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Ab Initio Studies of Radicals HBX (X=H, F, Cl, Br): Molecular Structure, Vibrational Frequencies and Potential Energy *

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We describe high-level ab initio calculations on the BH_2, HBF, HBCl and HBBr radicals. Molecular structure, vibrational frequencies and potential energy curves of the ground state and the first excited state, which are two Renner–Teller components for a $^2\Pi$ state at linearity, are studied using the basis sets aug-cc-pVTZ and icMRCI+Q technique. On the basis of the potential energy curves, a reliable potential energy barrier to dissociation HB+X (X=F, Cl, Br) fragments and to linearity are given. The ab initio results will add some understanding on the spectrum and the photo-dissociation dynamics of the series of radicals.

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Boron-containing free radicals are reactive molecular species playing key roles in a wide variety of applications, such as doping of semiconductors, plasma etching and reactive ion etching of circuit elements, the production of boron-containing films, and the incorporation of boron in steel. In 2005, He *et al.*[1] reported the discovery of a series of boron-containing radicals HBX (X=F, Cl, Br). Since then, researchers[2–6] have performed a series of experiments and MO theory on the spectrum of the series radicals, suggesting that the ground state of the radicals is a bending state while the first excited state is a linearity state and they are the two Renner–Teller components of the $^2\Pi$ state at linear geometry. Due to the nature of the electronic states, the laser-induced fluorescences of those series of radicals are very complicated and the assignments of the excited state vibrational levels are very challenging.

However, the analysis of elaborate spectrum needs detailed information of potential energy curves. With the aim of facilitating the assignment of the spectrum data, in this Letter we present quantitative quantum chemical calculations at a quantitatively accurate level on the spectrum parameters and potential energy curves of the series of boron-containing free radicals BH_2, HBF, HBCl and HBBr radicals. Equilibrium geometries, vibrational frequencies and excitation energies of the $\tilde{X}$ and $\tilde{A}$ states are obtained. The results are compared with the previous experimental data available. The potential energy curves (PECs) of these two states along the bond lengths and bond angles are also calculated. The theoretical results will add some understanding on the spectrum of the series radicals.

We perform the ab initio calculations on electronic states of the radicals BH_2, HBF, HBCl and HBBr using the Molpro 2012 program[7] and using the internally contracted multi reference configuration interaction (icMRCI)[8,9] method based on a full valence complete active space SCF (CASSCF)[10,11] wave function as reference with 11 active electrons in 12 active orbitals. The energetic effect of higher excitations is estimated using Davidson's formula.[12] The standard uncontracted all-electron correlation-consistent basis set of triple zeta quality with polarization functions aug-cc-pVTZ[13,14] (the Cl with aug-cc-pV(T+d)Z[15]) is used. The active space consists of 11 valence electrons and 9 valence orbitals (11e, 9o) corresponding to $n = 2$ atomic orbitals of B atoms and outer valence orbitals of an X atom.

The PECs of ground and first excited states of the radicals computed at icMRCI+Q/aug-cc-pVTZ level are given as functions of the bond angles and bond lengths, respectively, keeping the other two parameters fixed at their ground state with equilibrium values. The calculations are carried out in the C_{2v} point group, when the potential energy cuts change along the H–B–H bond angle, and in the C_s point group when the potential energy cuts change along the B–X bond length.

Except for BH_2, which has a C_{2v} symmetry, the other HBX radicals are in a lower C_s point group. The ground states of all HBX radicals are doublet ($^2A_1$ for BH_2, $^2A'$ for HBX). The first doublet excited states are $^2B_1$ for BH_2, $^2A''$ for HBX. The equilibrium bond lengths, bond angles, vibrational frequencies, transition energies of the $\tilde{X}$ and $\tilde{A}$ states of radicals computed at the icMRCI/aug-cc-pVTZ level are presented in Table 1, together with the experimental and theoretical results previously reported.

The calculated B–X bond lengths of the $\tilde{X}$ ($^2A'$) state for different boron-containing free radicals rang-

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ing from 1.189 Å to 1.880 Å from BH_2 to HBBr increase in going from hydrogen to bromine. With the hydrogen atom's low steric requirements, there is slight difference among the B–H bond lengths of the series radicals. The $\tilde{X}$ states are nonlinear structures with the bond angles from 128.9° of the BH_2 radical to 121.0° of the HBF radical, consistent with the experimental prediction of the group of Clouthier in 2005.[1] As seen from Table 1, the bond angle becomes smaller with the increasing electronegativity of the substituent atom and the trend in bond angles is consistent with Bent's rule, which predicts that the p character of bonding orbitals increases with the substituent electronegativity.

