Structural Parameters of the Ground States of the Quasi-Stable Diatomic Anions CO\(^-\), BF\(^-\), and BCl\(^-\) as Obtained by Conventional Ab Initio Methods

Ilias Magoulas, Aristotele Papakondylis,* and Aristides Mavridis

The experimental electron affinity (EA) of CO(\(^{1}\Sigma^+\)) is \(-1.5\) eV, signifying the metastability of the CO\(^-(X^2\Pi)\) anion. The electronic structure and bonding of CO\(^-\), BF\(^-\), and BCl\(^-\) vis-à-vis their neutral counterparts have been studied by conventional coupled-cluster (CCSD(T)) and multireference (MRCI) methods. Our results are in agreement with experiment for the CO/CO\(^+\) coupled-cluster (CCSD(T)) and multireference (MRCI) methods.

### Introduction

The calculation of accurate electron affinities (EA) of molecules and atoms (or ionization energies (IE) or detachment energies (DE) of their anions) is a recondite task. The N + 1 electron anion has quite different characteristics from the parent N electron neutral system, therefore, the computational approach and basis sets are of critical importance; see for example, Refs. [1–6]. By convention, the EA (of the neutral) and the DE (of the anion) is a positive number, provided that the total equilibrium energy \(E_0\) \(=\) \(E_0 + \) zero point energy (ZPE) of the N + 1 \(e^-\) species is lower (more negative) than that of the N \(e^-\) one (neutral). Focusing henceforth exclusively on diatomic molecules XY and referring to adiabatic EA\(^{[2]}\) for reasons of clarity, we write

\[
EA_0(XY) = E_0(XY) - E_0(XY^+), \text{ or} \\
EA_0(XY) = EA(Y) + D_0(XY^+) - D_0(XY) > 0
\]

assuming that \(EA(Y) > EA(X) > 0\); \(D_0 = D_0 - ZPE\) is the dissociation energy of the corresponding diatomic species. This, in turn, means that the stability of the \(XY^-\) anion is dictated by the obvious relation

\[
D_0(XY^-) - [D_0(XY) - EA(Y)] > 0
\]

It is instructive to apply the above relation to a diatomic molecule whose EA is close to 0, like NO(\(^{1}\Sigma^+\)). The latter’s experimental EA is \(+0.026 \pm 0.005\) eV.\(^{[7]}\) Indeed, \(D_0(\text{NO}^-; X^2\Sigma^-) - D_0(\text{NO}; X^2\Pi) - EA(O; \Sigma^+) = 5.056 - [6.496 - 1.461] = +0.021\) eV \((= EA_0)\) (Experimental values taken from Ref. [8]).

Disregarding, however, the ZPE, that is, using \(D_0 = D_0 + \omega_{\Sigma^+}/2 - \omega_{\Pi}/4\) instead of \(D_0\) we get \(EA_0 = -0.013\) eV. See also the interesting theoretical work on the EA\(_0\) of NO by Dunning and coworkers.\(^{[5]}\)

Now, when the equilibrium energy \(E_0(XY^-)\) is located above \(E_0(XY)\), the \(EA_0\) of XY is negative (or the DE of \(XY^-\) for that matter), signaling the metastability (quasi-boundedness) of the \(XY^-\) anion with respect to \(XY + e^-\). The energy difference \(E_0(...) = E_0(...) = -EA_0(XY)\) is the kinetic energy of the ejected electron. Under these circumstances, the \(XY^-\) complex is also called “temporary negative ion” or “resonance,”\(^{[9]}\) It has a very short life time, usually in the range \(10^{-16} \text{ to } 10^{-13}\) s, while its first principle calculation requires special attention (vide infra). The essence of the previous discussion is captured in Figure 1, a schematic representation of the potential energy curves (PEC) of XY and XY\(^-\); \(r_e\) is the “crossing” point (vide infra).

