



Research paper

Accurate ab initio investigation of the ground and some low-lying electronic states of boron monoiodide, BI, and its ions BI⁺ and BI⁻

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ARTICLE INFO

Article history:

Received 1 November 2017

In final form 14 December 2017

Available online 24 December 2017

Keywords:

Boron monoiodide
MR-CISDBinding energy
Electron affinity
Ionization potential

ABSTRACT

The lowest electronic states of boron monoiodide, BI, and its ions BI[±] have been theoretically studied by the multireference configuration interaction technique employing basis sets of quadruple and quintuple- ζ quality. Scalar relativistic effects and spin-orbit coupling are taken into account as well. For all states we report potential energy curves, binding energies, and spectroscopic constants. Some quantities such as electron affinity, ionization potential, and dipole moment of BI are evaluated for the first time. The nature of the bonding in the systems under scrutiny is also discussed in some detail.

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1. Introduction

Boron forms a large variety of binary halides with different coordination numbers. The most stable of them are boron trihalides, BX₃ with X = F, Cl, Br, and I, with important chemical properties (e.g. Lewis acid catalysts for Friedel-Crafts reactions) as well as technological applications (e.g. in electronics, chemical vapor deposition processes or doping Si or Ge with B) [1]. Other types of boron halides are diboron tetrahalides in which the ratio between the boron and halogen atoms is two, and the polyhedral boron halides with general formula B_nX_n with cage structures and boron coordination numbers greater than three [2,3]. Admittedly all these compounds of boron show an increased complexity which can only be rationalized on the basis of the properties of their elementary building blocks i.e. the diatomic haloborylenes, BX. All these species although having a closed shell X¹Σ⁺ ground state, they also possess a relatively low-lying a³Π state with two unpaired electrons (some people call it hybridization) combined with an empty p orbital on B (vide infra). These characteristics are responsible for the extreme complexity of boron halides. A large number of studies on BF, BCl, and BBr are available and a thorough compilation of the literature on these species can be found in a recent paper by Krasowska et al. [4]. Iodoborylene, BI, is the least studied between them and will make the subject of the present theoretical study together with its ions BI⁺ and BI⁻.

A first attempt to observe and study BI was through flash photolysis of BI₃ by Briggs and Piercy [5] in 1973. They observed two bands near 349 nm (~3.55 eV) together with numerous bands in the range 266–279 nm. However, the first definitive spectroscopic identification of BI was provided by Lebreton et al. [6] in 1974 from a “Schüler-type” discharge experiment where they observed the a³Π → X¹Σ⁺ band system of the molecule. In 1985 Coxon and Naxakis [7] recorded the a³Π (0⁺,1) → X¹Σ⁺ bands of BI excited by the reaction of discharged helium with BI₃. In this work they reported spectroscopic constants (T_e, ω_e, and ω_ex_e) for all states studied. Two years later the same authors presented [8] a rotational analysis from which they obtained the B_e, a_e, and D_e spectroscopic constants of the a³Π (0⁺,1) and X¹Σ⁺ states. Finally, in 1990, Lebreton et al. [9] carried out a new study of the same band system and gave precise molecular constants including spin-orbit and Λ-doubling constants for the a³Π state of BI.

There are only two theoretical works on BI by Yang et al. In the first one [10] they performed TDDFT calculations to obtain segments of potential energy curves (PEC) for 12 valence and 8 Rydberg excited states. In the second work [11] they employed the more accurate ab initio MR-CISD methodology combined with basis sets of triple- ζ quality and constructed full PEC's for 12 valence Λ-S electronic states and also for the 23 Ω states that arise by including the spin-orbit coupling. For all bound states they provided equilibrium distances, spectroscopic constants T_e, ω_e, and ω_ex_e as well as binding energies D_e.

In the present work we aim to complete the aforementioned rather limited literature on BI with very accurate ab initio results

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concerning its spectroscopic constants and binding energies as well as to report for the first time quantities such as dipole moment, ionization potential, and electron affinity. Moreover, insights are provided on the bonding mechanisms of all species studied. We focus to the three lowest electronic states of BI and one or two states of its ions BI^+ and BI^- . The latter ions are reported for the first time in the literature.

2. Computational details

Through all our calculations we used for the B and I atoms the following correlation consistent basis sets of quadruple and quintuple- ζ quality:

B: aug-cc-pV5Z [12] contracted as (15s9p5d4f3g2h) \rightarrow [7s6p5d4f3g2h]

I: aug-cc-pwCVQZ [13] contracted as (31s24p18d6f4g1h) \rightarrow [12s11p9d6f4g1h]

and also

aug-cc-pV5Z-PP [14] contracted as (17s14p14d4f3g2h) \rightarrow [8s8p6d4f3g2h]

The latter employs a relativistic effective core potential to replace 28 core electrons ($[Kr]4d^{10}$) of iodine. Now, these basis sets were combined as

$B(\text{aug-cc-pV5Z}) + I(\text{aug-cc-pwCVQZ}) \equiv \text{AQ}\zeta$ and

$B(\text{aug-cc-pV5Z}) + I(\text{aug-cc-pV5Z-PP}) \equiv \text{A5}\zeta\text{-PP}$

Our computational approach was based on the multireference configuration interaction method CASSCF + single + double replacements \equiv MRCl. The CASSCF configuration space was constructed by distributing the 10 (9, 11) valence electrons of BI (BI^+ , BI^-) to 10 orbitals corresponding to 8 valence orbitals of B and I + 2 complementary orbitals of π symmetry necessary

for a correct description of the BI^- anion. The active space comprised 4800–7400 configuration functions (CF) depending on the system studied. At the MRCl level the maximum number of CF's was $\sim 8 \times 10^8$ reduced to $\sim 5 \times 10^6$ CF's through the internal contraction technique [15]. When the $4d^{10}$ electrons of I were included in the CISD correlation treatment (C-MRCl), the $\sim 1.1 \times 10^{10}$ CF's C-MRCl space was internally contracted to $\sim 1.1 \times 10^8$ CF's.

