of $^1\Sigma^+$ symmetry correlating to $B(2s^22p^1;\ ^2P,\ M_L = 0) + F(2s^22p^5;\ ^2P,\ M_L = 0)$. The equilibrium CASSCF wavefunction and corresponding Mulliken atomic populations are

$$|X^1\Sigma^+(1)\rangle \approx 0.95\left|3\sigma^2 4\sigma^2 5\sigma^2 1\pi_x^2 1\pi_y^2\right\rangle,$$

$$2s^{1.73}2p_z^{0.57}2p_x^{0.18}2p_y^{0.18}(3d)^{0.12}/_B\, 2s^{1.86}2p_z^{1.67}2p_x^{1.80}2p_y^{1.80}(3d)^{0.04}/_F,$$

$$q_B = +0.17,$$

where $3\sigma \sim (0.98)2s^F$, $4\sigma \sim (0.89)2s^F - (0.55)2s^B - (0.38)2p_z{}^B$, $5\sigma \sim (0.82)2s^B - (0.56)2p_z{}^B + (0.31)2s^F$, $1\pi \sim 2p_\pi{}^F$, clearly show the formation of a σ bond with a rather strong charge transfer from the B $2p_z$ to the F $2p_z$ orbital and a concomitant π-backdonation from the F $2p_\pi$ to the empty $2p_\pi$ B orbitals. The bonding characteristics can be nicely described by the following valence-bond-Lewis (vbL) diagram:



The intense charge migration along the σ-frame is due to the strong interaction with the $^1\Sigma^+$ state correlating to the ion-pair $B^+(^1S) + F^-(^1S)$ limit, lying 5.19 (5.02) [4.90] eV above the ground asymptotic channel at the MRCI(+Q)[expt][53] level. This is evident from both the morphology of the corresponding PECs and the large charge transfer of ~0.25 e^- along the σ-frame at the large distance of ~7 bohr. The equilibrium bond length and dissociation energy are found to be $r_e = 1.2635$ (1.267) [1.2668] Å and $D_e = 184.25$ (182.7) [181.54] kcal/mol at the valence MRCI(+Q)[RCCSD(T)]/A6ζ level of theory. Scalar relativistic and core-valence correlation effects considered at the C-RCCSD(T)-DK/AC5ζ-DK level of theory give, $r_e = 1.2631$ Å and $D_e = 181.91$ kcal/mol in perfect agreement with the experimental values of $r_e = 1.262711672$ Å and $D_e = 182 \pm 3$ kcal/mol (see Table II). Also in excellent agreement are

TABLE I. Energies E (E_h), bond distances r_e (Å), dissociation energies D_e (kcal/mol), harmonic frequencies ω_e (cm^{-1}), anharmonic corrections $\omega_e x_e$ (cm^{-1}), rotation-vibration coupling constants α_e (cm^{-1}), centrifugal distortion constants $\bar{D}_e$ (cm^{-1}), dipole moments μ (Debye), and energy gaps T_e (cm^{-1}) of 13 ^{11}BF states at the MRCI(+Q)/A6ζ level of theory; experimental results in square brackets.

State	$-E$	r_e	D_e	ω_e	$\omega_e x_e$	α_e	$\bar{D}_e \times 10^6$	$\langle\mu\rangle/\mu_{FF}$[a]	T_e
$X^1\Sigma^+$	124.53721	1.2635	184.25	1408.57	11.80	0.0188	7.0	0.99/0.94	0.0
	(124.5540)	(1.267)	(182.7)	(1394.3)	(12.20)	(0.0190)	(7.0)	/0.84	(0.0)
		[1.262711672][b]	[182 ± 3][c]	[1402.15865][b]	[11.82106][b]	[0.01904848][b]	[7.09528][b]	[0.5 ± 0.2][d]	[0.0]
$a^3\Pi(2)$	124.40346	1.3049	100.32	1350.68	9.15	0.0154	6.3	−0.55/−0.57	29 355.63
	(124.4208)	(1.311)	(99.1)	(1324.5)	(9.30)	(0.0158)	(6.4)	/−0.55	(29 238.2)
		[1.3081][e]	[98.7 ± 3]	[1323.9][e]	[9.20][e]	[0.0158][e]	[6.3][e]		[29 144.3][f]
$A^1\Pi(3)$	124.30479	1.3076	38.5	1240.41	23.43	0.0218	7.4	0.10/0.20	51 009.59
	(124.3232)	(1.309)	(37.8)	(1261.7)	(12.52)	(0.0181)	(7.1)	/0.01	(50 668.5)
		[1.3038][g]	[35.7 ± 3]	[1264.96][h]	[12.53][h]	[0.0180][g]	[7.3][g]		[51 157.45][g]
$b^3\Sigma^+(4)$	124.26319	1.2176	12.2	1659.78	18.61	0.0189	6.3	−4.39/−4.03	60 140.72
	(124.2772)	(1.218)	(9.0)	(1624.0)	(16.37)	(0.0198)	(6.6)	/−4.12	(60 759.73)
		[1.2149][g]	[7.49 ± 3]	[1629.28][e]	[22.255][e]	[0.0200][g]	[6.3][g]		[61 035.3][e,f]
$B^1\Sigma^+(5)$	124.24361	1.2099		1697.76	12.68	0.0170	6.3	−7.36/−7.12	64 438.58
	(124.2579)	(1.211)		(1690.7)	(12.15)	(0.0169)	(6.3)	/−6.95	(64 984.8)
		[1.2074][g]		[1692.9][g]	[12.4][g]	[0.0178][g]	[7.6][g]		[65 353.9$_3$][g]
$c^3\Sigma^+(6)$	124.23612	1.2253		1591.93	19.65	0.0215	6.6	7.49/8.89	66 082.08
	(124.2503)	(1.230)		(1517.8)	(29.67)	(0.0252)	(7.1)	/10.02	(66 661.1)
		[1.228][g]		[1540.7][g]			[5.5][g]		[67 045][e,f]
$C^1\Sigma^+(7)$	124.22708	1.2227		1617.37	13.75	0.0185	6.5	9.52/9.91	68 066.17
	(124.2412)	(1.224)		(1606.4)	(14.19)	(0.0185)	(6.5)	/9.63	(68 663.3)
		[1.2204][g]		[1613.2][g]	[14.5][g]	[0.0194][g]	[7.3][g]		[69 030.3$_8$][g]
$d^3\Pi(8)$	124.22086	1.2136		1696.87	10.96	0.0164	6.2	−1.31/−1.01	69 429.74
	(124.2352)	(1.214)		(1689.5)	(11.18)	(0.0165)	(6.2)	/−0.78	(69 986.6)
		[1.2100][g]		[1696.81][g]	[11.0][g]	[0.0176][g]	[6.5][g]		[70 710.4][f,g]
$D^1\Pi(9)$	124.21514	1.2255		1682.84	11.12	0.0164	5.9	−1.18/−1.14	70 685.15
	(124.2278)	(1.223)		(1677.5)	(11.03)	(0.0165)	(6.0)	/−1.05	(71 600.8)
		[1.2188][i]		[1661.96][i]	[11.7][i]	[0.0170][i]	[6.3][i]		[72 144.42][g]
$e^3\Pi(10)$	124.17776	2.1383	36.28	644.39	6.22	0.0039	1.4	−0.58/	78 883.45
	(124.1998)	(2.188)	(42.42)	(591.18)	(2.28)	(0.0013)	(1.5)		(78 933.5)
$^3\Sigma^-(11)$	124.14907	1.5485	18.11	938.17	15.12	0.0154	4.7	−1.13/	85 180.26
	(124.1780)	(1.543)	(28.66)	(1196.74)	(20.73)	(0.0097)	(2.9)		(82 537.3)
$^1\Sigma^+(12)$	124.13419	1.5668	40.30	1863.87	44.57	0.0014	1.1	−2.35/	88 453.69
	(124.1604)	(1.547)	(49.0)	(1796.6)	(30.2)	(0.0022)	(1.3)		(86 403.9)
$^1\Delta(13)$	124.11926	1.4466	55.38	1363.91	34.15	0.0205	3.3	−1.12/	91 722.16
	(124.1610)	(1.470)	(73.0)	(1405.0)	(31.6)	(0.0125)	(2.8)		(86 267.8)