For different relative positions of the PECs and/or complications, see also Ref. [6]. It should be clear at this point that resonances are not stationary states, that is, the continuum of the neutral XY in which the XY\(^-\) anion is embedded leads to autodetachment, XY\(^-\) \(\rightarrow\) XY + e\(^-\). In other words, the discrete (square-integrable) space of the stationary states should be extended onto the continuum, followed by a “confinement” procedure for reasons of normalization. There is a variety of methodologies that can lead to the calculational determination of resonance states, some of which are described in Ref. [6]. The most effective and rather popular approach, however, is the complex absorbing potential (CAP) method; see Refs. [10,11] and references therein. For reasons of clarity and nomenclature, a brief outline is given here.

In the CAP method, the Hermitian Hamiltonian \(\hat{H}\) is modified by adding to it an imaginary potential,

\[
\hat{H}_{\text{CAP}}(\eta) = \hat{H} - i\eta \hat{W}
\]

where \(\hat{W}\) is a real potential function and \(\eta\) is a positive number reflecting the CAP strength. Clearly, \(\hat{H}_{\text{CAP}}(\eta)\) is a non-Hermitian operator. The corresponding Schrödinger equation reads

\[\text{vide infra}\]

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anion BF\(^{-}\), it is stated that “we expect our PEC to represent nevertheless a reasonably good approximation of the anion, as the bound state calculations using not too diffuse basis sets yield often surprisingly accurate PECs for metastable states.”

In this work, we study by single reference coupled-cluster (CCSD(T)) and multireference variational methods (MRCI) the lowest state of the quasi-stable anions CO\(^{-}\), BF\(^{-}\), and BCl\(^{-}\). The quasi-stability of the BF\(^{-}\)(X\(^2\)II) anion has been discovered for the first time by Dreuw et al.\([10]\) These workers used both the CCSD(T)/aug-cc-pCVTZ and the CAP method, the latter combined with the MRCI(5s3p1d+1s12p) approach. Through CCSD(T)/aug-cc-pCVTZ, they also located the high spin states 2\(^{2}\Sigma\)\(^{-}\) and 2\(^{2}\)II of BF\(^{-}\). Some of their findings will be compared with ours later on. To the best of our knowledge, no other work, either experimental or theoretical, on BF\(^{-}\) exists in the literature.

The BCl\(^{-}\) anion, quasi-stable according to our calculations (vide infra), is reported here for the first time, whereas the CO\(^{-}\)(X\(^2\)II) anion is a well-documented metastable system\([11]\) used here as a “guide”; nevertheless, it should be stated that complete CO\(^{-}\) PECs are reported for the first time.

In Computational Outline section, we briefly discuss the calculational map followed; in General Considerations and the Quasi-stable CO\(^{-}\) Anion section, after a few general remarks on diatomic metastable anions, we monitor the methods of Computational Outline section against the quasi-stable CO\(^{-}\)(X\(^2\)II), while Results and Discussion section refers to results and discussion on the BF/BF\(^{-}\) and BCI/BCI\(^{-}\) systems. We close with a short summary of our findings in Summary and Remarks section.

### Computational Outline

The single reference CC\(_s\), singles + doubles + perturbative connected triples CCSD(T)\([12,13]\) and the complete active space self consistent field (SCF) (CASSCF) + singles + doubles (+Q) = MRCI (+Q) methods have been used through this work; +Q refers to the Davidson nonextensivity cluster correction.\([14,15]\) Our reported MRCI(+Q) results are within the internal contraction (ic) scheme as implemented in the MOLPRO package.\([16]\) The MRCI numbers are at the valence level of theory that is the \(\sim 1s^2/_{\text{B,C,O,F}}\) and \(1s^22s^22p^6/_{\text{Cl}}\) inner electrons were kept closed except if stated otherwise.