To take into account the size non-extensivity we applied to our numbers the Davidson correction [16] for unlinked quadruples, MRCl+Q and C-MRCl+Q.

Scalar relativistic effects were introduced at the MRCl/AQ ζ and C-MRCl/AQ ζ levels by using the one electron Douglas-Kroll-Hess Hamiltonian [17–19] of third order, MRCl-DKH and C-MRCl-DKH, respectively. Basis sets were recontracted appropriately.

Spin-orbit coupling effects were obtained by diagonalizing the Breit-Pauli operator [20] in the space of all 12 Λ -S states emerging from the $B(^2P) + I(^2P)$ asymptote at the MRCl-DKH(+Q)/AQ ζ level. For the BI^+ and BI^- ions we used the two state space ($^2\Sigma^+$ and $^2\Pi$) stemming from the $BI^+(^1S) + I(^2P)$ and $B(^2P) + I^-(^1S)$, respectively. All calculations were performed considering the C_{2v} abelian subgroup of $C_{\infty v}$.

All spectroscopic constants were extracted by numerically solving the nuclear rovibrational Schrödinger equation using the ^{11}B and ^{127}I isotopic masses.

Dipole moments were calculated through the finite field method by applying a uniform electric field of 5×10^{-6} a.u. along the BI axis.

All calculations were performed with the MOLPRO2012.1 [21] program.

3. Results and discussion

A. BI. The ground state asymptotic atomic channel, $B(^2P) + I(^2P)$, of boron monoiodide gives rise to 12 Λ -S electronic states, namely

Table 1
Energies E (E_h), bond lengths r_e (Å), binding energies D_0 (kcal/mol), harmonic frequencies ω_e (cm^{-1}), anharmonicity constants $\omega_e x_e$ (cm^{-1}), rotation-vibration coupling constants a_e (cm^{-1}), centrifugal distortion constants \bar{D}_e (cm^{-1}), total Mulliken charges on B q_B (e), electric dipole moments μ (D), and energy gaps T_0 (cm^{-1}) of the $X^1\Sigma^+$, $a^3\Pi$, and $A^1\Pi$ electronic states of BI.

Method	$-E$	r_e	D_0	ω_e	$\omega_e x_e$	$a_e \times 10^3$	$\bar{D}_e \times 10^7$	q_B	μ	T_0
$X^1\Sigma^+$										
MRCl/A5 ζ -PP	319.544004	2.145	83.9	575.4	2.758	2.778	5.37	-0.42	1.17	0.00
MRCl+Q/A5 ζ -PP	319.557712	2.148	83.9	571.0	2.683	2.783	5.98	-	1.17	0.00
MRCl-DKH/AQ ζ	7137.929472	2.143	83.6	575.5	2.287	2.759	6.70	-0.35	1.18	0.00
MRCl-DKH+Q/AQ ζ	7137.942977	2.146	83.4	571.4	2.723	2.720	5.80	-	1.18	0.00
C-MRCl-DKH/AQ ζ	7138.380897	2.128	85.0	586.7	2.800	2.740	5.71	-0.35	1.17	0.00
C-MRCl-DKH+Q/AQ ζ	7138.438760	2.130	85.2	582.1	2.762	2.751	5.90	-	1.18	0.00
Expt.		2.13079 ^a	-	575.3 ^a	2.693 ^a	2.726 ^a	5.97 ^a	-	-	-
				574.8 ^b	3.035 ^b					
					2.97 ^c					
$a^3\Pi$										
MRCl/A5 ζ -PP	319.468869	2.074	37.8	647.5	4.90	3.67	5.97	-0.48	0.44	16,534
MRCl+Q/A5 ζ -PP	319.482380	2.074	37.5	642.8	4.69	3.36	5.72	-	0.48	16,534
MRCl-DKH/AQ ζ	7137.854530	2.072	36.7	646.9	4.9	3.68	6.05	-0.47	0.46	16,454
MRCl-DKH+Q/AQ ζ	7137.868069	2.072	36.4	642.8	4.61	3.16	5.63	-	0.50	16,534
C-MRCl-DKH/AQ ζ	7138.305239	2.061	37.9	657.2	4.35	3.28	5.62	-0.46	0.39	16,615
C-MRCl-DKH+Q/AQ ζ	7138.363310	2.060	37.9	654.3	4.49	3.82	5.74	-	0.42	16,615
Expt.		2.0579 ^a	-	649.3 ^b	4.96 ^b	3.49	5.89	-	-	16,355 ^c
$A^1\Pi$										
MRCl/A5 ζ -PP	319.408363	2.127	-0.9	452.2	23.14	3.38	14.80	-0.56	1.25	29,681
MRCl+Q/A5 ζ -PP	319.425013	2.119	+0.8	461.0	17.62	6.34	12.27	-	1.27	29,036
MRCl-DKH/AQ ζ	7137.794102	2.126	-1.0	450.9	22.69	3.52	14.86	-0.52	1.26	29,601
MRCl-DKH+Q/AQ ζ	7137.810558	2.117	+0.6	459.5	17.48	6.41	12.46	-	1.30	29,036
C-MRCl-DKH/AQ ζ	7138.240945	2.120	-2.2	423.6				-0.51	1.22	30,649
C-MRCl-DKH+Q/AQ ζ	7138.302705	2.106	-0.1	424.7				-	1.24	29,843

^a Ref. [8].

