

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

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The experimental electron affinity (EA) of $\text{CO}(\chi^1\Sigma^+)$ is -1.5 eV, signifying the metastability of the $\text{CO}^-(\chi^2\Pi)$ 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^- system, indicating as well the metastable nature of the

$\text{BF}^-(\chi^2\Pi)$ and $\text{BCl}^-(\chi^2\Pi)$ anions, their MRCI EAs being -0.8 ± 0.1 and -0.3 ± 0.1 eV, respectively. Our work clearly shows the usefulness of stationary state *ab initio* methods to the elucidation of metastable species. © 2015 Wiley Periodicals, Inc.

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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 ($= E_e + \text{zero point energy [ZPE]}$) 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 EAs^[2] for reasons of clarity, we write

$$\begin{aligned} \text{EA}_0(\text{XY}) &= E_0(\text{XY}) - E_0(\text{XY}^-), \text{ or} \\ \text{EA}_0(\text{XY}) &= \text{EA}(\text{Y}) + D_0(\text{XY}^-) - D_0(\text{XY}) > 0 \end{aligned}$$

assuming that $\text{EA}(\text{Y}) > \text{EA}(\text{X}) > 0$; D_0 ($= D_e - \text{ZPE}$) 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

$$D_0(\text{XY}^-) - [D_0(\text{XY}) - \text{EA}(\text{Y})] > 0$$

It is instructive to apply the above relation to a diatomic molecule whose EA is close to 0, like $\text{NO}(\chi^2\Pi_r)$. The latter's experimental EA is $+0.026 \pm 0.005$ eV.^[7] Indeed, $D_0(\text{NO}^-; \chi^3\Sigma^-) - [D_0(\text{NO}; \chi^2\Pi) - \text{EA}(\text{O}; ^3\text{P})] = 5.056 - [6.496 - 1.461] = +0.021$ eV ($= \text{EA}_0$) (Experimental values taken from Ref. [8]).

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

Now, when the equilibrium energy $E_0(\text{XY}^-)$ is located above $E_0(\text{XY})$, 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 $\text{XY} + e^-$. The energy difference $E_0(\text{XY}^-) - E_0(\text{XY}) = -\text{EA}_0(\text{XY})$ 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 τ , usually in the range 10^{-16} 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_c 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, $\text{XY}^- \rightarrow \text{XY} + e^-$. 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 η is a positive number reflecting the CAP strength. Clearly, $\hat{H}_{\text{CAP}}(\eta)$ is a non-Hermitian operator. The corresponding Schrödinger equation reads

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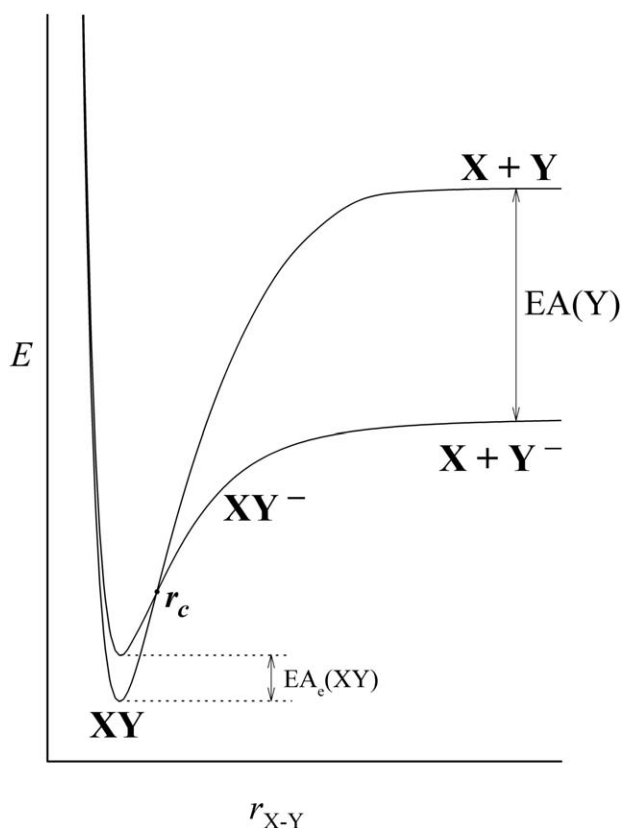


Figure 1. Schematic PECs of the XY diatomic and its metastable XY^- anion; r_c is the crossing point.

$$\hat{H}_{CAP}(\eta)\psi(\eta) = E(\eta)\psi(\eta)$$

The eigenstate of $\hat{H}_{CAP}(\eta)$ is the Siegert complex energy of the resonance state

$$E_{res} = E_R - i\frac{\Gamma}{2}$$

where E_R is the resonance energy and Γ the associated width related to the lifetime of the resonance state $\tau = \hbar/\Gamma$; see Ref. [11]. The physical meaning of the CAP method is to confine the outgoing electron, that is, to avoid the variational collapse to the XY neutral molecule (+ a free e^-), hence transforming the wave function of the resonance state to square-integrable.^[10,11] The CAP approach is combined to a standard highly correlated method, for instance coupled-cluster (CC) including triple excitations, or multireference configuration interaction (MRCI), for the location of resonances (E_R) and their width (Γ).