Table 1. Equilibrium geometries of electronic states of HBX radicals. The excited state imaginary bending frequencies are discarded.

	BH_2			HBF			HBCl			HBBr		
	Our	Exp.	Theory	Our	Exp.	Theory	Our	Exp.	Theory	Our	Exp.	Theory
						$\tilde{X}$ state						
R_{B-H} (Å)	1.189	1.197[a]	1.184[a]	1.199	1.214[b]	1.203[c]	1.190		1.191[d]	1.189		1.186[e]
R_{B-X} (Å)	1.189	1.197[a]	1.184[a]	1.303	1.303[b]	1.309[c]	1.720		1.724[d]	1.880		1.863[e]
∠H–B–X (deg)	128.9	129.6[a]	129.1[a]	121.0	120.7[b]	121.1[c]	123.6		123.3[d]	123.7		123.5[e]
ω_1	2506.7		2508.1[a]	1012.1	1002.8[b]	1008.0[c]	844.6	836[b]	842[d]	719.3		725[e]
ω_2	974.6		972.9[a]	1325.6	1319.4[b]	1320.1[c]	914.1	894[b]	909[d]	834.7	834[b]	845[e]
ω_3	2657.3		2658.4[a]	2557.4	2432.8[b]	2541.0[c]	2649.5		2641[d]	2654.3		2656[e]
						$\tilde{A}$ state						
R_{B-H} (Å)	1.170		1.167[a]	1.164		1.167[c]	1.166		1.167[d]	1.168		1.166[e]
R_{B-X} (Å)	1.170		1.167[a]	1.307		1.307[c]	1.680		1.690[d]	1.835		1.824[e]
∠H–B–X (deg)	180.0		180.0[a]	180.0		180.0[c]	180.0		180.0[d]	180.0		180.0[e]
ω_1	2590.3		2592.1[a]	1306.3		1313.1[c]	928.5		926[d]	790.0		791[e]
ω_2	951.2		953.0[a]	699.5		702.4[c]	682.7		682[d]	674.3		674[e]
ω_3	2825.2		2829.0[a]	2890.9		2890.6[c]	2859.5		2861[d]	2843.0		2845[e]
T_e (cm^{-1})	2790.08		2743[e]	10433.9		10084[e]	6143.21		6073[e]	5549.99		5607[e]

[a]Ref. [6], [b]Ref. [3], [c]Ref. [2], [d]Ref. [4], and [e]Ref. [5]

The $\tilde{A}$ states produced by promotion of an electron from the HOMO (an in-plane antibonding π orbital) to the LUMO which is an out-of-plane $2p_z$ nonbonding orbital localized on the boron atom from the ground state have a linear geometry with the bond angle at 180° for all the HBX radicals. Compared with the bond lengths of the ground state, there is slight decrease of the B–H and B–X bond lengths of the excited states. The B–X bond lengths also show the same trend of increase from hydrogen to bromine.

For comparison, the adopted experimental and latest theoretical geometric values are also listed in Table 1. However, as the weakness of laser-induced fluorescence (LIF) signals of the HBCl[4] and HBBr[5] radicals precludes the acquisition of high resolution, rotationally resolved spectra from which molecular structure may be derived, there are only the experimental molecular structures of the ground states of HBF[3] and BH_2[6] radicals. Our calculations are in good agreement with the experimental results: for BH_2 radical, only 0.008 Å (the B–H bond length) and 0.7° (the H–B–F bond angle) differ from the experimental result; for HBF radical, only 0.005 Å (the B–H bond length) and 0.3° (the H–B–F bond angle) differ from the experimental result. Our icMRCI results have also been compared with the latest theoretical results,[2–5,16] and they are in good agreement with each other.

The ab initio calculated frequencies ω_1, ω_2 and ω_3 in Table 1 refer to the frequencies of low-frequency (B–X, X=H, F, Cl, Br) stretch modes, bending modes, and high-frequency (B–H) stretch modes of the HBX radicals, respectively. Compared with the available experimental results, the ab initio calculated frequencies are slightly larger than the experimental data as the anharmonic effect is included in the measured values. The ab initio calculated frequencies are also compared with the previous theoretical results[1–6] and are in good agreement with them. From Table 1, we can see obvious increments in the frequencies of the stretching vibrations between the ground states and the excited states.