^b Ref. [9].

^c Ref. [7].

$1,3\Delta\oplus 1,3\Pi(x2)\oplus 1,3\Sigma^+(x2)\oplus 1,3\Sigma^-$. These states, in turn, lead to 23 Ω states ($\Omega = 0^-$ (x5), 0^+ (x5), 1 (x8), 2 (x4), 3) when spin-orbit coupling is taken into account. The latter states correlate to the four $B(^2P_{1/2,3/2}) + I(^2P_{3/2,1/2})$ asymptotes. In the present study we have focused on the lowest $X^1\Sigma^+(X\ 0^+)$, $a^3\Pi$ (0^- , 0^+ , 1 , 2), and $A^1\Pi$ (1) Λ -S(Ω) electronic states of BI. Tables 1 and 2 list all our numerical

results on those states while Fig. 1 displays the corresponding potential energy curves (PEC) at the MRCI-DKH+Q/AQ ζ level of theory.

The ground $X^1\Sigma^+$ (or $X\ 0^+$) state correlates to the ground $B(^2P_{1/2}) + I(^2P_{3/2})$ atomic fragments. It is a closed-shell system and the bonding can be described by the valence bond-Lewis (vbl) diagram

Table 2

Energies E (E_h), bond lengths r_e (\AA), binding energies D_e and D_0 (kcal/mol), harmonic frequencies ω_e (cm^{-1}), anharmonicity constants $\omega_e x_e$ (cm^{-1}), vibration-rotation coupling constants a_e (cm^{-1}), centrifugal distortion constants D_e (cm^{-1}), and energy gaps T_e (cm^{-1}) of the six lowest electronic Ω states of the BI molecule.

Method	$-(E+7137)$	r_e	D_e^a	D_0^a	ω_e	$\omega_e x_e$	$a_e \times 10^3$	$\bar{D}_e \times 10^7$	T_e
$X0^+$									
MRCI-DKH/AQ ζ	0.929207	2.143	77.4	76.5	577	2.95	2.69	5.61	0
MRCI-DKH+Q/AQ ζ	0.944928	2.148	77.9	77.1	570	2.95	2.71	5.69	0
Expt.		2.13079 ^b	–	–	575.3 ^b 574.8 ^c	2.693 ^b , 3.035 ^c , 2.97 ^d	2.726 ^b	5.97 ^b	0
$0^-(1)$									
MRCI-DKH/AQ ζ	0.856236	2.073	31.6	30.7	645	4.41	3.11	5.60	16,015
MRCI-DKH+Q/AQ ζ	0.871039	2.072	31.5	30.6	638	4.13	3.61	5.73	16,217
$0^+(1)$									
MRCI-DKH/AQ ζ	0.855970	2.071	31.4	30.5	652	4.86	3.06	5.49	16,073
MRCI-DKH+Q/AQ ζ	0.870741	2.071	31.3	30.4	649	5.76	3.65	5.93	16,282
Expt.		2.0579 ^b	–	–	652 ^d , 649.3 ^c	5.52 ^d , 4.58 ^b , 4.96 ^c	3.49 ^b	5.89 ^b	16,049 ^d
$1(1)$									
MRCI-DKH/AQ ζ	0.854453	2.076	30.5	29.6	644	5.69	3.17	5.56	16,406
MRCI-DKH+Q/AQ ζ	0.869274	2.076	30.4	29.5	636	5.67	3.69	6.02	16,604
Expt.					644.2 ^d	5.47 ^d			16,355 ^d
$2(1)$									
MRCI-DKH/AQ ζ	0.852514	2.081	29.3	28.4	622	4.55	3.17	5.56	16,812
MRCI-DKH+Q/AQ ζ	0.867344	2.080	29.2	28.3	623	4.22	3.69	6.02	17,028
$1(II)$									
MRCI-DKH/AQ ζ	0.796532	2.186	–5.8						29,119
MRCI-DKH+Q/AQ ζ	0.814508	2.167	–6.3						28,624
Expt.									28,653 ^e

^a Binding energies with respect to $B(^3P_{1/2})+I(^3P_{3/2})$ except from $0^+(1)$ which is with respect to $B(^3P_{3/2}) + I(^3P_{3/2})$.

^b Ref. [8].

^c Ref. [9].

^d Ref. [7].

^e Ref. [5].