Although the CAP methodology is mathematically “proper,” albeit phenomenological, there are technical problems, (a) related to the mathematical form of the operator \hat{W} which perturbs the Hermitian Hamiltonian, (b) the quest for the optimum value of the η parameter which is basis set dependent, and so forth. Therefore, the avoidance of the CAP approach and the use of standard conventional (bound) techniques whenever deemed possible should be given a chance. As a matter of fact, in Ref. [10] and in relation to the metastable

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^- ($X^2\Pi$) 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 (even tempered diffuse functions)] approach. Through CCSD(T)/aug-cc-pCVTZ, they also located the high spin states $^4\Sigma^-$ and $^6\Pi$ 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^- ($X^2\Pi$) 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^- ($X^2\Pi$), while Results and Discussion section refers to results and discussion on the BF/BF^- and BCl/BCl^- systems. We close with a short summary of our findings in Summary and Remarks section.

Computational Outline

The single reference CC 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 $\sim 1s^2/B,C,O,F$ and $1s^22s^22p^6/Cl$ 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- ζ quality, that is, aug-cc-pV6Z (=A6 ζ for brevity). The generally contracted basis sets for the group of atoms (B, C, O, F) and Cl are [8s7p6d5f4g3h2i] and [9s8p6d5f4g3h2i], 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

$(ns+np)\times 2+\pi p'_x+\pi p'_y$ (where $\pi p'_x$, $\pi p'_y$ denote molecular orbitals of b_1 and b_2 symmetries purporting to increase the flexibility of the reference space [CAS]), resulting in 4984 (neutrals) and 6940 (anions) configuration functions (CF). The corresponding MRCI (icMRCI) spaces number 5.8×10^8 (4.2×10^6) and 1.3×10^9 (6.2×10^6) 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.^[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 $\text{Ng} = \text{He}$ to Xe ,^[18] the H_2 , CO , N_2 molecules, and the hydrogen halides HY , $\text{Y} = \text{F}$, Cl , Br , and I ,^[8] see also the extended article on the HF/HF^- system by Piecuch.^[19] Going systematically through the Huber–Herzberg compilation,^[8] besides the HY^- anions only the H_2^- ($X^2\Sigma_u^+$), 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^- , $\text{IE} = 0.10_0 \pm 0.1_8$ given in Ref. [8], proved to be definitely positive many years later through negative ion photoelectron spectroscopy, $\text{IE} = 0.739 \pm 0.008$ eV,^[20] thus stable. As for H_2^- , it is a resonance state with a negative IE of nearly -2 eV.^[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.^[25] See also Ref. [26] for a useful discussion related to Ref. [25] on CO^- . We remind at this point that BF ($X^1\Sigma^+$) is a closed shell molecule, isoelectronic to CO and N_2 , and strongly bound with $D_0 = 182.0$ kcal/mol,^[27] therefore, one would expect a quasi-stable BF^- anion.^[10] To summarize, as these lines are written, the literature uncovers no more than 10 diatomic anionic resonance states, namely, HY^- ($\text{Y} = \text{F}$, 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 ζ PECs of CO ($X^1\Sigma^+$) and CO^- ($X^2\Pi$), whereas Table 1 lists numerical results of the CO/CO^- system at the CCSD(T) and MRCI (+Q)/A6 ζ levels of theory. Notice first the excellent agreement between the experimental^[8] and the calculated results on CO at the