The one electron basis functions used belong to the family of the Dunning correlation consistent cc-pVnZ \((n = 5\) and 6) basis sets.\([17]\) After substantial experimentation, (a) the addition of diffuse functions (augmentation) to describe the quasi-stable anions along the entire PEC was deemed necessary and (b) the cardinalities \(n = 5\) and 6 were found as better describing the well known CO\(^{-}\) quasi-stable anion, particularly the \(n = 6\) set for the MRCI calculations. Therefore, our final basis sets are of sextuple-\(\zeta\) quality, that is, aug-cc-pV6Z \(\sim\) A6\(\zeta\) for brevity. The generally contracted basis sets for the group of atoms \(\text{B, C, O, F}\) and \(\text{Cl}\) are \([8s7p6d5f4g3h2i]\) and \([9s8p6d5f4g3h2l]\), respectively. The valence reference space for both the neutral and negative species was generated by allotting 10 and 11 e\(^-\), respectively, to 10 orbitals, namely
(\(ns + np\)) \times 2 + np_1 + np_2(\text{where } np_1, \, np_2 \text{ denote molecular orbitals of } b_1 \text{ and } b_2 \text{ symmetries purporting to increase the flexibility of the reference space} \text{ (CAS)}, \text{ resulting in } 4984 \text{ (neutrals) and } 6940 \text{ (anions) configuration functions} \text{ (CF)}). \text{ The corresponding MRCI (icMRCI) spaces number } 5.8 \times 10^6 \text{ (4.2} \times 10^6) \text{ and } 1.3 \times 10^9 \text{ (6.2} \times 10^9) \text{ CFs for the neutrals and anions, respectively. All calculations were done under C_2v symmetry constraints, whereas spectroscopic parameters were obtained by solving numerically the radial Schrödinger equation for two nuclei.}

All calculations were performed by the MOLPRO 2012.1 suite of codes.\textsuperscript{[16]}

**General Considerations and the Quasi-stable CO\(^{−}\) Anion**

We believe that it is useful to summarize a few facts and to express some thoughts on the XY\(^{−}\) quasi-stable anions. One intuitively expects close to zero, or negative EAs for closed shell atoms or closed shell tightly bound diatomic molecules, and indeed this is the case for the noble gas atoms Ng = He to Xe\textsuperscript{[18]} the H\(_2\), CO, N\(_2\) molecules, and the hydrogen halides HY, Y = F, Cl, Br, and I.\textsuperscript{[8]} see also the extended article on the HF/HF\textsuperscript{−} system by Piecuch.\textsuperscript{[19]} Going systematically through the Huber–Herzberg compilation,\textsuperscript{[8]} besides the HY\(^−\) anions only the H\(_2\) (\(X^2\Sigma^+\)), CO (\(X^2\Pi\)), and N\(_2\) (\(X^2\Pi_g\)) species are definitely characterized as resonances with negative EAs, −1.5 and −1.90 eV for CO and N\(_2\), respectively. Conversely, the IE of As\(_2\)\(^{−}\), IE = 0.10\(\pm\) 0.1 eV given in Ref. [8], proved to be definitely positive many years later through negative ion photoelectron spectroscopy, IE = 0.739 ± 0.008 eV\textsuperscript{[20]} thus stable. As for H\(_2\)\(^{−}\), it is a resonance state with a negative IE of nearly −2 eV.\textsuperscript{[21]} See also the theoretical work on H\(_2\)\(^{−}\) in Refs. [22–24] and references cited therein.

The above discussion shows a relative scarcity of quasi-stable diatomic anions, and it is not without interest to mention that even CO\(^{−}\), one of the best established resonance states, was disputed (erroneously) in a 1976 experimental publication.\textsuperscript{[25]} See also Ref. [26] for a useful discussion related to Ref. [25] on CO\(^{−}\). We remind at this point that BF(X\(^2\Sigma^+\)) is a closed shell molecule, isoatomic to CO and N\(_2\), and strongly bound with D\(_0\) = 1820 kcal/mol\textsuperscript{[27]} therefore, one would expect a quasi-stable BF\(^{−}\) anion.\textsuperscript{[10]} To summarize, as these lines are written, the literature uncovers no more than 10 diatomic anionic resonance states, namely, HY\(^{−}\) (Y = F, Cl, Br, I), H\(_2\)\(^{−}\), CO\(^{−}\), N\(_2\)\(^{−}\), and BF\(^{−}\).