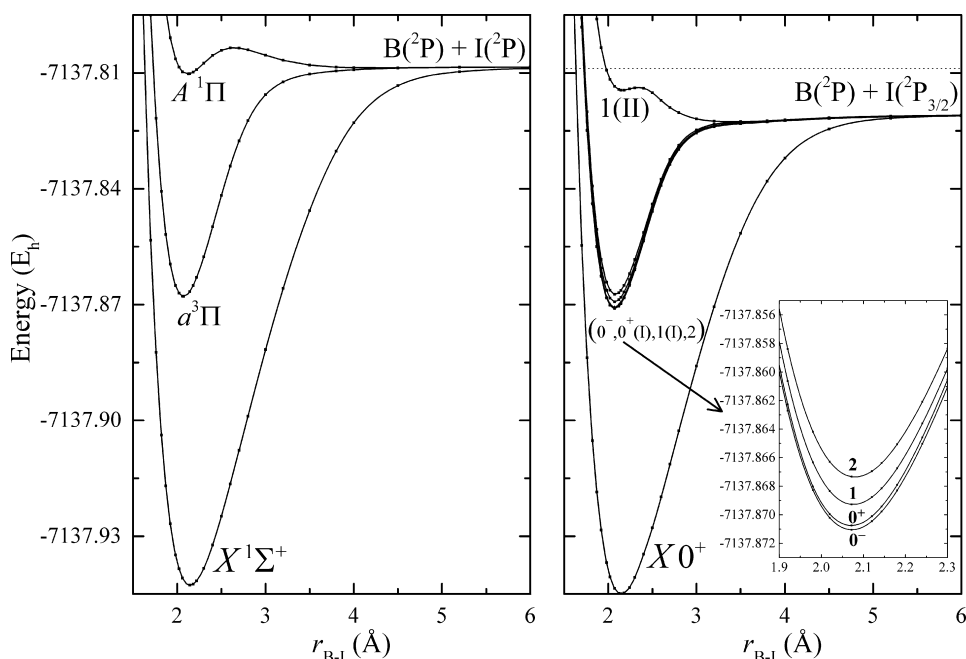
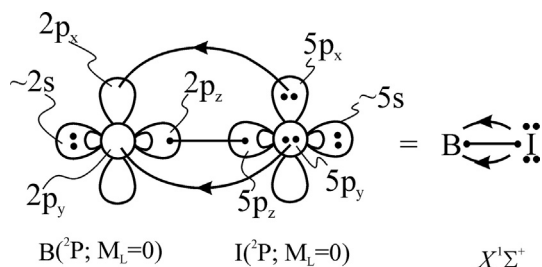
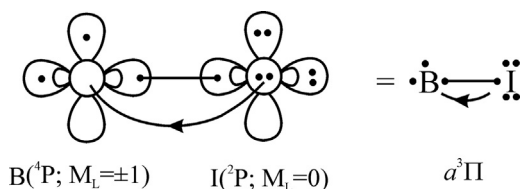


Fig. 1. Potential energy curves of the lowest $X^1\Sigma^+$, $a^3\Pi$, and $A^1\Pi$ Λ -S(Ω) states (left) and of the $X0^+$, 0^- , $0^+(1)$, $1(1)$, 2 , and $1(II)$ Ω states (right) of the boron moniodide, BI, system at the MRCI-DKH+Q/AQ ζ level of theory.



Scheme 1.

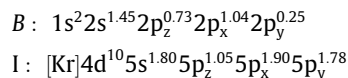
of Scheme 1 which is consistent with the atomic Mulliken populations: B: $1s^2 2s^{1.92} 2p_z^{0.86} 2p_x^{0.29} 2p_y^{0.29}$ – I: $[\text{Kr}] 4d^{10} 5s^{1.85} 5p_z^{1.19} 5p_x^{1.80} 5p_y^{1.80}$. As we can see there is a covalent σ bond accompanied by two dative B – I π bonds. This bonding mode is expected to lead to a negatively charged B end of the molecule. Indeed, by applying an external electric field the polarity was found to be $(^-)\text{BI}^{(+)}$ with a permanent electric dipole moment of 1.18 D, Table 1. From Tables 1 and 2 we can see that our numbers fit nicely the existing experimental data. Concerning the binding energy there is no experimental number. At the MRCI-DKH+Q/AQ ζ level we found $D_0 = 83.4$ kcal/mol which increased by 1.8 kcal/mol including core effects, Table 1. Of course these numbers will diminish when spin-orbit coupling is introduced due to the important I ($^2P_{3/2}$ – $^2P_{1/2}$) splitting [24]. From Table 2 we have for the X^0 state $D_0 = 77.9$ kcal/mol at the MRCI-DKH+Q/AQ ζ level. Now taking into



Scheme 2.

account and the I $4d^{10}$ core effect, our recommended value is $D_0 = 79.7$ kcal/mol. We believe that our value is more reliable than the $D_e = 83.7$ kcal/mol value reported by Yang et al. [11].

The first excited Λ -S state of BI is of $a^3\Pi$ symmetry. The leading MRCI configuration for this state is $|a^3\Pi\rangle \approx |\sigma^2 2\sigma^2 3\sigma^1 1\pi^4 2\pi^1\rangle$ where for simplicity only valence orbitals are counted. The latter combined with the atomic Mulliken populations:



lead to the vBL diagram of Scheme 2. According to this diagram we have the formation of a single σ bond whereas some weak π -bonding occurs through a B – I electron transfer. The corresponding binding energy was found to be less than half the ground state's binding energy, Tables 1 and 2. It is interesting at this point to notice that the in situ electronic configuration of the B atom corresponds to its first excited 4P state lying ~ 3.55 eV [24] higher than the ground state. The two unpaired electrons of the BI($a^3\Pi$) state can form σ bonds with e.g. two additional I atoms to give planar BI_3 . Moreover, the (quasi) empty p orbital on the boron atom can host an electron pair from an incoming species resulting in a dative bond. The BI($a^3\Pi$) unit with its bonding capabilities is the elementary building block of a great variety of boron halides (e.g. B_9I_9 [22]) as is $\text{BH}(a^3\Pi)$ for the different boron hydrides (e.g. B_4H_4 [23]).

Now considering the spin-orbit coupling, $a^3\Pi$ splits into four Ω states, namely $^3\Pi_0$, $^3\Pi_{0+}$, $^3\Pi_1$, and $^3\Pi_2$, in ascending energy order, dubbed 0^- , $0^+(1)$, $1(1)$, and 2 , see Fig. 1. From Table 2 we observe a very good agreement of our calculated spectroscopic constants with existing experimental data for the states $0^+(1)$ and $1(1)$. As we can see our accuracy is better than Yang et al.'s [11] probably due to our larger basis sets.