The adiabatic transition excitation energies for $\tilde{X} \rightarrow \tilde{A}$ have been obtained for the series radicals, as listed in Table 1. The transition excitation energies show the tendency, that is, T_e(HBF) > T_e(HBCl) > T_e(HBBr) > T_e(BH_2) as the electronegativity of substituted atoms H<Br<Cl<F.

Additional MRCI calculations are performed on the BH_2 radical using aug-cc-pVNZ (N= T, Q and 5) basis sets to show the effects of basis sets on the calculated geometries and frequencies. The results are listed in Table 2. The calculated bond lengths of both the ground state and the excited state decrease while the bond angle of the ground state increases as the basis sets change from aug-cc-pVTZ to aug-cc-pV5Z. In Table 2, the convergence behavior for the geometrical parameters can be found as the basis sets increase. Generally, the deviation between aug-cc-pVQZ and aug-cc-pV5Z basis sets is obviously less than that between aug-cc-pVTZ and aug-cc-pVQZ. The less deviation indicates that the accuracy is systemically improved by using the larger basis set. However, the deviation between aug-cc-pVTZ and aug-cc-pV5Z is only 0.0021 Å, and it seems that the aug-cc-pVTZ basis set is enough to accurately determine the geometrical parameters of BH_2 radical. The three harmonic vibrational frequencies of the two states change

slightly from aug-cc-pVTZ to aug-cc-pV5Z, and the largest change observed is ω_1 of the ground state, of which the frequency increases 43 cm^{-1} (only 1.7% of the ω_1). For the frequencies, the results also show that the deviation between aug-cc-pVQZ and aug-cc-pV5Z is less than that between cc-pVTZ and cc-pVQZ, indicating that the accuracy is systemically improved using a larger basis set.

Table 2. Equilibrium geometries and frequencies of electronic states of BH_2 radical calculated at the icMRCI+Q/aug-cc-pVNZ level (N=T, Q and 5).

	icMRCI+Q/aug-cc-pVTZ	icMRCI+Q/aug-cc-pVQZ	icMRCI+Q/aug-cc-pV5Z
		$\tilde{X}$ state	
R_{B-H} (Å)	1.1897	1.1882	1.1876
∠H–B–H (deg)	128.925	128.948	128.953
ω_1	2506.7	2532.2	2549.6
ω_2	974.6	972.3	971.6
ω_3	2567.3	2584.3	2593.9
		$\tilde{A}$ state	
R_{B-H} (Å)	1.1722	1.1708	1.1701
∠H–B–H (deg)	180.0	180.0	180.0
ω_1	2590.3	2596.4	2600.2
ω_2	951.2	949.3	950.2
ω_3	2825.2	2829.6	2830.2

Table 3. VTE and electron configuration of electronic states of HBX radicals (X=H, F, Cl, Br).

	Radicals	VTE (eV)	Configuration
$\tilde{X}$ state	BH_2	0	$(2-3a')^2(4a')^1$
	HBF	0	$(3-5a')^2(1a'')^2(6a')^2(7a')^1$
	HBCl	0	$(6-8a')^2(2a'')^2(9a')^2(10a')^1$
	HBBr	0	$(12-14a')^2(5a'')^2(15a')^2(16a')^1$
$\tilde{A}$ state	BH_2	1.172	$(2-3a')^2(1a'')^1$
	HBF	2.290	$(3-5a')^2(1a'')^2(6a')^2(7a')^0(2a'')^1$
	HBCl	1.712	$(6-8a')^2(2a'')^2(9a')^2(10a')^0(3a'')^1$
	HBBr	1.592	$(12-14a')^2(5a'')^2(15a')^2(16a')^0(6a'')^1$

To our knowledge, the electronic spectrum of the HBX radicals has been investigated in recent years.[1–6] LIF and single vibrational level emission spectra have been recorded to map out the ground state and excited state vibrational energy levels. However, the reliable assignment of the spectrum needs accurate information of potential energy curves. The potential energy curves of the $\tilde{X}$ state and the $\tilde{A}$ state of the series radicals HBX (X=H, F, Cl, Br) along the bond angles and bond lengths calculated at the icMRCI/aug-cc-pVTZ are displayed in Figs. 1–3. The calculations of the potential energy curves are carried out in the C_s point group, except for the potential energy curve along the H–B–H angles of the states of BH_2 radical, which are calculated in the C_{2v} point group. The configuration and vertical transition energies of the electronic state are calculated and the results are listed in Table 3.