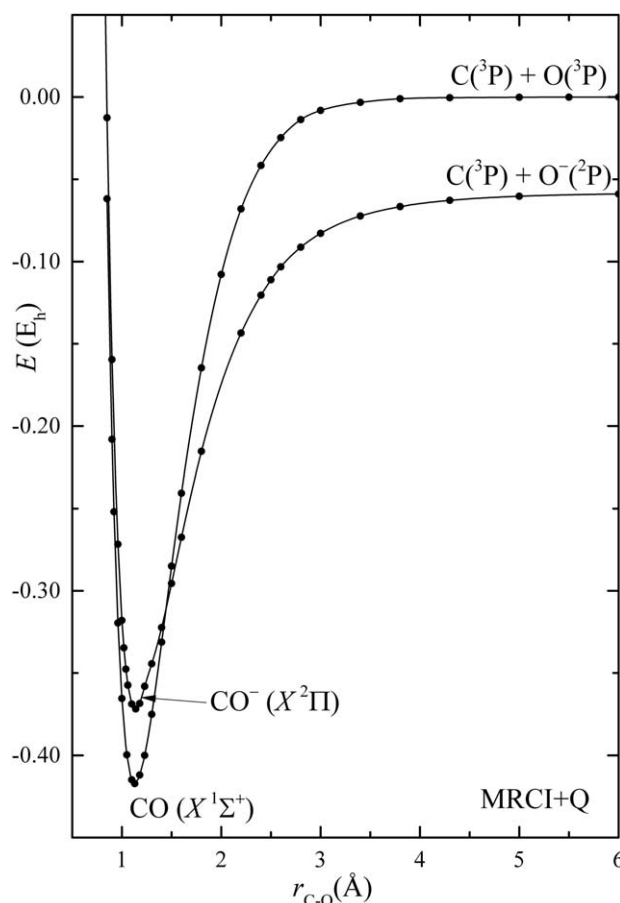


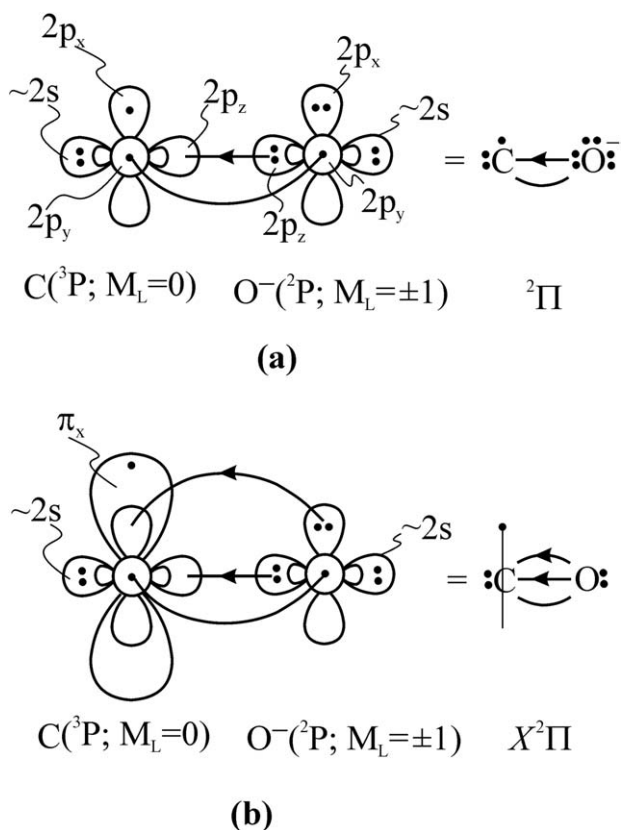
Figure 2. PECs of CO ($X^1\Sigma^+$) and CO^- ($X^2\Pi$) at the MRCI+Q/A6 ζ level. Both curves are shifted by $+112.784711 E_h$.

CCSD(T)(MRCI+Q)/A6 ζ level. Small discrepancies on the spectroscopic constants $\delta r_e = -0.0004(+0.0005)$ Å, $\delta D_0 = -0.02(+0.13)$ eV, $\delta \omega_e = -8.2(-0.8)$ cm^{-1} , and $\delta \omega_e x_e = -0.13(+0.5)$ cm^{-1} are due, mainly, to the omission of core ($\sim 1s^2/c_o$) correlation effects. Incidentally, the best experimental dissociation energy of CO so far is $D_0^0(X^1\Sigma^+) = 89592 \pm 15$ cm^{-1} ($=11.080 \pm 0.002$ eV).^[29]

Table 1. Structural parameters of the $^{12}\text{C}^{16}\text{O}$ ($X^1\Sigma^+$) and CO^- ($X^2\Pi$) at the valence CCSD(T), MRCI, and MRCI+Q/A6 ζ levels. Total energies E (E_h), bond distances r_e (Å), dissociation energies D_0 (eV), harmonic and anharmonic frequencies ω_e and $\omega_e x_e$ (cm^{-1}), and adiabatic electron affinities EA_0 (eV). Experimental results are also included for easy comparison.

Method	$-E$	r_e	D_0 ^[a]	ω_e	$\omega_e x_e$	EA_0 ^[b]
CO ($X^1\Sigma^+$)						
CCSD(T)	113.202431	1.1311	11.07	2161.6	13.16	-1.14
MRCI	113.188766	1.1342	11.23	2150	12.7	-1.31
MRCI+Q ^[c]	113.20196	1.132	11.22	2169	13.8	-1.22
Expt ^[d]		1.1315	11.09	2169.81	13.288	-1.50
CO^- ($X^2\Pi$)						
CCSD(T)	113.159956	1.139	8.49	1971.9	64.0	
MRCI	113.140081	1.136	8.55	1958	32.0	
MRCI+Q	113.15647	1.139	8.43	1812	22.6	
Expt		~ 1.17 ^[e]	8.1 ^[d]			

[a] $D_0 = D_e - \omega_e/2$. [b] $\text{EA}_0 = \text{EA}_e + \Delta\omega_e/2$. [c] +Q refers to Davidson correction. [d] Ref. [8]. [e] Ref. [28].



Scheme 1.