Next we studied the $A^1\Pi$ (or $1(\text{II})$) state of BI stemming, also, from the $\text{B}(^2P_{1/2}) + \text{I}(^2P_{3/2})$ asymptote. As shown in Fig. 1 the corresponding potential energy curve possesses a local minimum which is unbound with respect to the asymptotic atomic fragments, Tables 1 and 2. This minimum is the result of an avoided crossing with a curve coming from the $\text{B}(^2D) + \text{I}(^2P)$ excited asymptotic

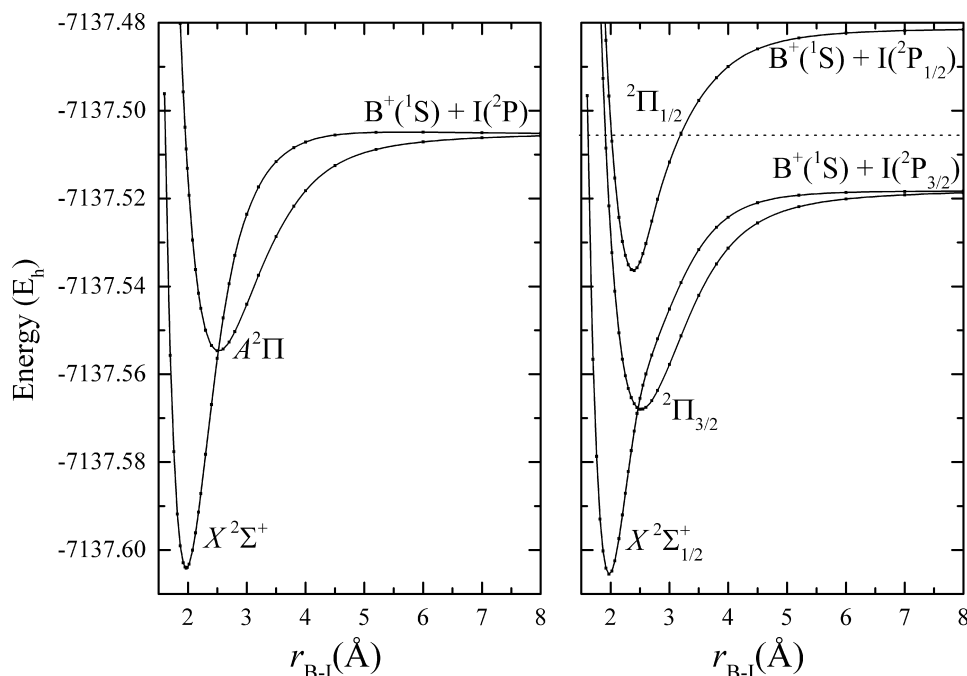
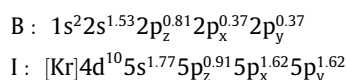


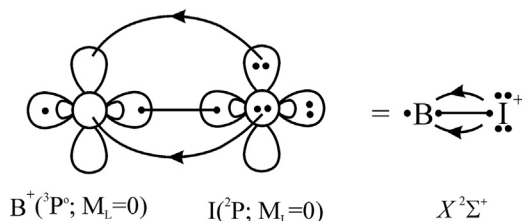
Fig. 2. Potential energy curves of the lowest $X^2\Sigma^+$ and $A^2\Pi$ Λ -S states (left) and of the $X^2\Sigma_{1/2}^+$, $^2\Pi_{3/2}$, and $^2\Pi_{1/2}$ Ω states (right) of the BI^+ cation at the MRCI-DKH+Q/AQ ζ level of theory.

channel as indicated by the in situ electronic configuration of the B atom which can be depicted by the vBL diagram of Scheme 2 but with the two unpaired electrons coupled into an open singlet. The barrier to dissociation was found 4.4 kcal/mol at the MRCI-DKH+Q/AQ ζ level but including spin-orbit effects it was reduced to 0.6 kcal/mol at the same level. The $T_e = 28,624 \text{ cm}^{-1}$ value for this state (Table 2) might correspond to the diffuse transient bands near 349 nm ($=28,653 \text{ cm}^{-1}$) observed by Briggs and Piercy [5].

B. BI $^+$. The ground state of the BI $^+$ cation is of $X^2\Sigma^+$ symmetry, Fig. 2, and correlates adiabatically to the B $^+(^1S) + I(^2P)$ atomic products. The leading MRCI configuration for this state is $|X^2\Sigma^+\rangle \approx |1\sigma^2 2\sigma^2 3\sigma^1 1\pi^4\rangle$, where only valence orbitals are counted. The corresponding atomic Mulliken populations at the MRCI-DKH/AQ ζ level are:



suggesting the vBL diagram of Scheme 3. As we can see there is a covalent σ bond followed by two dative π bonds. The overall bond-



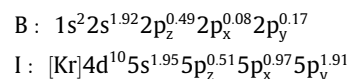
Scheme 3.

ing is of a formal triple character. The B $^+ \leftarrow I$ charge transfer makes the in situ B atom almost neutral. As shown in Scheme 3 the electronic distribution around B $^+$ corresponds to its excited $^3P^o$ state located $37,340 \text{ cm}^{-1}$ ($=106.8 \text{ kcal/mol}$) above the ground B $^+(^1S)$ state [24]. The binding energy $D_0 \approx 61 \text{ kcal/mol}$ (Table 3) is smaller than the D_0 value of the neutral BI species, Table 1. However, the intrinsic, i.e. with respect to B $^+(^3P^o) + I(^2P)$, binding energy is $61 + 106.8 \approx 168 \text{ kcal/mol}$ confirming the triple character of the bond. Considering the spin-orbit coupling we obtain a final value $D_0 = 53.6 \text{ kcal/mol}$ at the MRCI-DKH+Q/AQ ζ level, Table 4. We also notice that the B–I bond length is significantly shorter as compared to the ground state neutral BI system.