[a] μ_{FF} by the finite field approach, field strength ranging from -5×10^5 to 5×10^5 a.u.
[b] Reference 23.
[c] Reference 16.
[d] Reference 18.
[e] Reference 7.
[f] Reference 57.
[g] Reference 15.
[h] Reference 10.
[i] Reference 59.

the usual molecular constants for both ^{11}BF(^{10}BF) isotopologues which at the C-RCCSD(T)-DK/AC5ζ-DK level are $\omega_e = 1401.49$ (1444.96), $\omega_e x_e = 11.53$ (12.26), $\alpha_e = 0.0192$ (0.0210), and $\bar{D}_e(\times 10^6) = 7.1$ (8.0) cm^{-1}, with corresponding experimental values 1402.1587 (1445.7), 11.82 (12.574), 0.0198 (0.0209), and 7.6 (8.0208) cm^{-1}, respectively, attesting to the necessity of CV effects even for such a small molecular system; see Tables I and II. Recall that the natural abundance of two stable boron isotopes, ^{10}B and ^{11}B, are 19.8% and 80.2%, respectively.[54]

Concerning the dipole moment, an issue with a long history compounded with the accepted counterintuitive B^-F^+ polarity, all our calculations, even at the HF/cc-pVDZ level of theory, predict a *positive* charge on the B atom with a dipole moment value of $\mu = 0.88$ D. At our most accurate computational level, i.e., C-RCCSD(T)-DK/AC5ζ-DK, a value of $\mu = 0.84$ D is obtained through the finite field method[55] identical to the MRCI+Q/A6ζ value; see Table II. The 0.84 D value is in slight disagreement with the upper limit of the experimental value of 0.5 ± 0.2 D.[18]

The $B^1\Sigma^+(5)$ is the second state studied of $^1\Sigma^+$ symmetry originating from B(^{2}P) + F(^{2}P), but is of purely repulsive nature due to the asymptotic combination B($2s^2 2p^1$; ^{2}P, $M_L = \pm 1$) + F($2s^2 2p^5$; ^{2}P, $M_L = \mp 1$). Its vbL description

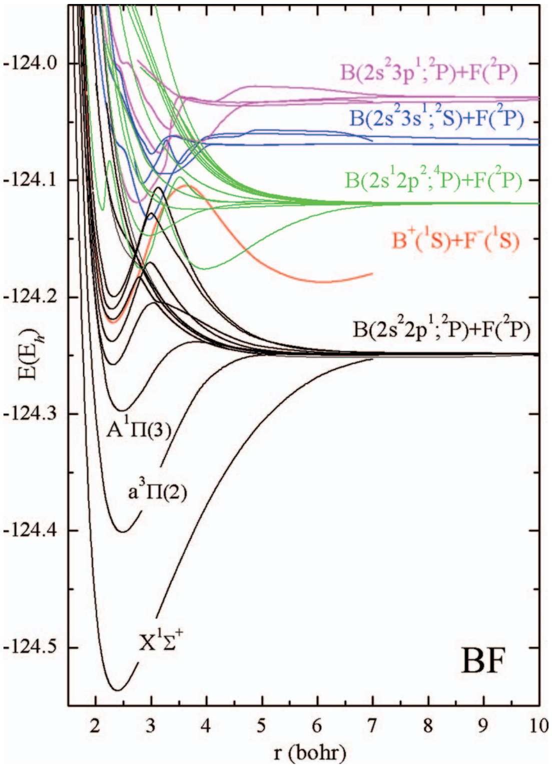


FIG. 1. Potential energy curves of all 33 BF states studied at the MRCI/A6ζ level of theory.

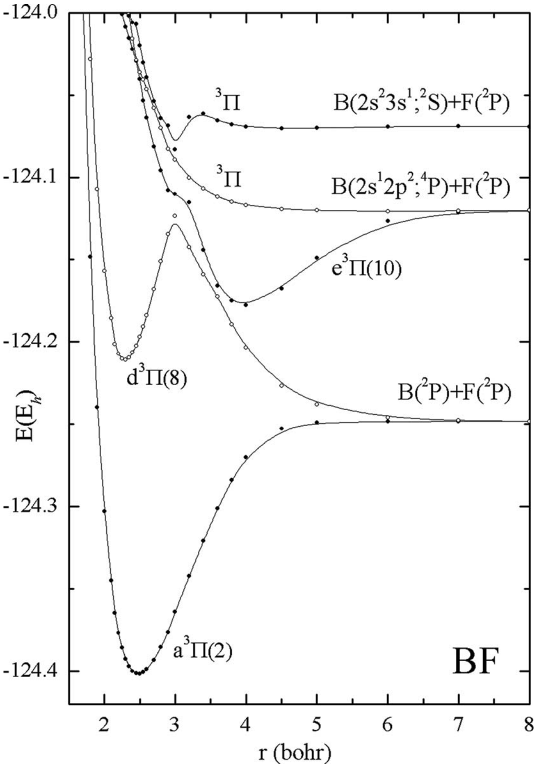


FIG. 3. MRCI/A6ζ potential energy curves of the $a^3\Pi(2)$, $d^3\Pi(8)$ and $e^3\Pi(10)$ BF states.

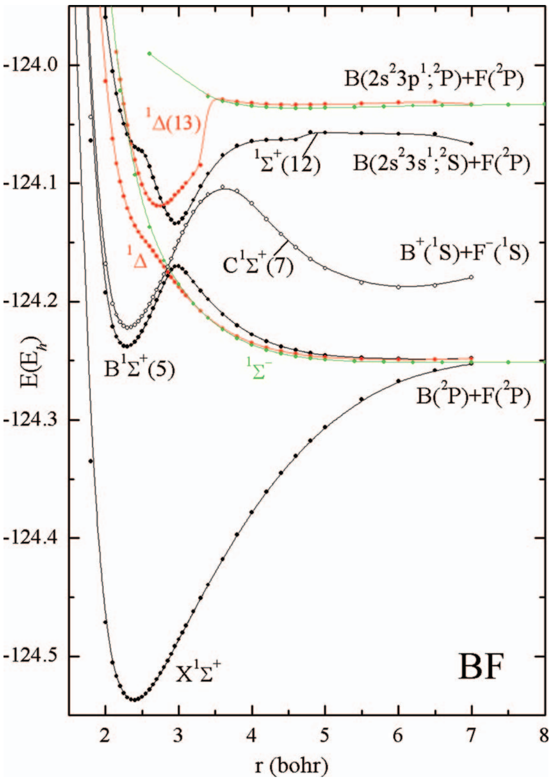


FIG. 2. MRCI/A6ζ potential energy curves of the $X^1\Sigma^+$, $B^1\Sigma^+(5)$, $C^1\Sigma^+(7)$, $^1\Sigma^+(12)$ and $^1\Delta(13)$ BF states.