Experimentally, the EA of CO (or the DE of CO^- , or the E_R position of CO^-) is $\text{EA} = -1.5$ ($\text{IE} = -1.5$, $E_R = 1.5$) eV at an estimated bond length $r(\text{CO}^-) \approx 1.17 \text{ \AA}$ 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

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

The above experimental findings on CO^- compare favorably with our CCSD(T)(MRCI+Q)/A6 ζ stationary state results, that is, $\text{EA}_0(\text{CO}) = -1.14(-1.22) \text{ eV}$, $r_e(\text{CO}^-) = 1.139(1.139) \text{ \AA}$, and $D_0 = 8.49(8.43) \text{ eV}$; see Table 1. Also the MRCI + Q vibrational energy differences are (the experimental values from Ref. [28] in parentheses) $\Delta E_{v+1,v}(\text{CO}^-)$, $v = 0, 1, 2, 3, 4 = 252$ (230), 233 (220), 208 (210), 198 (200), 192 meV, whereas the calculated crossing point of the $\text{CO}-\text{CO}^-$ PECs at both CC or MRCI is $r_c = 1.45-1.47 \text{ \AA}$; see Figure 2.

It is of interest to compare our calculated CO^- parameters with the most recent CAP-type calculations.^[11] The CAP-EOM-CCSD results depend strongly on the basis set size; monitoring the basis set with respect to experiment, at the d-aug-cc-pVDZ+p level (see Ref. [11] for details), $E_R = 1.30 \text{ eV}$, $r_e \approx 1.13 \text{ \AA}$ (see Fig. 2 of Ref. [11]), $r_c = 1.48 \text{ \AA}$, and $\Gamma = 0.52 \text{ eV}$.

The similarity between our “traditional” results and those of Ref. [11] (of course Γ is considered to be zero in our calculations), indicates that under certain circumstances bound state methods can be profitably used in calculating ground state resonances, see also Refs. [10,19]. In addition, the

MRCI approach is to be preferred over the CC one, because the former allows the construction of full PECs, thus the determination of the stationary state region of the XY^- anion to the right of the crossing point r_c with the PEC of the stable target species XY. The full PECs of Figure 2 clarify these arguments: between r_c and $r_\infty (= 20 \text{ bohr})$, $r_c < r < r_\infty$ the CO^- ion is a stationary state succinctly described at infinity by the valence bond-Lewis (vbl) Scheme 1a, and corroborated by the MRCI Mulliken atomic distributions $2s^{2.00}2p_z^{1.00}2p_x^{1.00}2p_y^{1.00}/_C \quad 2s^{2.00}2p_z^{2.00}2p_x^{2.00}2p_y^{1.00}/_{O^-}$

To the left of the crossing point, $0 < r < r_c$, the CO^- ($X^2\Pi$) switches from a stationary state to a scattering state of the same symmetry, better described around its PEC minimum as $\text{CO}(X^1\Sigma^+) +$ an electron distributed over a diffuse orbital of π symmetry residing mainly on the C atom and away from the parent molecule. A schematic vbl illustration is given in the Scheme 1b. The leading equilibrium configurations of $\text{CO}(X^1\Sigma^+)$ and $\text{CO}^-(X^2\Pi)$ along with the corresponding MRCI Mulliken populations are in agreement with the diagram (1b)

$$\begin{aligned} \text{CO} : |X^1\Sigma^+ \rangle &\approx 0.94 | 3\sigma^2 4\sigma^2 5\sigma^2 1\pi_x^2 1\pi_y^2 \rangle \\ &2s^{1.65} 2p_z^{0.99} 2p_x^{0.55} 2p_y^{0.55} \sim d^{0.23} /_C \\ &2s^{1.79} 2p_z^{1.44} 2p_x^{1.36} 2p_y^{1.36} \sim d^{0.08} /_O, q_c = +0.03 \end{aligned}$$

$$\begin{aligned} \text{CO}^- : |X^2\Pi \rangle &\approx 0.94 | 3\sigma^2 4\sigma^2 5\sigma^2 1\pi_x^2 1\pi_y^2 2\pi_x \rangle \\ &2s^{1.70} 2p_z^{0.98} 2p_x^{1.53} 2p_y^{0.55} \sim d^{0.35} /_C \\ &2s^{1.75} 2p_z^{1.43} 2p_x^{1.18} 2p_y^{1.18} \sim d^{0.16} /_O, q_c = -1.11 \end{aligned}$$

Observe that while the *in situ* C and O net Mulliken charges are practically zero in CO, as it should, more than one e^- has been transferred from O^- to C in the CO^- species. Increasing systematically the one electron diffuse space, we ended up with $\text{CO}(X^1\Sigma^+) +$ a detached electron of π symmetry (variational 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/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 $r_e = 1.26712 \text{ \AA}$ 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 (*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 $\text{BF}(X^1\Sigma^+)$ and $\text{BF}^-(X^2\Pi)$ at the CCSD(T) and MRCI(+Q)/A6 ζ 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

Table 2. Total energies E (E_h), bond distances r_e (Å), dissociation energies D_0 (eV), harmonic and anharmonic frequencies ω_e and $\omega_e x_e$ (cm^{-1}), and adiabatic electron affinities EA_0 (eV) of the ground states of $^{11}\text{B}^{19}\text{F}(\text{X}^1\Sigma^+)$ and $\text{BF}^-(\text{X}^2\Pi)$ at the valence CCSD(T), MRCI, and MRCI+Q/A6 ζ level.