In this work, the BF\(^{−}\) and BCl\(^{−}\) PECs along with the PECs of the neutrals BF and BCl, are studied by stationary state techniques as described in Computational Outline section, whereas the methods and basis sets have been tested by contrasting our results to the experimental findings on the CO/CO\(^{−}\) system.

Figure 2 displays full MRCI+Q/A6\(^c\) PECs of CO(X\(^3\Sigma^+\)) and CO (\(X^2\Pi\)), whereas Table 1 lists numerical results of the CO/CO\(^{−}\) system at the CCSD(T) and MRCI (+Q)/A6\(^c\) levels of theory. Notice first the excellent agreement between the experimental\textsuperscript{[8]} and the calculated results on CO at the

\[
\begin{align*}
{\text{Method}} & \quad {\text{E}} & \quad {r_\text{a}} & \quad D_0^{(a)} & \quad \Delta_\text{E} & \quad \text{EA}_{\text{E}}^{[b]} \\
\text{CCSD(T)} & \quad 113.202431 & \quad 1.1311 & \quad 11.07 & \quad 2161.6 & \quad 13.16 & \quad -1.14 \\
\text{MRCI} & \quad 113.188766 & \quad 1.1342 & \quad 11.23 & \quad 2150.7 & \quad 12.70 & \quad -1.31 \\
\text{MRCI+Q}\textsuperscript{[c]} & \quad 113.20196 & \quad 1.132 & \quad 11.22 & \quad 2169.1 & \quad 13.88 & \quad -1.22 \\
\text{Expt}\textsuperscript{[d]} & \quad 1.1315 & \quad 11.09 & \quad 2169.8 & \quad 13.288 & \quad -1.50 \\
\text{CCSD(T)} & \quad 113.159956 & \quad 1.139 & \quad 8.49 & \quad 1971.9 & \quad 64.0 \\
\text{MRCI} & \quad 113.140081 & \quad 1.136 & \quad 8.53 & \quad 1958.3 & \quad 32.0 \\
\text{MRCI+Q} & \quad 113.15647 & \quad 1.139 & \quad 8.43 & \quad 1812.2 & \quad 22.6 \\
\text{Expt}\textsuperscript{[e]} & \quad \sim 1.17^{[e]} & \quad 8.1^{[e]} \\
\end{align*}
\]

\textsuperscript{[a]} D\(_0\) = D\(_0\) − \Delta_\text{E}/2. \textsuperscript{[b]} \text{EA}_{\text{E}} = \text{EA}_0 + \Delta_\text{E}/2. \textsuperscript{[c]} \text{Q refers to Davidson correction.} \textsuperscript{[d]} \text{Ref. [8].} \textsuperscript{[e]} \text{Ref. [28].}
Experimentally, the EA of CO (or the DE of CO\(^-\), or the \(E_R\) position of CO\(^-\)) is \(E_A = -1.5\) (IE = -1.5, \(E_R = 1.5\)) eV at an estimated bond length \(r(\text{CO})\approx 1.17\ \text{Å}\) and width \(\Gamma = 0.40\ \text{eV}\), thus \(\tau = 1.6 \times 10^{-15}\ \text{s}\).\(^{[28]}\) Using the experimental EA of CO, the “binding energy” of CO\(^-\) is

\[
D_0(\text{CO}) = D_0(\text{CO}) - [\text{EA(O)} - \text{EA(CO)}] = 11.08 - (1.46 + 1.5)\ \text{eV} \\
\approx 8.1\ \text{eV};\text{ see also Ref. [8].}
\]