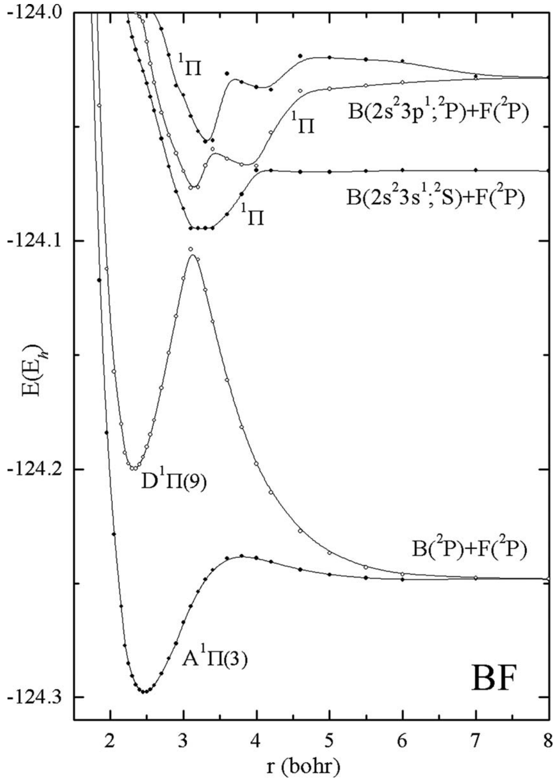


FIG. 4. MRCI/A6ζ potential energy curves of the $A^1\Pi(3)$ and $D^1\Pi(9)$ BF states.

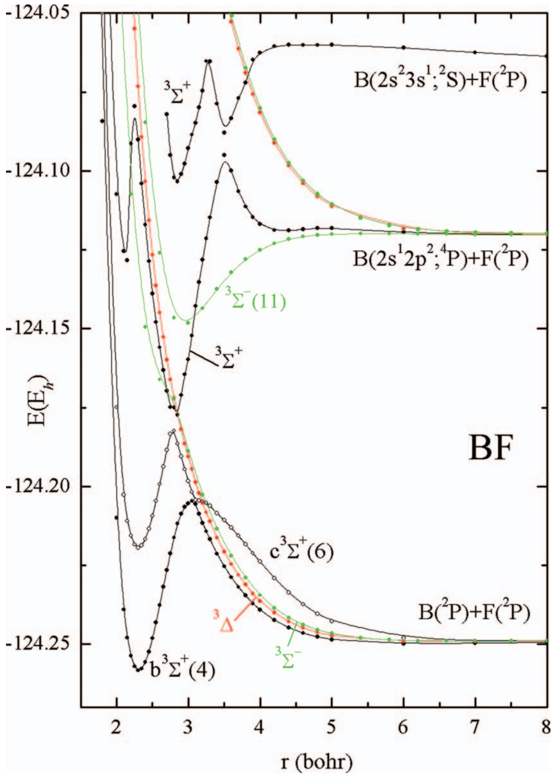
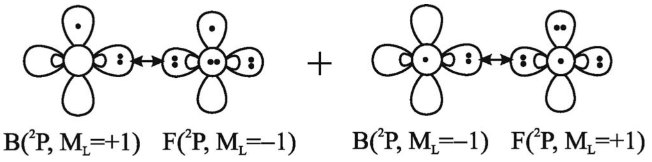


FIG. 5. MRCI/A6ζ potential energy curves of the $b^3\Sigma^+(4)$, $c^3\Sigma^+(6)$ and $^3\Sigma^-(11)$ BF states.



is indicative of an electronic congestion along the σ-frame due to the similarity of the 2s and 2p radial distributions[58] that obstructs of any chemical bonding. This is also the case for the symmetry related $^1\Sigma^-$ and $^1\Delta$ states that also share similar vbL icons (see Fig. 2). Due to a severe avoided crossing, however, at 3.0 bohr the $B^1\Sigma^+(5)$ state results into a potential well of Rydberg nature with a barrier to dissociation of 42.6(33.8) kcal/mol at the MRCI(+Q)/A6ζ level of theory. The avoided crossing is due to the $^1\Sigma^+$ state emanating from the B($2s^23s^1$; ^{2}S) + F($2s^22p^5$; ^{2}P) limit. The valence MRCI(+Q)/A6ζ equilibrium bond distance is r_e = 1.2099 (1.211) Å. Correcting now by $\delta r_e = -0.003$ Å (contraction due to CV effects in the $X^1\Sigma^+$ state) for CV effects in the $B^1\Sigma^+(5)$ state, we find an r_e = 1.207 (1.208) Å in perfect agreement with the experimental value of r_e = 1.2074 Å[15]; see Table I. It is also noticeable the agreement with the $r_e(X^2\Sigma^+)$ = 1.211 Å of the BF$^+$ system to which this $B^1\Sigma^+(5)$ Rydberg state converges.

The $C^1\Sigma^+(7)$ is the third studied $^1\Sigma^+$ state that originates from the ion-pair limit B$^+$(^{1}S) + F$^-$(^{1}S). A local minimum of purely ionic nature appears at r_e = 3.219 Å (=6.1 bohr) which is due to the repulsive character of the $B^1\Sigma^+(5)$ state (Fig. 2). To the left of the r = 3.6 bohrs point and due to an avoided crossing with the $^1\Sigma^+(12)$, the $C^1\Sigma^+(7)$ state approaches its Rydberg minimum at r_e = 1.223 (1.224) Å at the MRCI(+Q)/A6ζ level.

The main CASSCF equilibrium configurations and orbital synthesis (common for both states) of $B^1\Sigma^+(5)$ and $C^1\Sigma^+(7)$ are

$$\begin{aligned}|B^1\Sigma^+(5)\rangle \approx\ & \left|3\sigma^2 4\sigma^2 5\sigma^1[0.87(6\bar{\sigma}^1)+0.33(7\bar{\sigma}^1)]1\pi_x^2 1\pi_y^2\right\rangle \\ & +0.15\left|3\sigma^2 4\sigma^2 5\sigma^1 6\bar{\sigma}^1\left(1\pi_x^2 1\pi_y^1 2\bar{\pi}_y^1\right.\right. \\ & \left.\left.+\,1\pi_x^1 2\bar{\pi}_x^1 1\pi_y^2\right)\right\rangle, \\ \left|C^1\Sigma^+(7)\right\rangle \sim\ & \left|3\sigma^2 4\sigma^2 5\sigma^1[0.89(7\bar{\sigma}^1)\right. \\ & \left.-\,0.34(6\bar{\sigma}^1)]1\pi_x^2 1\pi_y^2\right\rangle \\ & +0.14\left|3\sigma^2 4\sigma^2 5\sigma^1 6\bar{\sigma}^1\left(1\pi_x^2 1\pi_y^1 2\bar{\pi}_y^1\right.\right. \\ & \left.\left.+\,1\pi_x^1 2\bar{\pi}_x^1 1\pi_y^2\right)\right\rangle,\end{aligned}$$

$3\sigma \sim (0.98)2s^{F}$, $4\sigma \sim (0.89)2p_z{}^{F} - (0.55)2s^{B} - (0.38)2p_z{}^{B}$, $5\sigma \sim (0.82)2s^{B} - (0.56)2p_z{}^{B} + (0.31)2p_z{}^{F}$, $6\sigma \sim 3s^{B}$, $7\sigma \sim 3p_z{}^{B}$, $1\pi \sim 2p_\pi{}^{F}$, $2\pi \sim 2p_\pi{}^{B}$.

The latter are indicative of their Rydberg character, while their spectroscopic MRCI(+Q)/A6ζ constants ω_e = 1697.76(1690.7)/$_B$, 1617.37(1606.4)/$_C$, and $\omega_e x_e$ = 12.68(12.15)/$_B$, 13.75(14.19)/$_C$ cm^{-1} are practically identical to the corresponding ω_e = 1700.05(1692.2) and $\omega_e x_e$ = 11.00(10.62) cm^{-1} values of the $X^2\Sigma^+$ state of BF$^+$ to which both B and C BF states converge; see Table III.