Method	$-E$	r_e	$D_0^{[a]}$	ω_e	$\omega_e x_e$	$EA_0^{[b]}$
BF($\text{X}^1\Sigma^+$)						
CCSD(T)	124.555611	1.2668	7.78	1395	11.8	-0.60
MRCI	124.538674	1.2739	7.98	1378	12.0	-0.92
MRCI+Q ^[c]	124.54748	1.275	7.96	1371	11.6	-0.72
Expt		1.2627 ^[d]	7.806 \pm 0.13 ^[e]	1402.1 ^[f]	11.8 ^[f]	
BF$^-(\text{X}^2\Pi)$						
CCSD(T)	124.533349	1.2834	3.77	1243	22	
MRCI	124.504896	1.2793	3.62	1328	9.4	
MRCI+Q	124.52099	1.286	3.62	1242	-	

[a] $D_0 = D_e - \omega_e/2$. [b] $EA_0 = EA_e + \Delta\omega_e/2$. [c] +Q refers to Davidson correction. [d] Ref. [30]. [e] Ref. [31]. [f] Ref. [8].

-0.60 (CCSD(T)) and -0.92 (MRCI), or -0.72 eV (MRCI+Q). These negative EAs are more or less in agreement with those of Dreuw et al.^[10] who obtained $EA(\text{adiabatic}) = -0.806$ eV at the CCSD(T)/aug-cc-pCVTZ level and $r_e = 1.3092$ Å. Using the CAP/CI 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/CI approach $r_c = 1.63$ and 1.75 Å, (estimated from Figs.

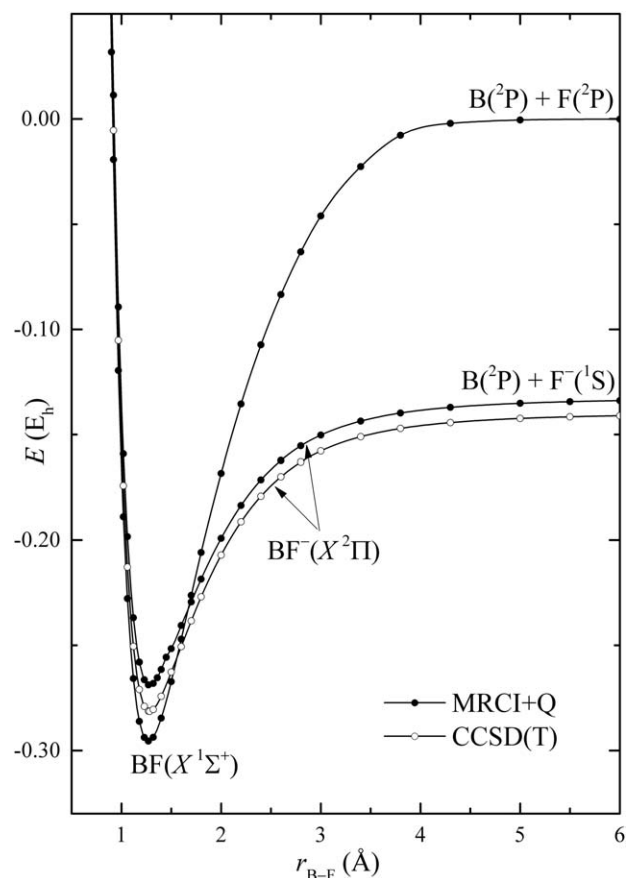
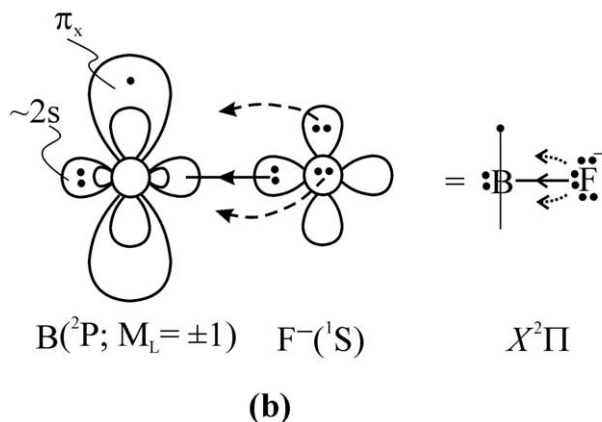
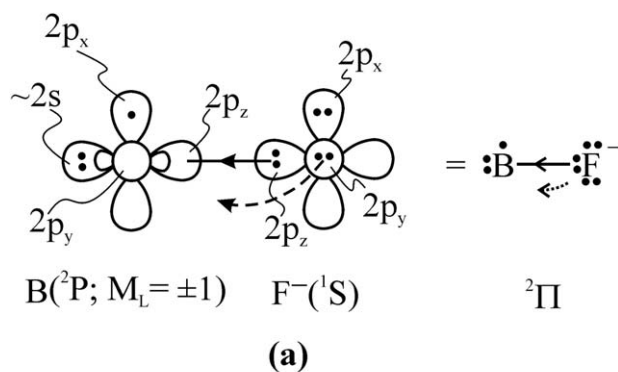