The above experimental findings on CO\(^-\) compare favorably with our CCSD(T)/MRCI+Q/A6\(_J\) stationary state results, that is, \(E_{A(\text{CO})} = -1.14(-1.22)\) eV, \(r(\text{CO}) = 1.139(1.139)\ \text{Å}\), and \(D_0 = 8.49(8.43)\ \text{eV};\text{ see Table 1. Also the MRCI + Q vibrational energy differences are (the experimental values from Ref. [28] in parentheses) } \Delta E_v = 1.5 \text{ eV} \times 10^{-15}\ \text{s}\).\(^{[28]}\) The leading equilibrium configurations of the \(X^1\Sigma^+\) state, indicated by Cederbaum and coworkers.\(^{[10]}\) The latter is the only work on BF that could be transferred from O\(^-\) to C in the CO\(^-\) species. Increasing systematically the one electron diffuse space, we ended up with CO\((X^1\Sigma^+)\) plus a detached electron of \(\pi\) symmetry (variations collapse).

The previous exposition indicates that bound state methods, if appropriately handled, can lead to useful results on the molecular structure of nonstationary states.

### Results and Discussion

**BF/\(\text{BF}^-\)**

The BF molecule is a (formally) triply bonded closed shell system, isoelectronic to CO, and strongly bound; its experimental bond length\(^{[30]}\) and binding energy\(^{[31]}\) are \(r_c = 1.26712\ \text{Å}\) and \(D_0 = 180 \pm 3\ \text{kcal/mol} (=7.806 \pm 0.130\ \text{eV})\), respectively; see also Ref. [27]. For another point of view as to the binding nature of BF, that is, (formally) triply or singly bonded, see Ref. [32]. The negative ion of BF is a perfect candidate for being a resonance (\textit{vide supra}), and indeed it is according to Cederbaum and coworkers.\(^{[10]}\) The latter is the only work on BF\(^-\) in the literature till now; see also the introduction.

Table 2 collects our findings on BF\((X^1\Sigma^+)\) and BF\(^-\)\((X^2\Pi)\) at the CCSD(T) and MRCI+Q/A6\(_J\) level, whereas Figure 3 displays the corresponding PECs. Observe first the very good agreement between experiment and theory on the neutral molecule; see also Ref. [27]. The calculated EA ranges between

\[
\text{CO:} \quad \left|X^1\Sigma^+\right| \approx 0.94[3\sigma^24\pi^25\sigma^27\pi^21\pi^2] \\
2s^22p^2[2p_0^22p_5^05\pi^0\sim\Delta_{\text{III}}] \\
2s^12p_5^14p^13p_0^14p_2^0\sim\Delta_{\text{III}}/c \\
2s^12p_5^14p^{1.36}4p_0^{1.36}\sim\Delta_{\text{III}}/c \\
\text{CO}:\quad \left|X^2\Pi\right| \approx 0.94[3\sigma^24\pi^25\sigma^27\pi^21\pi^2] \\
2s^17.022p_0^02p_{0.53}^12p_{0.55}^0\sim\Delta_{\text{III}}/c \\
2s^17.732p_2^14p_1^{1.38}2p_{0.18}^{1.36}\sim\Delta_{\text{III}}/c, q_c = -1.11
\]
Concerning the MRCI approach, the same workers reported an EA of about $-0.72$ eV (MRCI+Q). These negative EAs are more or less in agreement with those of Dreuw et al.\textsuperscript{[10]} who obtained $\Delta E_{\text{ad}} = -0.806$ eV at the CCSD(T)/aug-cc-pVTZ level and $r_c = 1.3092$ Å. Using the CAP/Cl approach, the same workers reported an EA of about $-1$ eV around equilibrium. Concerning the MRCI(+Q) crossing point, we get $r_c = 1.75(1.67)$ Å (Fig. 3), as contrasted to the CCSD(T) and CAP/Cl approach $r_c = 1.63$ and $1.75$ Å, (estimated from Figs.