From Tables 1–4 our best value for the ionization potential (IP) of BI was found $\text{IP}_0(\text{BI}) = 9.25 \text{ eV}$. Interestingly this number approximately equals the mean value of $\text{IP}(\text{B}) = 8.30 \text{ eV}$ and $\text{IP}(\text{I}) = 10.83 \text{ eV}$ [24].

We move now to the first excited Λ -S state which is of $A^2\Pi$ symmetry. As Fig. 2 shows this term splits into its two, $\Omega = 3/2$ and $\Omega = 1/2$, components by introducing the spin-orbit coupling. The resulting curves correlate to the B $^+(^1S) + I(^2P_{3/2})$ and B $^+(^1S) + I(^2P_{1/2})$ asymptotes, respectively.

According to the Mulliken atomic populations of the $A^2\Pi$ state:



the bonding can be described by the vBL diagram of Scheme 4. This diagram shows a charge transfer from I to B $^+$. The final positive charge distribution is B $^{(+0.33)}I^{(+0.66)}$. The binding energies are much smaller as compared to the ground state (Tables 3 and 4), due to the dative character of the bonding, as well as, to the coulombic repulsion between the positively charged B and I atoms.

Table 3

Energies E (E_h), bond lengths r_e (Å), binding energies D_0 (kcal/mol), harmonic frequencies ω_e (cm^{-1}), anharmonicity constants $\omega_e x_e$ (cm^{-1}), rotation-vibration coupling constants a_e (cm^{-1}), centrifugal distortion constants D_e (cm^{-1}), total Mulliken charges on B q_B (e), and energy gaps T_0 (cm^{-1}) of the $X^2\Sigma^+$ and $A^2\Pi$ electronic states of the BI $^+$ cation.

Method	$-E$	r_e	D_0	ω_e	$\omega_e x_e$	$a_e \times 10^3$	$D_e \times 10^7$	q_B	T_0
$X^2\Sigma^+$									
MRCI/A5 ζ -PP	319.209098	1.972	60.6	781	4.66	3.37	4.97	-0.08	0
MRCI+Q/A5 ζ -PP	319.218331	1.973	60.9	779	4.74	3.38	4.99		0
MRCI-DKH/AQ ζ	7137.595157	1.970	60.6	780	4.58	3.41	4.83	-0.08	0
MRCI-DKH+Q/AQ ζ	7137.604248	1.972	60.9	776	4.40	3.08	5.21		0
C-MRCI-DKH/AQ ζ	7138.051383	1.961	60.4	808				-0.08	0
C-MRCI-DKH+Q/AQ ζ	7138.102137	1.961	61.5	804					0
$A^2\Pi$									
MRCI/A5 ζ -PP	319.159321	2.515	30.6	336	2.02	1.91	6.55	+0.31	10,727
MRCI+Q/A5 ζ -PP	319.169567	2.522	30.5	332	2.08	2.16	6.81		10,485
MRCI-DKH/AQ ζ	7137.545266	2.513	30.6	337	2.25	1.85	7.88	+0.34	10,728
MRCI-DKH+Q/AQ ζ	7137.555411	2.520	30.5	333	2.29	2.15	5.80		10,484
C-MRCI-DKH/AQ ζ	7137.998118	2.493	27.7	333				+0.33	11,453
C-MRCI-DKH+Q/AQ ζ	7138.050205	2.501	29.6	334					11,130

Table 4

Energies E (E_h), bond lengths r_e (Å), binding energies D_e and D_0 (kcal/mol), harmonic frequencies ω_e (cm^{-1}), anharmonicity constants $\omega_e x_e$ (cm^{-1}), vibration-rotation coupling constants a_e (cm^{-1}), centrifugal distortion constants D_e (cm^{-1}), and energy gaps T_e (cm^{-1}) of the three lowest electronic Ω states of the BI $^+$ cation.

Method	$-(E+7137)$	r_e	D_e	D_0	ω_e	$\omega_e x_e$	$a_e \times 10^3$	$D_e \times 10^7$	T_e
$X^2\Sigma_{1/2}^+$									
MRCI-DKH/AQ ζ	0.594451	1.977	53.8	52.8	760	5.70	3.38	5.20	0
MRCI-DKH+Q/AQ ζ	0.604918	1.975	54.7	53.6	765	5.89	3.07	5.28	0
$^2\Pi_{3/2}$									
MRCI-DKH/AQ ζ	0.557746	2.516	30.8	30.3	334	2.25	1.85	7.88	7946
MRCI-DKH+Q/AQ ζ	0.568410	2.489	31.4	30.8	335	2.20	2.45	6.79	8013
$^2\Pi_{1/2}$									
MRCI-DKH/AQ ζ	0.526289	2.385	34.1	33.4	499	4.00	0.70	3.87	14,960
MRCI-DKH+Q/AQ ζ	0.536450	2.397	34.6	33.9	500	3.70	0.60	4.00	15,027