The last studied $^1\Sigma^+(12)$ state correlates adiabatically to the first boron Rydberg state B($2s^23s^1$; ^{2}S) + F($2s^22p^5$; ^{2}P, M_L = 0) and presents a minimum at r_e = 1.567 Å at the MRCI/A6ζ level, which is of mixed valence-Rydberg nature as evidenced by its leading MRCI configurations

$$\begin{aligned}\left|^1\Sigma^+(12)\right. \approx\ & 0.65\left|3\sigma^2 4\sigma^2 5\sigma^1 6\bar{\sigma}^1 1\pi_x^2 1\pi_y^2\right\rangle \\ & -0.40\left|3\sigma^2 4\sigma^2 5\sigma^2\left(1\pi_x^2 1\pi_y^1 2\bar{\pi}_y^1 + 1\pi_x^1 2\bar{\pi}_x^1 1\pi_y^2\right)\right\rangle.\end{aligned}$$

2. $a^3\Pi(2)$, $d^3\Pi(8)$, and $e^3\Pi(10)$

The first excited $a^3\Pi(2)$ state correlates adiabatically to B($2s^22p^1$; ^{2}P, M_L = ±1) + F($2s^22p^5$;^{2}P, M_L = 0) with the B(^{2}P, M_L = 0) + F(^{2}P; M_L = ±1) combination being of repulsive character (see Fig. 3). Although in principle, there is no reason for an attractive B(^{2}P, M_L = ±1) + F(^{2}P; M_L = 0) but repulsive B(^{2}P, M_L = 0) + F(^{2}P; M_L = ±1) PEC, an intense interaction with the $^3\Pi$ state correlating to the B(^{4}P, M_L = ±1) + F(^{2}P; M_L = 0) channel creates a potential well with a D_e = 100.3 (99.1) kcal/mol and r_e = 1.305 (1.311) Å at the MRCI(+Q)/A6ζ level. The main equilibrium CASSCF configuration and Mulliken populations along with the valence orbitals

$$\left|a^3\Pi(2)\right\rangle \approx 0.95\left|3\sigma^2 4\sigma^2 5\sigma^1 1\pi_x^2 2\pi_x^1 1\pi_y^2\right\rangle,$$

$$2s^{0.93}2p_z^{0.46}2p_x^{1.05}2p_y^{0.16}(3d)^{0.11}/_B\, 2s^{1.89}2p_z^{1.65}2p_x^{1.89}2p_y^{1.87}/_F,$$

$$q_B = +0.25,$$

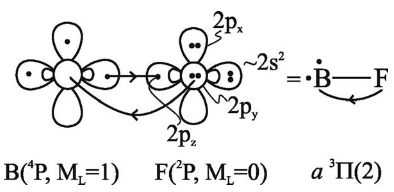
where $3\sigma \sim (0.99)2s^{F}$, $4\sigma \sim (0.48)2s^{B} + (0.34)2p_z{}^{B} - (0.89)2p_z{}^{F}$, $5\sigma \sim (0.88)2s^{B} - (0.49)2p_z{}^{B} + (0.30)2p_z{}^{F}$, $1\pi \sim 2p_\pi{}^{F}$, 2π

TABLE II. Energies E (E_h), bond distances r_e (Å), dissociation energies D_e (kcal/mol), harmonic frequencies ω_e (cm^{-1}), anharmonic corrections $\omega_e x_e$ (cm^{-1}), dipole moments μ (Debye), and energy gaps T_e (cm^{-1}) of the $X^1\Sigma^+$ and $a^3\Pi(2)$ ^{11}BF states at different levels of theory.

State	Method[a]	$-E$	r_e	D_e	ω_e	$\omega_e x_e$	$\langle\mu\rangle/\mu_{FF}$[b]	T_e
$X^1\Sigma^+$	MRCI	124.53387	1.2639	184.01	1407.86	12.02	0.99/0.94	0.0
	MRCI+Q	124.5506	1.2671	182.41	1393.53	12.28	/0.84	0.0
	C-MRCI-DK	124.73758	1.2591	184.88	1420.00	11.83	1.05/0.99	0.0
	C-MRCI-DK+Q	124.75914	1.2621	183.07	1404.71	11.72	/0.89	0.0
	RCCSD(T)	124.55204	1.2671	181.28	1393.40	11.36	/0.82	0.0
	RCCSD(T)-DK	124.64588	1.2670	181.12	1393.03	11.54		0.0
	C-RCCSD(T)	124.66866	1.2633	182.07	1402.91	12.00		0.0
	C-RCCSD(T)-DK	124.76295	1.2631	181.91	1401.49	11.53	/0.84	0.0
	Expt.		1.262711672[c]	182 ± 3[d]	1402.15865[c]	11.82106[c]	0.5 ± 0.2[e]	0.0
$a^3\Pi(2)$	RCCSD(T)	124.41875	1.3120	97.64	1320.28	9.24	/−0.54	29 253.35
	RCCSD(T)-DK	124.51242	1.3119	97.37	1319.45	9.21		29 291.88
	C-RCCSD(T)	124.53617	1.3084	98.93	1326.04	9.28		29 078.69
	C-RCSD(T)-DK	124.63027	1.3083	98.65	1325.22	9.23	/−0.55	29 118.89
	Expt.		1.3081[f]	98.7 ± 3	1323.86[f]	9.20[f]		29 144.3[g]

[a] Valence, core-valence, DK, and combined core-valence/DK MRCI and RCCSD(T) calculations with the A5ζ, AC5ζ, A5ζ-DK, and AC5ζ-DK basis sets, respectively.
[b] μ_{FF} by the finite field approach, field strength ranging from -5×10^5 to 5×10^5 a.u.
[c] Reference 23.
[d] Reference 16.
[e] Reference 18.
[f] Reference 7.
[g] Reference 57.

$\sim 2p_\pi{}^B$, allude to an *in situ* excited B(^{4}P) atom making the intrinsic bond strength of the $a^3\Pi(2)$ state equal to $D_e^{diab} = D_e^{adiab} + \Delta E_B(^4P \leftarrow {}^2P) = 100.3\ (99.1) + 80.5\ (82.8) = 180.8\ (181.9)$ kcal/mol at the valence MRCI(+Q)/A6ζ level of theory, practically the same as of the $X^1\Sigma^+$ state. Correcting for scalar relativistic and CV correlation effects at the C-RCCSD(T)-DK/AC5ζ-DK level of theory, we find perfect agreement with the experimental data (values in parenthesis) $r_e = 1.308$ (1.3081) Å, $\omega_e = 1325.22$ (1323.86), $\omega_e x_e = 9.23$ (9.20) cm^{-1}, $D_e = 98.7$ (98.7) kcal/mol, and $T_e = 29\,118.9$ (29 144.3) cm^{-1}; see Table II. The bonding characteristics can be safely accounted for by the following vbL icon:



The above diagram suggests a genuine σ bond with a large charge transfer from B to F of ∼ 0.5 e$^-$ and a smaller π-migration from F to B. The overall effect is a positive charge on B of about 0.25 e$^-$ with a C-RCCSD(T)-DK/AC5ζ-DK dipole moment of $\mu_{FF} = -0.55$ D. Notice the inverse

TABLE III. Energies E (E_h), bond distances r_e (Å), dissociation energies D_e (kcal/mol), harmonic frequencies ω_e (cm^{-1}), anharmonic corrections $\omega_e x_e$ (cm^{-1}), rotation-vibration coupling constants α_e (cm^{-1}), centrifugal distortion constants $\bar{D}_e$ (cm^{-1}), and energy gaps T_e (cm^{-1}) of five ^{11}BF$^+$ states at the MRCI(+Q)/A6ζ level of theory. Experimental results in square brackets.