Figure 3. PECs of $\text{BF}(\text{X}^1\Sigma^+)$ and $\text{BF}^-(\text{X}^2\Pi)$ at the MRCI+Q/A6 ζ and CCSD(T)/A6 ζ (BF^-) levels of theory. All curves are shifted by +124.251198 E_h .



Scheme 2.

1 and 2 of Ref. [10]). In addition, $\Gamma \approx 1$ eV, or $\tau(\text{BF}^-) = \hbar/\Gamma = 6 \times 10^{-16}$ s,^[10] perhaps shorter than that of CO^- .

An experimental "binding energy" of BF^- can be estimated through the energy conservation relation $D_0(\text{BF}^-) = D_0(\text{BF}) - [\text{EA}(\text{F}) - \text{EA}(\text{BF})] = (7.806 \pm 0.13) - [3.40 - (-0.8 \pm 0.1)] = 3.6 \pm 0.2$ eV, taking the EA of BF as -0.8 ± 0.1 eV. This value is in agreement with the directly calculated CC or multireference D_0 values of 3.77 and 3.62 eV, respectively; see Table 2. We also report the MRCI+Q vibrational energy differences of $\text{BF}^-(\text{X}^2\Pi)$, $\Delta E_{v+1,v}$ ($v = 0, 1, 2, 3$) = 153, 146, 132, 120 meV.

We turn now to the bonding character of BF^- . As in the CO^- description, between the crossing point r_c and r_∞ ($= 20$ bohr), $r_c < r < r_\infty$ the BF^- ion is stable, described at r_∞ by the vbL diagram of Scheme 2a and clearly confirmed by the Mulliken populations $2s^{2.00}2p_z^{0.00}2p_x^{1.00}2p_y^{0.00}/_B$ $2s^{2.00}2p_z^{2.00}2p_x^{2.00}2p_y^{2.00}/_{\text{F}^-}$.

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

$$\begin{aligned} \text{BF} : |\text{X}^1\Sigma^+ \rangle &\approx 0.94 | 3\sigma^2 4\sigma^2 5\sigma^2 1\pi_x^2 1\pi_y^2 \rangle \\ &2s^{1.68} 2p_z^{0.59} 2p_x^{0.17} 2p_y^{0.17} \sim d^{0.18} /_B \\ &2s^{1.87} 2p_z^{1.68} 2p_x^{1.80} 2p_y^{1.80} \sim d^{0.06} /_{\text{F}}, q_B = +0.21 \end{aligned}$$

Table 3. Total energies E (E_h), bond distances r_e (Å), dissociation energies D_0 (eV), harmonic and anharmonic frequencies ω_e and $\omega_e x_e$ (cm^{-1}), rotation–vibration coupling constants a_e (cm^{-1}), centrifugal distortions D_e (cm^{-1}), dipole moments μ_e (D), net Mulliken charges on the B atom q_B (e), and electron affinities EA_0 (eV) of $^{11}\text{B}^{35}\text{Cl}(\chi^1\Sigma^+)$ and $\text{BCl}^-(\chi^2\Pi)$ at the valence CCSD(T), MRCI, and MRCI+Q/A6 ζ level.

Method	$-E$	r_e	$D_0^{[a]}$	ω_e	$\omega_e x_e$	$a_e \times 10^2$	$D_e \times 10^6$	$\mu_{\text{ff}} (\langle \mu \rangle)^{[b]}$	q_B	EA_0
$\text{BCl}(\chi^1\Sigma^+)$										
CCSD(T)	484.500407	1.7228	5.26	836	4.93	0.67	1.96	1.35		-0.10
MRCI	484.484784	1.7195	5.27	847	5.28	0.65	1.76	1.34(1.34)	-0.12	-0.44
MRCI+Q ^[c]	484.50100	1.722	5.22	838	5.30	0.66	1.78	1.35		-0.18
MRCI+DK/A5 ζ ^[d]		1.713	5.29	845.7	5.49	0.646				
Expt		1.715 ₉ ^[e]	5.26 ± 0.05 ^[f]	839.12 ^[e]	5.11 ^[e]	0.646 ^[e]	1.72 ^[e]			
$\text{BCl}^-(\chi^2\Pi)$										
CCSD(T)	484.496091	1.8919	1.52	510	10.1	4.1	1.24			
MRCI	484.467782	1.8898	1.43	518	7.0	7.0	1.00		-0.71	
MRCI+Q ^[c]	484.49378	1.890	1.49	514	6.8	6.9	1.00			