As we can see from Table 3, the electronic configuration of the ground state of the series radicals is $(a'')^2(a')^2(a')^1(a'')^0$ in the simplest approximation, where $(a')^1$ (HOMO) and $(a'')^0$ (LUMO) are the in-plane and out-of-plane BX π antibonding orbitals. One electron is promoted from the HOMO to the LUMO (which is predominantly an out-of-plane $2p_z$ boron orbital) yielding a $(a'')^2(a')^2(a')^0(a'')^1$ excited state configuration symbolized as $\tilde{A}^2A''\Pi$, which should have a linear geometry according to the Walsh diagrams. The VTEs calculated at the ground states equilibrium conformation of the excited states are also listed in Table 3.

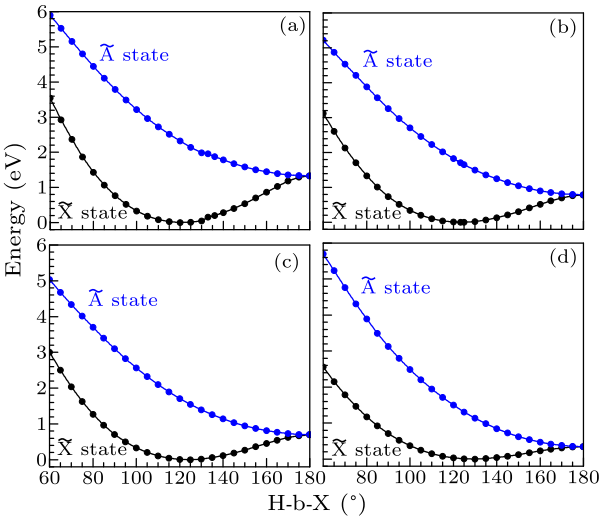

Fig. 1. Potential energy curves of the lowest two states along the H–B–X bond angle of the serious radicals HBF (a), HBCl (b), HBBr (c) and BH_2 (d).

Potential energy curves as a function of the bond angle illustrating the nature of the electronic states are shown in Fig. 1. In the calculation, the other two geometry parameters B–H bond lengths and B–X bond lengths are fixed at their respective values of the $\tilde{X}$ states. As shown in Fig. 1, the ground states of the series of radicals are all bending states. From the potential energy curves, the barriers to the linearity

decrease as the electronegativity of the substituent X increases, and are calculated to be 2776.3 cm^{-1}, 10732.9 cm^{-1}, 6299.66 cm^{-1} and 5567.76 cm^{-1}, including the zero point energy, for BH_2, HBF, HBCl and HBBr radicals, which are consistent with the calculated values from the report of Gharaibeh *et al.*[5] in 2016. As presented in Table 3, the $\tilde{A}$ states of the HBX radicals are conformed by promoting an electron from the HOMO orbitals to the LUMO from the ground state. As we can see, the $\tilde{A}$ states of the radicals are all linear states, having the energy minima at 180° in agreement with the prediction in Clouthier's report. The $\tilde{A}$ states and the $\tilde{X}$ states degenerate the state $^2\Pi$ at the linear geometry as shown in Fig. 1. The linear geometry of the $\tilde{A}$ state would lead to the complexity of the LIF spectra.

The potential energy curves along the B–H bond length are displayed in Fig. 2. From Fig. 2, we can see that the $\tilde{X}$ and $\tilde{A}$ states are all bound states and obviously there is no evidence of dissociation barriers on the ground states and the excited states. Along the change of the electronegativity of the substituent X, the depths of the potential well of the ground states and the excited states becomes larger. The dissociation energies of the $\tilde{X}$ states along the B–H bond are calculated to be at 17502.6 cm^{-1}, 22664.7 cm^{-1}, 23140.6 cm^{-1} and 29117.3 cm^{-1} for HBF, HBCl, HBBr and BH_2 radicals. In Ref. [3], the LIF spectra of the HBF radical have been scanned. The fluorescence decays fastest in the high-energy region and terminates above 15900 cm^{-1}. They suggest that the fluorescences are broken off, which may be a pre-dissociation of an excited state into $H(^2S)+BF(^1\Sigma^+)$ product on the ground state potential energy surface. However, in our calculation, the ground state is not a predissociation state. We have also examined the higher excited states of the HBF radical including $2^2A'$, $3^2A'$, $2^2A''$ and $3^2A''$ states and there is no avoided crossing between the ground state and the higher excited states, which may yield the dissociation barrier on the potential curve of the ground state. Further insights into experimental and theoretical studies are necessary to retrieve the dissociation dynamics of HBF radical.