State	$-E$	r_e	D_e	ω_e	$\omega_e x_e$	α_e	$\bar{D}_e \times 10^6$	T_e
$X^2\Sigma^+$	124.13414	1.2110	114.84	1700.05	11.00	0.0163	6.2	0.0
	(124.1508)	(1.213)	(119.1)	(1692.2)	(10.62)	(0.0162)	(6.2)	(0.0)
	124.14477[a]	1.2122[a]	115.84[a]	1698.74[a]	10.54[a]	0.0162[a]	6.2[a]	0.0[a]
	124.35543[b]	1.2088[b]	117.05[b]	1706.92[b]	10.89[b]	0.0162[b]	6.2[b]	0.0[b]
		[1.208 ± 0.005][c]	[117.4 ± 3.2][c]	[1765 ± 20][c]				
$2\,^2\Pi$	123.87770	1.3833	61.24	1610.41	19.29	0.0061	3.1	56 282.07
	(123.8937)	(1.390)	(64.8)	(1603.3)	(19.21)	(0.0058)	(3.0)	(56 416.4)
$3\,^2\Sigma^+$	123.86134	1.8197	51.0	792.84	6.06	−0.0049	2.5	59 872.46
	(123.8792)	(1.852)	(55.6)	(841.7)	(11.83)	(−0.0074)	(2.0)	(59 604.5)
$4\,^2\Delta$	123.81281	1.6735	20.52	536.21	10.02	0.0212	9.0	70 523.78
	(123.8239)	(1.683)	(20.9)	(528.0)	(9.98)	(0.0208)	(8.9)	(71 732.4)
$5\,^2\Sigma^-$	123.81066	1.6801	19.18	524.91	10.33	0.0217	9.1	70 996.75
	(123.8216)	(1.689)	(19.5)	(516.7)	(9.14)	(0.0213)	(9.1)	(72 243.1)

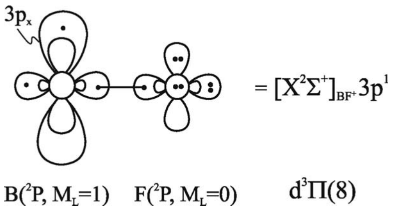
[a] Results based on RCCSD(T)/A5ζ calculations.
[b] Results based on C-RCCSD(T)-DK/AC5ζ-DK calculations.
[c] Reference 56.

direction of the dipole moment vector compared to the $X^1\Sigma^+$ state, $\mu = -0.55$ vs 0.84 D, although both states are of similar charge polarity, i.e., B^+F^-.

The $d^3\Pi(8)$ state owes its potential minimum to an avoided crossing at 3.0 bohrs with an incoming Rydberg state tracing its origin to B($2s^2 3p^1$; ^{2}P, $M_L = \pm 1$) + F(^{2}P, $M_L = 0$). Its potential minimum at $r_e = 1.214$ Å (Table I) along with its main equilibrium CF testify to its Rydberg nature

$$|d^3\Pi(8)\rangle \approx 0.93|3\sigma^2 4\sigma^2 5\sigma^1 1\pi_x^2 3\pi_x^1 1\pi_y^2\rangle$$

with $3\sigma \sim (0.99)2s^F$, $4\sigma \sim (0.50)2s^B + (0.40)2p_z{}^B - (0.92)2p_z{}^F$, $5\sigma \sim (0.85)2s^B - (0.55)2p_z{}^B + (0.25)2p_z{}^F$, $1\pi \sim 2p_\pi{}^F$, $3\pi \sim 3p_\pi{}^B$. The bonding is captured by the following vbL diagram, showing the Rydberg character of the $d^3\Pi(8)$ state:



Its spectroscopic parameters $\omega_e(\omega_e x_e) = 1696.9$ (10.96) cm^{-1} and $r_e = 1.214 - \delta r_e = 1.214 - 0.003 = 1.211$ Å are in complete agreement with both the experimental data and the corresponding values of the $X^2\Sigma^+$ BF$^+$ state; see Table III. Although this state is unbound with respect to its adiabatic limit, B($2s^2 2p^1$; ^{2}P) + F(^{2}P), its intrinsic bond strength with respect to B($2s^2 3p^1$; ^{2}P, $M_L = \pm 1$) + F(^{2}P, $M_L = 0$) is 112.63(118.7) kcal/mol at the MRCI(+Q)/A6ζ level of theory.

The last bound state studied, $e^3\Pi(10)$, owes its existence to the congruent interaction between the repulsive part of the $d^3\Pi(8)$ and strongly attractive part of the $^3\Pi$ diabatic state converging to B(^{4}P, $M_L = \pm 1$) + F(^{2}P, $M_L = 0$). Its main equilibrium CFs

$$\begin{aligned} |e^3\Pi(10)\rangle \approx\ & 0.63|3\sigma^2 4\sigma^1 5\sigma^2 1\pi_x^2 2\pi_x^1 1\pi_y^2\rangle \\ & + 0.36|3\sigma^2 4\sigma^2 5\sigma^1 1\pi_x^2 2\pi_x^1 1\bar{\pi}_y^1 2\pi_y^1\rangle \\ & - 0.36|3\sigma^2 4\sigma^1 5\bar{\sigma}^1 6\sigma^1 1\pi_x^2 2\pi_x^1 1\pi_y^2\rangle \\ & - 0.30|3\sigma^2 4\sigma^2 5\sigma^1 1\pi_x^2 2\pi_x^1 1\pi_y^2\rangle \end{aligned}$$

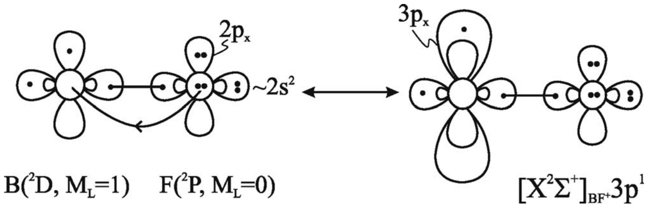
with $3\sigma \sim 2s^F$, $4\sigma \sim 2p_z{}^F$, $5\sigma \sim 2s^B$, $6\sigma \sim 2p_z{}^B$, $1\pi \sim 2p_\pi{}^F$, $2\pi \sim 2p_\pi{}^B$, are a mixture of these two components leading to a minimum at $r_e = 2.138$ Å.

3. $A^1\Pi(3)$ and $D^1\Pi(9)$

These two $^1\Pi$ states are in fact the singlet analogues of the $a^3\Pi(2)$ and $d^3\Pi(8)$ states correlating adiabatically to B($2s^2 2p^1$; ^{2}P, $M_L = \pm 1$, 0) + F($2s^2 2p^5$; ^{2}P, $M_L = 0$, ± 1), respectively (see Fig. 4). Both states behave in a repulsive way at large distances as the *a* and *d* $^3\Pi$ states did. At around 3.8 bohrs and after passing a barrier of 6.37 kcal/mol (MRCI/A6ζ), the interaction with the Rydberg $^1\Pi$ stemming from the B($2s^2 3p^1$; ^{2}P, $M_L = 0$) + F($2s^2 2p^5$; ^{2}P, $M_L = \pm 1$) channel having already interacted with the Rydberg state arising from the B($2s^2 3s^1$; ^{2}S) + F(^{2}P, $M_L = \pm 1$) asymptote, creates a potential well at $r_e = 1.308(1.309)$ Å with a $D_e = 38.5(37.8)$ kcal/mol at the MRCI(+Q)/A6ζ level. Its leading equilibrium CASSCF CFs

$$\begin{aligned} |A^1\Pi(3)\rangle \approx\ & 0.87|3\sigma^2 4\sigma^2 5\sigma^1 1\pi_x^2 2\bar{\pi}_x^1 1\pi_y^2\rangle \\ & - 0.36|3\sigma^2 4\sigma^2 5\sigma^1 1\pi_x^2 3\bar{\pi}_x^1 1\pi_y^2\rangle \end{aligned}$$

with $3\sigma \sim 2s^F$, $4\sigma \sim (0.89)2s^F - (0.52)2s^B - 0.352p_z{}^B$, $5\sigma \sim (0.86)2s^B - (0.53)2p_z{}^B + (0.32)2p_z{}^F$, $1\pi \sim 2p_\pi{}^F$, $2\pi \sim 2p_\pi{}^B$, $3\pi \sim 3p_\pi{}^B$, clearly show a state of mixed valence-Rydberg character. The above CFs support the "resonance" of the following vbL diagrams



of valence and Rydberg character. The first diagram depicts a B atom in its ^{2}D($2s^1 2p^2$; $M_L = \pm 1$) state, where the second one a BF$^+$ core in its $X^2\Sigma^+$ state and an electron distributed in a Rydberg $3p_x$ type orbital.