Table 2. Total energies $E (E_h)$, bond distances $r_e$ (Å), dissociation energies $D_h$ (eV), harmonic and anharmonic frequencies $\omega_0$ and $\omega\nu_0$Xe (cm$^{-1}$), and adiabatic electron affinities $E_{\text{a}}$ (eV) of the ground states of $^1\text{B}^6\text{F}^o(X^e\Sigma^+)$ and BF $^1\text{X}^2\Pi$ at the valence CCSD(T), MRCI, and MRCI+Q/A6$^\dagger$ level.

<table>
<thead>
<tr>
<th>Method</th>
<th>$-E$</th>
<th>$r_e$</th>
<th>$D_h$[a]</th>
<th>$\omega_0$</th>
<th>$\omega\nu_0$Xe</th>
<th>$E_{\text{a}}$[b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF(X$^e\Sigma^+$)</td>
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<td></td>
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<td>1395</td>
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<td>1378</td>
<td>12.0</td>
<td>-0.92</td>
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<td>1.275</td>
<td>7.96</td>
<td>1371</td>
<td>11.6</td>
<td>-0.72</td>
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<td>0.806±0.13[e]</td>
<td>1402.11[f]</td>
<td>11.8[f]</td>
<td></td>
<td></td>
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<tr>
<td>BF $^1\text{X}^2\Pi$</td>
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<td>CCSD(T)</td>
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<td>3.77</td>
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<td>1.286</td>
<td>3.62</td>
<td>1242</td>
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[a] $D_h = D_0 - \omega_0/2$. [b] $E_{\text{a}} = E_{\text{a}} + \Delta\omega_0/2$. [c] +Q refers to Davidson correction. [d] Ref. [30]. [e] Ref. [31]. [f] Ref. [8].

![Figure 3. PECS of BF(X$^e\Sigma^+$) and BF(X$^1\text{X}^2\Pi$) at the MRCI+Q/A6$^\dagger$ and CCSD(T)/A6$^\dagger$ (BF) levels of theory. All curves are shifted by +124.251198 $E_h$.](image)

![Scheme 2. 1 and 2 of Ref. [10]]. In addition, $\Gamma \approx 1$ eV, or $\tau(BF^-) = \hbar/\Gamma = 6 \times 10^{-16}$ s,\textsuperscript{[10]} perhaps shorter than that of CO$^-$. An experimental “binding energy” of BF$^-$ can be estimated through the energy conservation relation $D_h(BF^-) = D_h(BF) - (EA(F) - EA(BF)) = (7.806 \pm 0.13) - (3.40 - (\text{--}0.8 \pm 0.1)) = 3.6 \pm 0.2$ eV, taking the EA of BF as $-0.8 \pm 0.1$ eV. This value is in agreement with the directly calculated CC or multireference $D_h$ values of 3.77 and 3.62 eV, respectively; see Table 2. We also report the MRCI+Q vibrational energy differences of BF $^1\text{X}^2\Pi$, $\Delta E_{\nu+1,\nu}$ ($\nu = 0,1,2,3$) = 153, 146, 132, 120 meV. We turn now to the bonding character of BF$^-$. As in the CO$^-$ description, between the crossing point $r_e$ and $r_{\infty}$ ($= 20$ bohr), $r_{\infty}<r<r_{\nu\omega}$ the BF$^-$ ion is stable, described at $r_{\infty}$ by the vbl diagram of Scheme 2a and clearly confirmed by the Mulliken populations $2s^2 2p_x^2 2p_y^2 2p_z^2 2s^2 2p_x 2p_y 2p_z / \beta$. $2s^2 2p_x^2 2p_y^2 2p_z^2 2p_x 2p_y 2p_z / \beta$.