[a] $D_0 = D_e - \omega_e/2$. [b] Finite field (μ_{ff}) and expectation value ($\langle \mu \rangle$) dipole moments. [c] +Q refers to Davidson correction. [d] Ref. [33]. [e] Ref. [8]. [f] Ref. [35].

$$\text{BF}^- : |\chi^2\Pi\rangle \simeq 0.96|3\sigma^2 4\sigma^2 5\sigma^2 1\pi_x^2 1\pi_y^2 2\pi_x^1\rangle$$

$$2s^{1.72} 2p_z^{0.60} 2p_x^{1.55} 2p_y^{0.15} \sim d^{0.11}/B$$

$$2s^{1.89} 2p_z^{1.67} 2p_x^{1.51} 2p_y^{1.80}/F, q_B = -1.13$$

Notice that more than one e^- has migrated from F^- to B in the BF^- anion ($\text{B}^{-1.1}\text{F}^{+0.1}$), identical to that of CO^- (*vide*

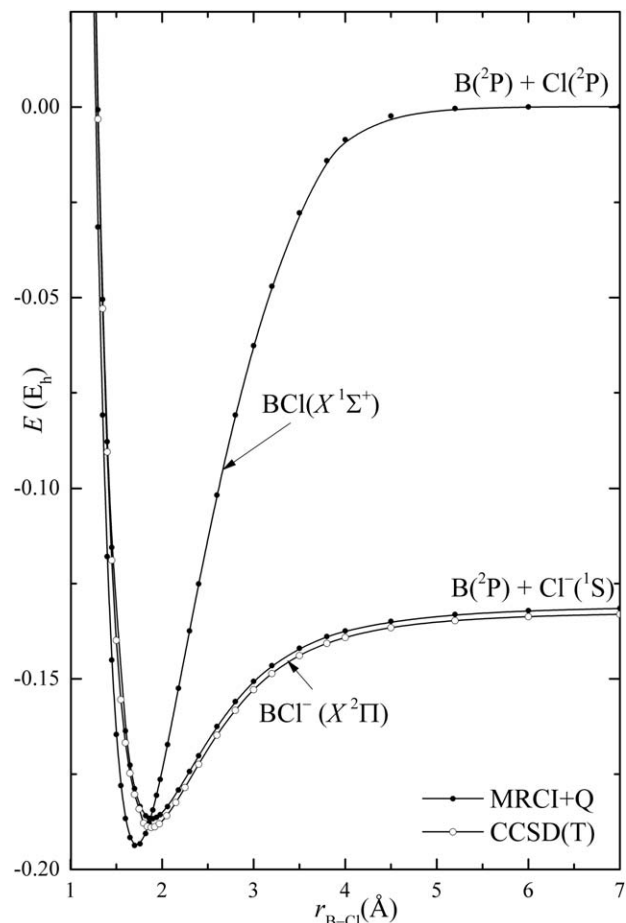


Figure 4. PECs of $\text{BCl}(\chi^1\Sigma^+)$ and $\text{BCl}^-(\chi^2\Pi)$ at the MRCI+Q/A6 ζ and CCSD(T)/A6 ζ (BCl^-) levels of theory. All curves are shifted by +484.307089 E_h .

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.

BCl/BCl⁻

The closed shell chloroborane ($\text{BCl}; \chi^1\Sigma^+$) molecule is isovalent 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 ζ spectroscopic parameters of $\text{BCl}(\chi^1\Sigma^+)$ along with experimental^[8,35] 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 ($1s^2/B$ $1s^2 2s^2 2p^6/C$) correlation effects. It is of interest, however, to notice the following: (a) the electric dipole moment μ 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, μ_{ff} . (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 BCl reported here for the first time is negative at both CC or MRCI methods. In particular, the MRCI(+Q) EA is $EA_0 = -0.44(-0.18)$ eV. This signifies that BCl^- is a resonance or a metastable state. PECs of $\text{BCl}(\chi^1\Sigma^+)$ and $\text{BCl}^-(\chi^2\Pi)$ are shown in Figure 4. As before an “experimental” binding energy of BCl^- can be obtained based on the MRCI EA of BCl, $EA_0 = -0.3 \pm 0.11$ eV, and the experimental values D_0 ^[35] and EA of Cl:

$$D_0(\text{BCl}^-) = D_0(\text{BCl}) - [\text{EA}(\text{Cl}) - \text{EA}(\text{BCl})] = (5.26 \pm 0.05) - [3.61 - (-0.3 \pm 0.1)] = 1.35 \pm 0.1 \text{ eV, in harmony with the MRCI } D_0 \text{ value of Table 3. The MRCI(+Q) crossing point between the PECs of BCl/BCl}^- \text{ is } r_c = 1.97(1.87) \text{ \AA, } 0.25(0.15) \text{ \AA to the right of the equilibrium distance } r_e = 1.72 \text{ \AA of the neutral, while the first four MRCI+Q vibrational energy differences of BCl}^-(\chi^2\Pi) \text{ are } \Delta E_{v+1,v} (v = 0,1,2,3) = 62, 61, 59, 57 \text{ meV.}$$