The $D^1\Pi(9)$ state, after a severe avoided crossing at 3.1 bohrs with the same Rydberg diabatic, i.e., the one starting from the B(^{2}P, $M_L = \pm 1$) + F(^{2}P, $M_L = 0$), presents a MRCI(+Q)/A6ζ minimum at $r_e = 1.226$ (1.223) Å of primarily Rydberg nature. The main equilibrium CFs

$$\begin{aligned} |D^1\Pi(9)\rangle \approx\ & 0.83|3\sigma^2 4\sigma^2 5\sigma^1 1\pi_x^2 3\bar{\pi}_x^1 1\pi_y^2\rangle \\ & - 0.44|3\sigma^2 4\sigma^2 5\sigma^1 1\pi_x^2 2\bar{\pi}_x^1 1\pi_y^2\rangle \end{aligned}$$

reflect a state that is the orthogonal complement of the $A^1\Pi(3)$ state.

4. $b^3\Sigma^+(4)$, $c^3\Sigma^+(6)$, and $^3\Sigma^-(11)$

Both the b and c $^3\Sigma^+$ states correlate adiabatically to the ground state atoms B(^{2}P, $M_L = 0$, ± 1) + F(^{2}P, $M_L = 0$, ∓ 1), respectively, and have a repulsive behavior up to around 3.0 bohrs; see Fig. 5. The minima of both states own their existence to an interesting interaction between them and a $^3\Sigma^+$ state related to the Rydberg B($2s^2 3s^1$; ^{2}S) + F(^{2}P, $M_L = 0$) asymptote. At r = 3.05 bohrs, the b and c $^3\Sigma^+$ states interact heavily and that creates a minimum at $r_e = 1.218$ (1.218) Å at the MRCI(+Q)/A6ζ level of theory. Correcting for CV effects, we find $r_e = 1.218 - \delta r_e = 1.218 - 0.003 = 1.215$ Å in perfect agreement with the experimental value of $r_e = 1.2149$ Å (see Table I). The two atoms are slightly bound by 12.2(9.0) kcal/mol at the valence MRCI(+Q)/A6ζ level as compared to an experimental value being 7.5 kcal/mol,[7,16,57] and a large barrier of 27.7 kcal/mol which prevents its dissociation. The equilibrium CFs

$$|b^3\Sigma^+(4)\rangle \approx |3\sigma^2 4\sigma^2 5\sigma^1[0.90(6\sigma^1) + 0.24(7\sigma^1)]1\pi_x^2 1\pi_y^2\rangle$$

with $3\sigma\sim 2s^{\mathrm{F}}$, $4\sigma\sim(0.91)2p_z{}^{\mathrm{F}}-(0.52)2s^{\mathrm{B}}-(0.38)2p_z{}^{\mathrm{B}}$, $5\sigma\sim(0.83)2s^{\mathrm{B}}-(0.54)2p_z{}^{\mathrm{B}}+(0.29)2s^{\mathrm{F}}$, $6\sigma\sim 3s^{\mathrm{B}}$, $7\sigma\sim 3p_z{}^{\mathrm{B}}$ reveal a charged core BF^+ ($\mathrm{X}^2\Sigma^+$) state and a Rydberg electron orbiting in a σ type orbital.

The $\mathrm{c}^3\Sigma^+(6)$ owes its minimum to the intense interaction with a Rydberg $^3\Sigma^+$ state correlating to $\mathrm{B}(2s^2 3s^1;\,^2\mathrm{S}) + \mathrm{F}(^2\mathrm{P}, \mathrm{M_L} = 0)$. Its equilibrium CFs reveal a complicated valence-Rydberg state

$$\left|c^3\Sigma^+(6)\right\rangle \approx \left|3\sigma^2 4\sigma^2 5\sigma^1[0.77(7\sigma^1) + 0.50(8\sigma^1) -0.22(6\sigma^1)]1\pi_x^2 1\pi_y^2\right\rangle$$

with the 8σ orbital being of valence character, the rest are identical to those of the $\mathrm{b}^3\Sigma^+(4)$ state.

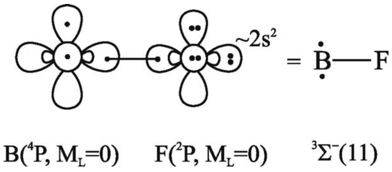
At this point, we should mention that the $^3\Delta$ and $^3\Sigma^-$ symmetries issued from the ground state channel $\mathrm{B}(^2\mathrm{P}, \mathrm{M_L} = \pm1)$ and $\mathrm{F}(^2\mathrm{P}, \mathrm{M_L} = \pm1)$ atoms, are completely repulsive as it was the case with their singlet analogues. An attractive $^3\Sigma^-(11)$ state results from the $\mathrm{B}(^4\mathrm{P}, \mathrm{M_L} = 0) + \mathrm{F}(^2\mathrm{P}, \mathrm{M_L} = 0)$ interaction. Both equilibrium CASSCF configuration and Mulliken atomic populations

$$\left|^3\Sigma^-(11)\right\rangle \approx 0.74\left|3\sigma^2 4\sigma^2 1\pi_x^2 2\pi_x^1 1\pi_y^2 2\pi_y^1\right\rangle,$$

$$2s^{0.78}2p_z^{0.09}2p_x^{0.97}2p_y^{0.97}/_B 2s^{1.94}2p_z^{1.29}2p_x^{1.92}2p_y^{1.92}/_F,$$

$$q_B = +0.12$$

support a genuine σ bond of 18.2 kcal/mol due to the unfavorite interaction with the purely repulsive $^3\Sigma^-$ originating from the ground state atoms. All the above can be nicely captured pictorially by the diagram



Two more minima of $^3\Sigma^+$ symmetry are shown in Fig. 5, the result of avoided crossings.

5. $^1\Delta(13)$

The last bound state studied for the neutral BF molecule is of $^1\Delta$ symmetry and correlates adiabatically to $\mathrm{B}(^2\mathrm{D}, \mathrm{M_L} = \pm2) + \mathrm{F}(^2\mathrm{P}, \mathrm{M_L} = 0)$. It presents a minimum at $\mathrm{r_e} = 1.447$ Å with $\mathrm{D_e} = 55.4$ kcal/mol at the MRCI/A6ζ level with corresponding CFs and Mulliken atomic distributions

$$\left|^1\Delta(13)\right\rangle \approx 0.65\left|3\sigma^2 4\sigma^2 1\pi_x^2 1\pi_y^2(2\pi_x^2 - 2\pi_y^2)\right\rangle,$$

$$2s^{0.74}2p_z^{0.17}2p_x^{0.91}2p_y^{0.91}/_B 2s^{1.88}2p_z^{1.49}2p_x^{1.84}2p_y^{1.84}/_F,$$