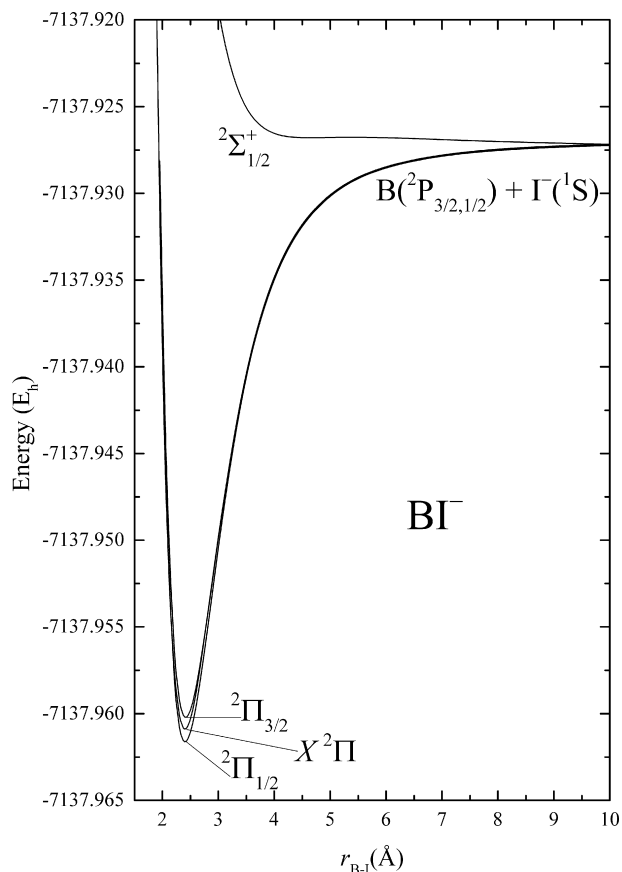
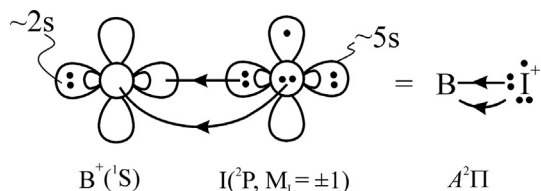


Fig. 3. Potential energy curves of the lowest $X^2\Pi$ Λ -S state and of the $X^2\Pi_{1/2}$, and $^2\Pi_{3/2}$ Ω states of the BI^- anion as obtained at the MRCI-DKH+Q/AQ ζ level of theory. The repulsive $^2\Sigma^+_{1/2}$ state is shown as well.

The above mentioned Mulliken populations show that the single electron is located on the iodine atom. This fact explains why the $\Delta E(^2\Pi_{3/2}-^2\Pi_{1/2}) = 7014 \text{ cm}^{-1}$ energy separation (Table 4) is close to the $I(^2P_{3/2}-^2P_{1/2})$ spin-orbit splitting of 7603 cm^{-1} [24]. Both, $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$, states are accessible from the ground $X^2\Sigma^+_{1/2}$ state according to $\Delta\Omega = 0, \pm 1$.

C. BI^- . We have only studied the ground $X^2\Pi$ state of the BI^- anion. Our main goals were to accurately determine the electron affinity (EA) of the BI molecule as well as to elucidate the electronic structure of the anion. Fig. 3 shows the corresponding Λ -S and Ω PEC's while Table 5 lists our numerical results. A first glance at Tables 2 and 5 reveals that the anion is stable but we will discuss later in this paragraph the electron affinity issue. The leading MRCI configuration for the $X^2\Pi$ state is $|X^2\Pi\rangle \approx |1\sigma^2 2\sigma^2 3\sigma 21\pi^4 2\pi^1\rangle$ with the corresponding atomic Mulliken populations:

$$\text{B} : 1s^2 2s^{1.99} 2p_z^{0.53} 2p_x^{1.02} 2p_y^{0.19}$$

$$\text{I} : [\text{Kr}]4d^{10} 5s^{1.98} 5p_z^{1.43} 5p_x^{1.94} 5p_y^{1.92}.$$

The boron atom bears a total Mulliken charge -0.73 . The additional electron of the system is placed in a π orbital mainly localized on B. On the other hand, the $\text{BI}^- (^2\Pi)$ system upon dissociation ends up to the $\text{B}(^2P) + \text{I}^- (^1S)$ asymptotic channel (Fig. 3) because $\text{EA}(\text{I}) > \text{EA}(\text{B})$. We attempt to illustrate the situation with the vbl diagram of Scheme 5. As it is shown in this diagram the bonding occurs through an electron transfer from I to B mostly in the σ frame and to a lesser extent in the π frame. The π orbital hosting the unpaired electron is localized on the B atom and acquires a diffuse character. The resulting binding energy is very low, $D_0 = 20\text{--}21 \text{ kcal/mol}$ (Table 5) and the bond is much

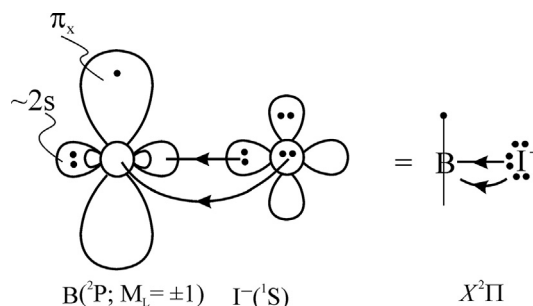


Table 5
(a) Energies E (E_h), bond lengths r_e (\AA), binding energies D_0 (kcal/mol), harmonic frequencies ω_e (cm^{-1}), anharmonicity constants $\omega_e x_e$ (cm^{-1}), rotation-vibration coupling constants a_e (cm^{-1}), centrifugal distortion constants \bar{D}_e (cm^{-1}), and total Mulliken charges on B q_B (e) of the ground $X^2\Pi$ electronic state of the BI^- anion.