The leading MRCI CFs of BCl and BCl⁻ and their Mulliken populations are given below, where the electronic structure of BCl⁻ (X²Π) at r_∞ (=20 bohr) and r_e (=1.72 Å) is adequately represented by the vbL Schemes 2a and 2b of the isovalent BF⁻.

$$\text{BCl} : |X^1\Sigma^+\rangle \simeq 0.92|(\text{core})^{12}5\sigma^26\sigma^27\sigma^22\pi_x^22\pi_y^2\rangle$$

$$2s^{1.72}2p_z^{0.79}2p_x^{0.21}2p_y^{0.21}\sim d^{0.19}/_B \quad 3s^{1.90}3p_z^{1.54}3p_x^{1.74}3p_y^{1.74}\sim d^{0.16}/_Cl$$

$$\text{BCl}^- : |X^2\Pi\rangle \simeq 0.92|(\text{core})^{12}5\sigma^26\sigma^27\sigma^22\pi_x^22\pi_y^23\pi_x^1\rangle$$

$$2s^{1.84}2p_z^{0.56}2p_x^{1.04}2p_y^{0.14}\sim d^{0.13}/_B \quad 3s^{1.93}2p_z^{1.47}2p_x^{1.86}2p_y^{1.85}\sim d^{0.18}/_Cl$$

The net Mulliken charges on the B atom are -0.12 and -0.71 for BCl and BCl⁻, respectively.

Summary and Remarks

The isovalent diatomic molecular systems CO(X¹Σ⁺)/CO⁻(X²Π), BF(X¹Σ⁺)/BF⁻(X²Π), and BCl(X¹Σ⁺)/BCl⁻(X²Π) have been studied by CCSD(T) and MRCI methods and correlation consistent basis sets of augmented valence quintuple and sextuple cardinality. The focus of this study is the metastable negative ions with the purpose to show that resonances, that is quasi-stable species with lifetimes of the order of 10⁻¹⁵ s, can be treated profitably by stationary state methods. It should be stated emphatically, however, that extreme caution should be exercised in treating resonances by stationary state methods. In addition, the systems examined in this work are isoelectronic or isovalent and of the same symmetry, X¹Σ⁺. We condense our findings below.

- Our general conclusions on the quasi-stable anions are in agreement with either experimental (CO⁻) or theoretical CAP results (CO⁻, BF⁻).
- It is reported for the first time that the BCl⁻(X²Π) anion is a resonance, with a negative adiabatic electron affinity EA₀ = -0.3 ± 0.1 eV.
- For all three quasi-stable anions, CO⁻, BF⁻, and BCl⁻ full MRCI+Q PECs are reported for the first time. Limited PECs at the CCSD(T)/aug-cc-pCVTZ level have been reported before for BF⁻.^[10]
- The calculated sequence of the EAs of the isovalent CO, BF, BCl, and BBr, the latter at the CCSD(T) CBS-limit^[36] is about -1.3 (expt. -1.5), -0.8 ± 0.1, -0.3 ± 0.1, and +0.20 eV, respectively. Preliminary MRCI+Q (CCSD(T))/[aug-cc-pV5Z/_B aug-cc-pV5Z-PP/_I] calculations of this laboratory on the BI(X¹Σ⁺)/BI⁻(X²Π) system, prove unequivocally that the BI⁻ anion is stable. More specifically, we find BI(X¹Σ⁺): r_e = 2.15 (2.15) Å, ω_e = 586 (584) cm⁻¹, while ω_e(expt) = 574.798 cm⁻¹.^[37] BI⁻(X²Π_{1/2}): r_e = 2.41 (2.40) Å, ω_e = 320 (308) cm⁻¹, with EA₀(BI) = +0.54 (+0.60) eV. Observe the monotonic increase of EA by ~0.5 eV from CO to BBr and BI, the BBr and BI anions being definitely stable.
- For a XY/XY⁻ PECs (XY⁻ metastable) of the morphology of Figure 1, a crossing point r_c always exists. Considering

EA as a function of the interatomic distance r, we can write that EA(r) > 0 for r > r_c (stationary region), EA(r) < 0 for r < r_c (metastable region), and EA(r) = 0 for r = r_c (transition point). The MRCI+Q transition points of CO⁻, BF⁻, and BCl⁻ are 1.46, 1.67, and 1.87 Å, respectively.

- Although closed shell diatomic molecules with negative EAs are very limited, the situation changes drastically for closed shell polyatomic molecules. For instance, CH₄⁻ is definitely metastable,^[38] whereas a variety of common unsaturated hydrocarbons like acetylene, butadiene, cyclohexene, benzene, and so forth have EA < 0.^[39] This means that the role of molecular resonances can be very important in certain chemical processes; see also Ref. [6].

A final observation warning is in order. Bound state methods, either variational or not, are not the best tool for studying quasi-stable negative species because of the lurking 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 · *ab initio*

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