Chemical Physics Letters 692 (2018) 367–373

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

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-CISD
Binding energy
Electron affinity
Ionization potential

ABSTRACT

The lowest electronic states of boron monoiodide, BI, and its ions $BI^{\pm}$ 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.

1. Introduction

Boron forms a large variety of binary halides with different coordination numbers. The most stable of them are boron trihalides, BX_3 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 $X^1\Sigma^+$ ground state, they also possess a relatively low-lying $a^3\Pi$ 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 BI_3 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 $a^3\Pi \rightarrow X^1\Sigma^+$ band system of the molecule. In 1985 Coxon and Naxakis [7] recorded the $a^3\Pi\ (0^+,1) \rightarrow X^1\Sigma^+$ bands of BI excited by the reaction of discharged helium with BI_3. In this work they reported spectroscopic constants (T_e, ω_e, and $\omega_e x_e$) 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 $\bar{D}_e$ spectroscopic constants of the $a^3\Pi\ (0^+,1)$ and $X^1\Sigma^+$ states. Finally, in 1990, Lebreton at 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 $a^3\Pi$ 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 $\omega_e x_e$ 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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https://doi.org/10.1016/j.cplett.2017.12.036
0009-2614/

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) → [7s6p5d4f3g2h]

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

and also

aug-cc-pV5Z-PP [14] contracted as (17s14p14d4f3g2h) → [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(aug-cc-pV5Z) + I(aug-cc-pwCVQZ) ≡ AQζ and
B(aug-cc-pV5Z) + I(aug-cc-pV5Z-PP) ≡ A5ζ-PP

Our computational approach was based on the multireference configuration interaction method CASSCF + single + double replacements ≡ MRCI. 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 MRCI 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-MRCI), the $\sim 1.1 \times 10^{10}$ CF's C-MRCI 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, MRCI+Q and C-MRCI+Q.

Scalar relativistic effects were introduced at the MRCI/AQζ and C-MRCI/AQζ levels by using the one electron Douglas-Kroll-Hess Hamiltonian [17–19] of third order, MRCI-DKH and C-MRCI-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(^{2}P) + I(^{2}P) asymptote at the MRCI-DKH(+Q)/AQζ level. For the BI^+ and BI^- ions we used the two state space ($^2\Sigma^+$ and $^2\Pi$) stemming from the BI^+(^{1}S) + I(^{2}P) and B(^{2}P) + I^- (^{1}S), 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(^{2}P) + I(^{2}P), 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_o (cm^{-1}) of the $X\ ^1\Sigma^+$, $a\ ^3\Pi$, and $A\ ^1\Pi$ electronic states of BI.

Method	$-E$	r_e	D_o	ω_e	$\omega_e x_e$	$a_e \times 10^3$	$\bar{D}_e \times 10^7$	q_B	μ	T_o
$X\ ^1\Sigma^+$										
MRCI/A5ζ-PP	319.544004	2.145	83.9	575.4	2.758	2.778	5.37	−0.42	1.17	0.00
MRCI+Q/A5ζ-PP	319.557712	2.148	83.9	571.0	2.683	2.783	5.98	–	1.17	0.00
MRCI-DKH/AQζ	7137.929472	2.143	83.6	575.5	2.287	2.759	6.70	−0.35	1.18	0.00
MRCI-DKH+Q/AQζ	7137.942977	2.146	83.4	571.4	2.723	2.720	5.80	–	1.18	0.00
C-MRCI-DKH/AQζ	7138.380897	2.128	85.0	586.7	2.800	2.740	5.71	−0.35	1.17	0.00
C-MRCI-DKH+Q/AQζ	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]					
$a\ ^3\Pi$										
MRCI/A5ζ-PP	319.468869	2.074	37.8	647.5	4.90	3.67	5.97	−0.48	0.44	16,534
MRCI+Q/A5ζ-PP	319.482380	2.074	37.5	642.8	4.69	3.36	5.72		0.48	16,534
MRCI-DKH/AQζ	7137.854530	2.072	36.7	646.9	4.9	3.68	6.05	−0.47	0.46	16,454
MRCI-DKH+Q/AQζ	7137.868069	2.072	36.4	642.8	4.61	3.16	5.63		0.50	16,534
C-MRCI-DKH/AQζ	7138.305239	2.061	37.9	657.2	4.35	3.28	5.62	−0.46	0.39	16,615
C-MRCI-DKH+Q/AQζ	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]
$A\ ^1\Pi$										
MRCI/A5ζ-PP	319.408363	2.127	−0.9	452.2	23.14	3.38	14.80	−0.56	1.25	29,681
MRCI+Q/A5ζ-PP	319.425013	2.119	+0.8	461.0	17.62	6.34	12.27		1.27	29,036
MRCI-DKH/AQζ	7137.794102	2.126	−1.0	450.9	22.69	3.52	14.86	−0.52	1.26	29,601
MRCI-DKH+Q/AQζ	7137.810558	2.117	+0.6	459.5	17.48	6.41	12.46		1.30	29,036
C-MRCI-DKH/AQζ	7138.240945	2.120	−2.2	423.6				−0.51	1.22	30,649
C-MRCI-DKH+Q/AQζ	7138.302705	2.106	−0.1	424.7					1.24	29,843

[a] Ref. [8].
[b] Ref. [9].
[c] Ref. [7].