$$q_B = +0.11$$

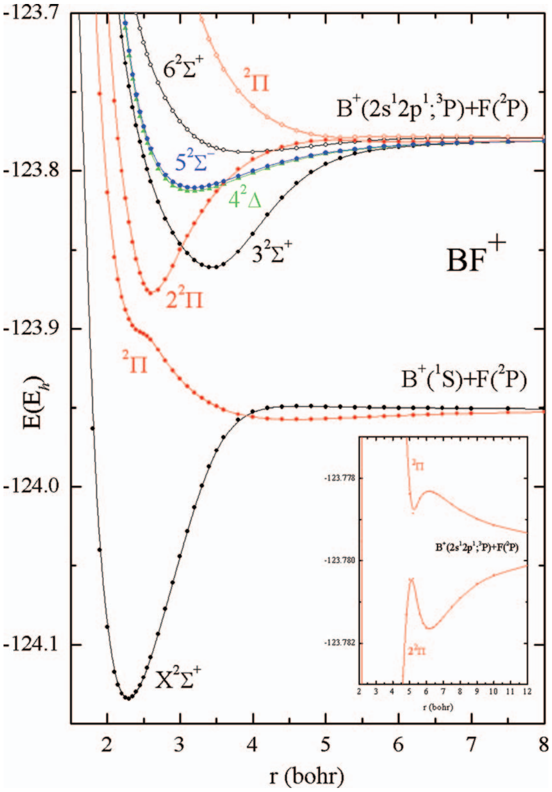
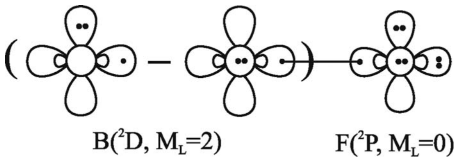


FIG. 6. MRCI/A6ζ potential energy curves of the $\mathrm{X}^2\Sigma^+$, $2^2\Pi$, $3^2\Sigma^+$, $4^2\Delta$, $5^2\Sigma^-$ and $6^2\Sigma^+$ BF^+ states. The inset displays the avoided crossing between the $2^2\Pi$ and a higher $^2\Pi$ state at 5.0 bohrs.

and schematically represented by the vbL diagram below featuring a genuine σ bond:



Twenty more states were calculated at the MRCI/A6ζ level of theory, 15 of which are of repulsive character, while 5 more are the result of multiple avoided crossings with lower states of the appropriate symmetry. Figure 1 shows 33 PECs, while in Figs. 4 and 5 we see the perturbations caused by the non-repulsive states to the lower ones and discussed previously (*vide supra*).

B. BF^+

Table III presents results on five doublets out of a total of 14 $^{2S+1}\Lambda$ BF^+ states dissociating to $\mathrm{B}^+(^1\mathrm{S}, {}^3\mathrm{P}) + \mathrm{F}(^2\mathrm{P})$ with corresponding PECs displayed in Fig. 6.

1. $X^2\Sigma^+$, $3^2\Sigma^+$, and $6^2\Sigma^+$

All three $^2\Sigma^+$ BF^+ states correlate adiabatically to $\mathrm{B}^+(^1\mathrm{S}) + \mathrm{F}(^2\mathrm{P}, \mathrm{M_L} = 0)$ and $\mathrm{B}^+(2s^1 2p^1;\,^3\mathrm{P}, \mathrm{M_L} = \pm1, 0) + \mathrm{F}(^2\mathrm{P}, \mathrm{M_L} = \mp 1, 0)$, respectively. Although their dissociation channels are separated by a MRCI/A6ζ (experimental)[53] energy gap of 4.65 (4.63) eV, these states interact heavily. The

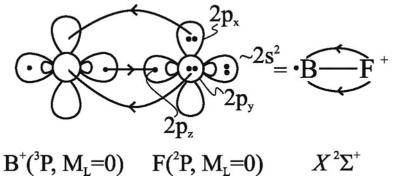
$B^+(^1S) + F(^2P, M_L = 0)$ interaction is as expected of repulsive character, but due to the mixing with the $|^3P, M_L = \pm 1, 0\rangle_{B^+} \otimes |^2P, M_L = \mp 1, 0\rangle_F$ states a deep minimum results at $r_e = 1.211$ (1.213) Å with a $D_e = 114.8$ (119.1) kcal/mol with respect to $B^+(^1S) + F(^2P)$ at the MRCI(+Q)/A6ζ level. The intrinsic bond strength, however, should refer to $B^+(^3P) + F(^2P)$; thus, $D_e^{\text{intrinsic}} = D_e + \Delta E(^3P \leftarrow {}^1S) = 114.8$ (119.1) kcal/mol + 4.65 (4.64) eV = 222.0 (226.1) kcal/mol, significantly larger than the dissociation energy of the neutral species. Correcting for scalar relativistic and CV effects, we find $r_e = 1.209$ Å and $D_e = 117.1$ kcal/mol (C-RCCSD(T)-DK/AC5ζ-DK), in perfect agreement with the corresponding experimental values of 1.208 ± 0.005 Å and 117.4 kcal/mol.[56] At the same level of theory the ionization energy is found to be IE = 11.09 eV while the most accurate experimental value is IE = 11.115 ± 0.004 eV.[15] The main equilibrium CF, Mulliken atomic populations, and natural molecular orbitals are

$$|X^2\Sigma^+\rangle \approx 0.92\left|3\sigma^2 4\sigma^2 5\sigma^1 1\pi_x^2 1\pi_y^2\right\rangle,$$

$$2s^{0.84}2p_z^{0.50}2p_x^{0.20}2p_y^{0.20}(3d)^{0.11}/_B 2s^{1.92}2p_z^{1.67}2p_x^{1.72}2p_y^{1.72}(3d)^{0.08}/_F,$$

$$q_B = +1.11,$$

$3\sigma \sim 2s^F$, $4\sigma \sim (0.94)2p_z{}^F - (0.41)2s^B - (0.41)2p_z{}^B$, $5\sigma \sim (0.92)2s^B - (0.59)2p_z{}^B$, $1\pi \sim 2p_\pi{}^F$. Our findings suggest the following vbL diagram



displaying a σ bond with a $\sim$0.6 e$^-$ charge transfer towards the F atom, while a π backdonation of $\sim$0.4 e$^-$ to the empty $2p_\pi$ B orbitals is responsible for two π bonds in close similarity with the $X^1\Sigma^+$ state of the neutral BF system.

The $3^2\Sigma^+$ state is bound by 51.0(55.6) kcal/mol with respect to its $B^+(^3P) + F(^2P)$ adiabatic limit at the MRCI(+Q)/A6ζ level with its equilibrium distance, $r_e = 1.820$ Å, located on the top of a "potential" avoided crossing with the $X^2\Sigma^+$ state (see Fig. 6). The main equilibrium CFs reflect its multiconfiguration nature due to the intense interaction of the X, 3rd, and 6th $^2\Sigma^+$ states

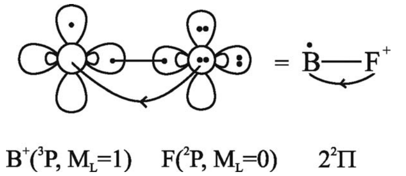
$$\begin{aligned}|3^2\Sigma^+\rangle \approx\ & 0.67\left|3\sigma^2 4\sigma^1 5\sigma^2 1\pi_x^2 1\pi_y^2\right\rangle \\ & + 0.36\left|3\sigma^2 4\sigma^2 5\sigma^1 \left(1\pi_x^2 1\bar{\pi}_y^1 2\pi_y^1 + 1\bar{\pi}_x^1 2\pi_x^1 1\pi_y^2\right)\right\rangle \\ & - 0.24\left|3\sigma^2 4\sigma^2 5\sigma^1 1\pi_x^2 1\pi_y^2\right\rangle.\end{aligned}$$

2. $2^2\Pi$

Considering the $X^2\Sigma^+$ state and moving the single electron from the B localized σ orbital to a π type orbital, we get the first excited state of the cation lying 161 kcal/mol above the X-state. It correlates adiabatically to $B^+(^3P, M_L = 0) + F(^2P, M_L = \pm 1)$, but diabatically to $B^+(^3P, M_L = \pm 1) + F(^2P, M_L = 0)$ due to an avoided crossing at 5.2 bohr (see inset of Fig. 6). Its main equilibrium CF

$$|2^2\Pi\rangle \approx 0.83\left|3\sigma^2 4\sigma^2 1\pi_x^2 2\pi_x^1 1\pi_y^2\right\rangle$$

can be accounted for by the following vbL diagram:



3. $4^2\Delta$ and $5^2\Sigma^-$

These two states related to $B^+(^3P, M_L = \pm 1, \pm 1) + F(^2P, M_L = \pm 1, \mp 1)$, are quasidegenerate and with practically identical molecular parameters; see Table III. Their CASSCF equilibrium configurations and atomic distributions (common for both states)

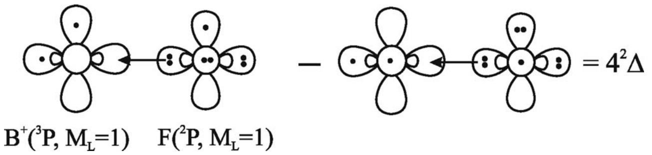
$$\begin{aligned}|4^2\Delta\rangle \approx\ & 0.60\left|3\sigma^2 4\sigma^2 5\sigma^1 (1\bar{\pi}_x^1 2\pi_x^1 1\pi_y^2 - 1\pi_x^2 1\bar{\pi}_y^1 2\pi_y^1)\right\rangle \\ & - 0.35\left|3\sigma^2 4\sigma^2 5\sigma^1 \left(1\pi_x^1 2\bar{\pi}_x^1 1\pi_y^2 - 1\pi_x^2 1\pi_y^1 2\bar{\pi}_y^1\right)\right\rangle,\end{aligned}$$

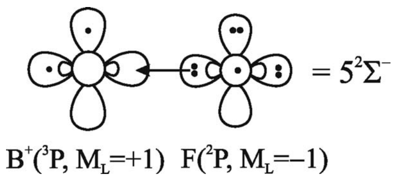
$$\begin{aligned}|5^2\Sigma^-\rangle \approx\ & 0.70\left|3\sigma^2 4\sigma^2 5\sigma^1 1\pi_x^2 2\bar{\pi}_x^1 1\pi_y^1\right\rangle \\ & + 0.60\left|3\sigma^2 4\sigma^2 5\sigma^1 1\bar{\pi}_x^1 1\pi_y^2 2\pi_y^1\right\rangle \\ & - 0.36\left|3\sigma^2 4\sigma^2 5\sigma^1 1\pi_x^1 1\pi_y^2 2\bar{\pi}_y^1\right\rangle,\end{aligned}$$

$$2s^{1.0}2p_z^{0.21}2p_x^{0.50}2p_y^{0.50}/_B 2s^{1.97}2p_z^{1.76}2p_x^{1.48}2p_y^{1.48}/_F,$$

$$q_B = +0.74,$$

can be schematically cast in the following diagrams:





A single σ bond is formed with a charge transfer of $\sim$0.2 e$^-$ to the $2p_z$ B orbital. For both states, the binding energy is $D_e \sim 20$ kcal/mol with $r_e \sim 1.68$ Å (Table III). It is interesting to notice at this point the difference in behavior of these two $4^2\Delta$ and $5^2\Sigma^-$ states with the $3^2\Sigma^+$ one, with which they share the same asymptotic products $B^+(^3P, M_L = \pm 1)$ and $F(^2P, M_L = \pm 1)$; their only difference being their combination mode.

IV. CONCLUDING REMARKS

The BF and BF^+ molecular systems have been studied by high level *ab initio* methods at both the valence (10 and 9 e^-) MRCI/aug-cc-pV6Z and combined core-valence/scalar relativity at the coupled-cluster C-RCCSD(T)-DK/aug-cc-pCV5Z-DK levels of theory. We have constructed 33 potential energy curves for BF and 8 for BF^+ correlating to B(^{2}P, ^{4}P, ^{2}S, ^{2}D, ^{2}P) + F(^{2}P), B^+(^{1}S) + F^-(^{1}S), and B^+(^{1}S, ^{3}P) + F(^{2}P), respectively.

The ground state of BF is of $^1\Sigma^+$ symmetry with binding energy $D_e = 181.9$ kcal/mol and equilibrium distance $r_e = 1.263$ Å at the C-RCCSD(T)-DK/AC5ζ-DK level of theory in complete agreement with the corresponding experimental values of $D_e = 182 \pm 3$ kcal/mol and $r_e = 1.262711672$ Å. The dipole moment value at both the MRCI + Q/A6ζ and C-RCCSD(T)-DK/CA5ζ-DK levels is $\mu_{FF} = 0.84$ D with the B atom positively charged. It is indeed remarkable that for the last 50 years starting with the Hartree–Fock work of Ransil,[24] the scientific community was led to believe that the (charge) polarity of the BF ($X^1\Sigma^+$) molecule was B^-F^+, the result of inappropriate methods and, perhaps, misunderstandings (see also Ref. 33). This counterintuitive charge distribution would require an interaction with the ionic B^-F^+ ($^1\Sigma^+$) state, the latter being $\Delta E = IE(F) - EA(B) = 17.42 - 0.28 = 17.1$ eV higher at infinity, a rather untenable process. On the other hand, the ionic state B^+F^- is located 4.90 eV above the ground state fragments. We would like to observe as well that while the dipole moment of the $X^1\Sigma^+$ state is 0.84 D, that of, for instance, the $a^3\Pi(2)$ is -0.55 D, but the charge polarity of the two states is the same, B^+F^-. This direction reversal of the dipole moment in the $a^3\Pi(2)$ state is due to the charge distribution which is developed on the back of the B atom (see text).

The two atoms are held together by a single σ bond while a charge transfer along the π frame is responsible for two weaker bonds. The first excited state is of $^3\Pi$ symmetry and lies at $T_e = 29\,118.89$ cm^{-1} (C-RCCSD(T)-DK/AC5ζ-DK) with the experimental value being $T_e = 29\,144.3$ cm^{-1}. The two atoms interact attractively through a single σ bond but the B atom is found in its excited $^4P(2s^12p^2)$ state, thus the F-to-B π-migration has dropped to its half as compared to the $X^1\Sigma^+$ state.

The ground state of the cation BF^+ is of $^2\Sigma^+$ symmetry and results from the X-state of the neutral by removing one electron from the $\sim 2s_B$ like orbital. The binding mode stays exactly the same (one σ and two π bonds) but the binding energy drops by 36% with respect to the ground state atoms to a value of $D_e = 117.0$ kcal/mol, in complete agreement with experiment. Its first excited state is of $^2\Pi$ symmetry in analogy to the $^3\Pi$ symmetry of the neutral species; it suffices to remove the single σ electron and get the $^2\Pi$ BF^+ state. It lies 6.98 eV above the $X^2\Sigma^+$ state and is bound by 61.2 kcal/mol with respect to its adiabatic limit.

In the neutral case, both the $X^1\Sigma^+$ and $a^3\Pi(2)$ states share the same binding mode and this is reflected to their binding energies; $D_e(X^1\Sigma^+) = 182$ kcal/mol, while the intrinsic bond strength of the $a^3\Pi(2)$ state is $D^{\text{diabatic}} = 181$ kcal/mol. Although the same should apply to the BF^+ case, the binding energies do not show the same similarities due to the avoided crossing between the bound $2^2\Pi$ and the repulsive PEC of $^2\Pi$ symmetry arising from B^+(^{1}S) + F(^{2}P); see Fig. 6.

In many of our studied BF states a valence-Rydberg mixing occurs resulting in molecular parameters similar to those of the ionic core, i.e., of the $X^2\Sigma^+$ BF^+ state. A perfect agreement with the available experimental data is achieved after considering the core-valence and scalar relativistic effects even for such a small (14 e^-) molecular system.

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