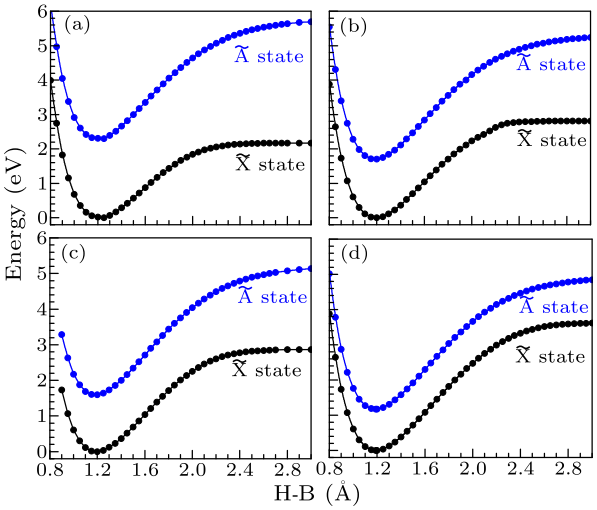

Fig. 2. Potential energy curves of the lowest two states along the H–B bond length of the serious radicals HBF (a), HBCl (b), HBBr (c) and BH_2 (d).

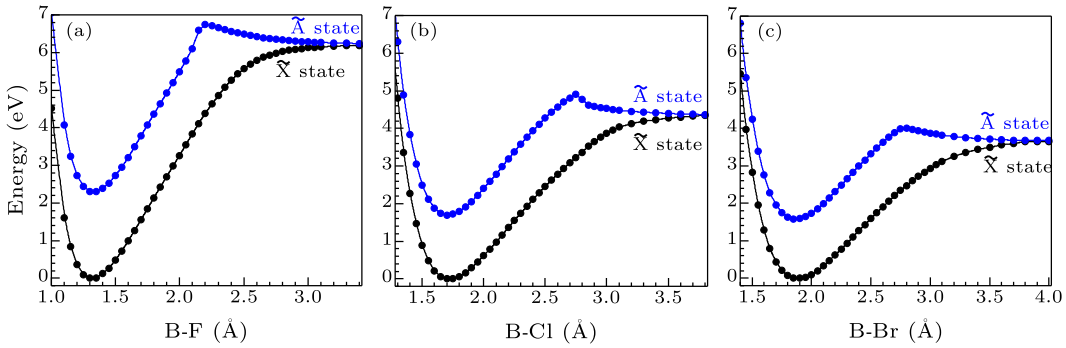

Fig. 3. Potential energy curves of the lowest two states along the B–X bond length of the serious radicals HBF (a), HBCl (b) and HBBr (c).

Figure 3 display the potential energy curves of the $\tilde{X}$ and $\tilde{A}$ states of the series radicals along B–X bond length. In the present calculation, the B–H bond length and the H–B–X bond angle are fixed at their respective values of the $\tilde{X}$ states. As shown in Fig. 3, the $\tilde{X}$ states of the series radicals are all bound states with the depth of the potential well going smaller from HBF to HBBr, which is different from the PECs along the B–H bond length. The dissociation energies of the $\tilde{X}$ states including the zero point energies are given as 50007.5 cm^{-1}, 34682.6 cm^{-1} and 28230.1 cm^{-1} for HBF, HBCl, and HBBr, respectively. Different from the PECs along the B–H bond length, the $\tilde{A}$ states along the B–X bond lengths of the series radicals are pre-dissociation states with a dissociation barrier in the PECs. We have examined the higher excited states of the HBBr and HBF radicals, and the dissociation barriers of the $\tilde{A}$ states could arise from the avoided crossing between the $\tilde{A}$ state and the $2^2A''$ state. On the basis of the PECs, the reliable barrier values are obtained as 36566.8 cm^{-1} in HBF, 25391.1 cm^{-1} in HBCl, and 20477.9 cm^{-1} in HBBr.

In summary, high-level ab initio calculations on the electronic states of a series of radicals BH_2, HBF,

HBCl and HBBr have been performed using the icMRCI technique with the aug-cc-pVTZ basis set. The molecular structures, vibrational frequencies and transition energies of the $\tilde{A}$ state and the $\tilde{X}$ state are carefully calculated at the icMRCI/aug-cc-pVTZ level. The ab initio results are compared with the available experimental values and the results are in good agreement with them. The PECs of the $\tilde{X}$ state and the $\tilde{A}$ state along the bond lengths and the bond angles are given at the icMRCI/aug-cc-pVTZ level. The barriers to dissociation and linearity are also obtained on the basis of PECs. Our ab initio calculations will shed more light on the spectrum of the radicals.

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