Around $r_c$, the BF $^1\text{X}^2\Pi$ changes character, its physical nature being a neutral BF(X$^e\Sigma^+$) + an electron moving away from the B atom in a $\pi$ fashion; see Scheme 2b. The qualitative vbl diagram (2b) is justified by the leading MRCI equilibrium ($r_e \approx 1.30$ Å) CSFs of BF(X$^e\Sigma^+$) and BF(X$^1\text{X}^2\Pi$), and the Mulliken distributions

$$\begin{align*}
\text{BF} : |X^e\Sigma^+\rangle &\approx 0.4(3s^2 4s^2 5s^2 2p_x^2 1^3p_y^2) \\
2s^1 2p_x^{1.68} 2p_y^{0.59} 2p_z^{0.17} 2p_y^{0.17} \sim d^{0.18}/\beta \\
2s^1 2p_x^{1.87} 2p_y^{1.68} 2p_z^{0.80} 2p_z^{0.80} \sim d^{0.06}/\beta, q_{\beta} = +0.21
\end{align*}$$
Table 3. Total energies $E$ (eV), bond distances $r_B$ (Å), dissociation energies $D_0$ (eV), harmonic and anharmonic frequencies $\omega_0$ and $\omega_0\alpha_0\lambda_0$ (cm$^{-1}$), rotation–vibration coupling constants $\alpha_0$ (cm$^{-1}$), centripetal distortions $D_\phi$ (cm$^{-1}$), dipole moments $\mu_D$ (D), net Mulliken charges on the B atom $q_B$ (e), and electronic affinities $E_A$ (eV) of $^{1}\Sigma^+(X)$ and BCI$^-$ ($^\chi^2\Pi$) at the valence CCESD(T), MRCI, and MRCI+Q/A6$^e$ level.

<table>
<thead>
<tr>
<th>Method</th>
<th>$-E$</th>
<th>$r_B$</th>
<th>$D_0$</th>
<th>$\omega_0$</th>
<th>$\omega_0\alpha_0\lambda_0$</th>
<th>$\alpha_0$</th>
<th>$D_\phi$</th>
<th>$\mu_D$</th>
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<tbody>
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<td>1.7228</td>
<td>5.26</td>
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<td>4.93</td>
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<tr>
<td>CCESD(T)</td>
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[a] $D_0 = D_0 - \omega_0/2$. [b] Finite field ($\mu_D$) and expectation value ($\langle \mu_D \rangle$) dipole moments. [c] $+Q$ refers to Davidson correction. [d] Ref. [33]. [e] Ref. [8]. [f] Ref. [35].

Notice that more than one $e^-$ has migrated from F$^+$ to B in the BF$^-$ anion (B$^{-1.3}$F$^{+0.1}$), identical to that of CO$^-$ (vide supra). The diagram (2b) rationalizes as well the fact that a smooth PEC of BF$^-$ can be constructed through the (single reference) CC method; see Figure 3.

BCI/BCI$^-$

The closed shell chloroborane (BCI; $^\chi^4\Sigma^+$) molecule is isostructural to BF and CO, and erroneously described as a radical in two recent publications.$^{[33,34]}$ The first part of Table 3 collects CC and MRCI(+Q)/A6$^e$ spectroscopic parameters of BCI($^\chi^4\Sigma^+$) along with experimental$^{[3,5]}$ and theoretical results from Ref. [33]. The overall comparison of the present results with experiment and those of Ref. [33] at the MRCI+scalar relativity (DK2)/aug-cc-pV5Z level shows that scalar relativistic effects are unimportant, whereas small deviations from experiment are due to missing core (1s 2/B) correlation effects. It is of interest, however, to notice the following: (a) the electric dipole moment $\mu$ reported here for the first time and unknown experimentally is 1.34–1.35 D, obtained either as an expectation value $\langle \mu \rangle$ or using the finite field approach, $\mu_D$. (b) The polarity of the molecule is B$^{-}Cl^+$ with a MRCI net Mulliken charge on B, $q_B = -0.12$. The negative charge on B has also been confirmed by following the sign of the interaction energy of a static electric field with the dipole moment. (c) Most importantly, the EA of BCI reported here for the first time is negative at both CC and MRCI methods. In particular, the MRCI(+Q) EA is $E_A = -0.44(-0.18)$ eV. This signifies that BCI$^-$ is a resonance or a metastable state. PECs of BCI($^\chi^4\Sigma^+$) and BCI($^\chi^2\Pi$) are shown in Figure 4. As before an "experimental" binding energy of BCI$^-$ can be obtained based on the MRCI EA of BCI, $E_A = -0.3 \pm 0.11$ eV, and the experimental values $D_0^{[35]}$ and EA of Cl:

$$D_0(BCI^-) = D_0(BCI) - [EA(Cl) - EA(BCI)] = (5.26 \pm 0.05) - [3.61 - (-0.3 \pm 0.1)] = 1.35 \pm 0.11$$ eV.

In harmony with the MRCI $D_0$ value of Table 3. The MRCI(+Q) crossing point between the PECs of BCI/BCI$^-$ is $r_B = 1.97(1.87)$ Å, 0.25(0.15) Å to the right of the equilibrium distance $r_B = 1.72$ Å of the neutral, while the first four MRCI(+Q) vibrational energy differences of BCI$^-$ ($^\chi^2\Pi$) are $\Delta E_{v+1} (v = 0,1,2,3) = 62, 61, 59, 57$ meV.
The leading MRCl CFs of BCI and BCI\(^-\) and their Mulliken populations are given below, where the electronic structure of BCI (X=\(^2\Pi\)) at r=\(r_\infty\) (=20 bohr) and r\(_c\) (=1.72 Å) is adequately represented by the vbL Schemes 2a and 2b of the isovalent BF\(^-\).

\[
\begin{align*}
\text{BCI} : |X^1\Sigma^+\rangle & \approx 0.92(|2s^22p^22^1\Pi\rangle - 1.5|2s^22p^62^3\Sigma^+\rangle) \\
& + 2s^12p^22s^22p^22^1\Pi \approx 0.16 \langle 2s^22p^62^3\Sigma^+ | 2s^22p^62^3\Sigma^/+1/2|2s^22p^62^3\Sigma^+ \rangle \\
\text{BCI}^- : |X^2\Pi\rangle & \approx 0.92(|2s^22p^22^1\Pi\rangle - 1.5|2s^22p^62^3\Sigma^+\rangle) \\
& + 2s^12p^22s^22p^22^1\Pi \approx 0.16 \langle 2s^22p^62^3\Sigma^+ | 2s^22p^62^3\Sigma^/+1/2|2s^22p^62^3\Sigma^+ \rangle
\end{align*}
\]

The net Mulliken charges on the B atom are \(-0.12\) and \(-0.71\) for BCI and BCI\(^-\), respectively.

### Summary and Remarks

The isovalent diatomic molecular systems CO(X=\(^1\Sigma^+\))/CO\(^-\) (X=\(^2\Pi\)), BF(X=\(^1\Sigma^+\))/BF\(^-\) (X=\(^2\Pi\)), and BCI(X=\(^1\Sigma^+\))/BCI\(^-\) (X=\(^2\Pi\)) have been studied by CCSD(T) and MRCl methods and correlation consistent basis sets of augmented valence quintuple and sextuple cardinality. The focus of this study is the metastable negative ions because of the larking variational cardinality. The focus of this study is the metastable negative ions because of the larking variational collapse to the parent molecule + a quasi-free e\(^-\). However, monitoring stationary state methods with experiment or more appropriate theoretical approaches like the CAP method, useful conclusions can be extracted.

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### Keywords:

- quasi-stable anions
- resonances
- electron affinities
- \textit{ab initio}

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