Method	$-E$	r_e	D_0	ω_e	$\omega_e x_e$	$a_e \times 10^3$	$\bar{D}_e \times 10^7$	q_B
MRCI/A5 ζ -PP	319.554088	2.409	19.5	314	5.49	3.11	9.13	-0.73
MRCI+Q/A5 ζ -PP	319.576059	2.405	20.6	316	3.88	3.81	8.57	
MRCI-DKH/AQ ζ	7137.937802	2.437	18.5	314	3.42	3.10	9.11	-0.67
MRCI-DKH+Q/AQ ζ	7137.960893	2.409	20.7	314	3.80	3.72	9.21	
C-MRCI-DKH/AQ ζ	7138.380980	2.393	17.8	315				-0.69
C-MRCI-DKH+Q/AQ ζ	7138.450547	2.388	20.0	313				

(b) Energies E (E_h), bond lengths r_e (\AA), binding energies D_0 (kcal/mol), harmonic frequencies ω_e (cm^{-1}), anharmonicity constants $\omega_e x_e$ (cm^{-1}), rotation-vibration coupling constants a_e (cm^{-1}), centrifugal distortion constants \bar{D}_e (cm^{-1}), and energy gaps T_e (cm^{-1}) of the two lowest Ω states ($^2\Pi_{1/2}$ and $^2\Pi_{3/2}$) of the BI^- anion.

Method	$-(E+7137)$	r_e	D_0	ω_e	$\omega_e x_e$	$a_e \times 10^3$	$\bar{D}_e \times 10^7$	T_e
$^2\Pi_{1/2}$								
MRCI-DKH/AQ ζ	0.938506	2.431	19.0	319	3.19	4.16	9.10	0
MRCI-DKH+Q/AQ ζ	0.961622	2.403	21.1	319	3.88	3.64	9.82	0
$^2\Pi_{3/2}$								
MRCI-DKH/AQ ζ	0.937145	2.443	18.2	310	3.61	4.09	9.21	299
MRCI-DKH+Q/AQ ζ	0.960212	2.415	20.3	312	4.69	4.41	9.58	309

longer than in neutral BI. The same stands for the ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ components which are very similar, Table 5. The spin-orbit coupling is very weak since the unpaired electron is mainly influenced by the B atom and ${}^2\Pi_{1/2}$ is the ground state (regular states) just as ${}^2P_{1/2}$ is in the case of the free B moiety [24]. A repulsive ${}^2\Sigma_{1/2}^+$ state which correlates to $B({}^2P_{3/2}) + I(^1S)$ is also shown in Fig. 3.

We turn now to the electron affinity discussion. In a previous paper [25] we have shown that the BF and BCl species have negative EA's of -0.8 and -0.3 eV, respectively, which means that BF^- and BCl^- are "temporary negative ions" or "resonances" [26]. On the other hand Peterson et al. [27] calculated a positive EA = $+0.20$ eV for the BBr diatomic. To our knowledge there is no experimental or theoretical number for BI. From Tables 1, 2, and 5 we find $EA_0(BI) = 0.50$ eV at the MRCI-DKH+Q/AQ ζ level and $EA_0(BI) = 0.52$ eV at the MRCI-DKH+Q/A5 ζ -PP level of theory. Including spin-orbit effects we find $EA_0 = 0.48$ eV with the MRCI-DKH+Q/AQ ζ methodology. Assuming that this value will increase with the A5 ζ -PP basis as before spin-orbit, our final recommended number is $EA_0 = 0.50 \pm 0.02$ eV. This result confirms the tendency for the electron affinity of boron monohalides to increase monotonically as $BF(-0.80) \rightarrow BCl(-0.30) \rightarrow BBr(+0.20) \rightarrow BI(+0.50)$ (all numbers in eV).

4. Summary and conclusions

The MRCI methodology in conjunction with large basis sets was used in order to study boron moniodide BI and its ions BI^\pm . Our calculations were completed by taking into account scalar relativistic effects and spin-orbit coupling. Below are briefly quoted our principal findings.

- (i) The ground state of BI is of $X^1\Sigma^+$ symmetry with a binding energy $D_0 = 79.7$ kcal/mol with respect to $B({}^2P_{1/2}) + I({}^2P_{3/2})$. Its dipole moment was calculated for the first time, $\mu = 1.18$ D, and it was clarified that the polarity of the molecule is $(^-)BI(^+)$. Its first excited state $a^3\Pi_0^-$ lies 2.0 eV higher and has a significantly lower binding energy, $D_0 = 31$ kcal/mol. It was stressed that this state is responsible for the great complexity of the different boron halides. For all Λ -S and Ω states studied, full potential energy curves have been constructed and spectroscopic constants T_e , ω_e , $\omega_e x_e$, a_e , and \bar{D}_e were extracted in very good agreement with existing experimental data.
- (ii) The lowest electronic states, $X^2\Sigma^+$ and $A^2\Pi_{3/2,1/2}$ of the BI^+ cation have been studied for the first time. The ground $X^2\Sigma^+$ is triply bonded with a much shorter bond, as compared to the neutral BI species, and a binding energy of 54 kcal/mol with respect to the adiabatic $B^+(^1S) + I({}^2P_{3/2})$ fragments.
- The ionization potential of BI has been calculated $IP_0(BI) = 9.25$ eV.
- (iii) The BI^- ($X^2\Pi$) anion has been found to be stable yielding a BI electron affinity $EA_0(BI) = 0.50 \pm 0.02$ eV. The unpaired electron finds itself in a diffuse π orbital localized on the B moiety. The anion has a very low binding energy, $D_0 = 21$ kcal/mol, and a significantly longer bond as compared to the neutral BI species.

It has been established that the electron affinity of boron monohalides increases monotonically going down from BF to BI.

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