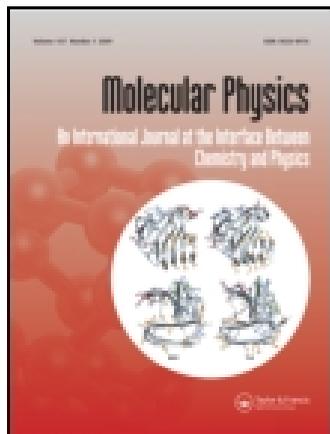


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## RESEARCH ARTICLE

### MRSDCI study on potential energy curves and ro-vibrational spectra of the BBr molecule

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Four low-lying electronic states of the BBr molecule, including  $\Sigma^+$  symmetry and  $\Pi$  symmetry with singlet and triplet spin multiplicities, have been studied using the complete active space self-consistent-field method followed by multi-reference single and double excitation configuration interaction calculation. For the ground state, four isotopes ( $^{11}\text{B}^{79}\text{Br}$ ,  $^{11}\text{B}^{81}$ ,  $^{10}\text{B}^{79}\text{Br}$ ,  $^{10}\text{B}^{81}\text{Br}$ ) of the BBr molecule have been studied, since their experimental spectroscopic constants and ro-vibrational energy levels are abundant. For the three excited states, just the most natural abundance isotope –  $^{11}\text{B}^{79}\text{Br}$  – is investigated. The spin-orbital coupling effect for the  $a^3\Pi$  state is also considered. Finally, the analytical potential energy functions of these states are fitted except for the  $^3\Sigma^+$  state because its potential well is too shallow to be fitted with available functions. These results have been compared in detail with those of the investigations reported in the literature.

**Keywords:** multi-reference configuration interaction; potential energy curve; analytical potential energy function; spectroscopic constants; spectroscopic line

#### 1. Introduction

With the development of the calculation methods of quantum chemistry, the basis set and extent of electronic correlation required for an accurate representation of the bond length and energies of the ground and low-lying electronic states is reasonably well understood [1,2]. Studies over the past several decades have shown that theoretical studies can provide accurate descriptions of diatomic molecule systems [3–5]. Moreover, one can determine the spectroscopic constants by solving the Schrödinger equation of nuclear motion. So this is found to be an effective way to research the spectroscopic properties of diatomic molecules.

Boron monohalides have been widely researched for a long time because of their utility in the etching processes of semiconductor and metal materials, and in the chemical vapour deposition both for bulk deposition and doping host material [6]. As one of the boron monohalide molecules, BBr has been studied over the past several decades. The first experimental study was conducted early in the 1930s by Miescher [7]. Investigations before 1979 have been collected together by Huber and Herzberg [8]. The transition actions of  $a^3\Pi \rightarrow X^1\Sigma^+$  and  $A^1\Pi \rightarrow X^1\Sigma^+$  were researched by Destoky *et al.* [9,10]. In 1997, Nomoto *et al.* [11] studied the microwave spectrum of the BBr molecule;

transition lines of its ground state were reported in their work. Another important experiment on the BBr molecule was conducted in 1998 by Hunt *et al.* [12]. They identified its infrared spectroscopy and measured 151 transition lines of the ground state for the four isotopes of the title molecule. In 2001, Martin *et al.* [13] computed the bond length, dissociation energy and harmonic frequency of the BBr molecule using CCSD (T)/(SDB-CC-PVQZ, CPP-CC-PVQZ...) method (SDB-Stuttgart-Dresden-Bonn relativistic pseudopotential [14]; CPP-core polarization potential [15]). Then Menconi *et al.* [16] studied the BBr molecule as well as other diatomic molecules to assess the validity of the exchange-correlation functionals. However, both Martin *et al.* [13] and Menconi *et al.* [16] only determined some spectroscopic constants of the ground state, while the excited states were not considered. In 2002, Zou and Yang *et al.* [17] calculated the ground state and a number of excited states using time-dependent density functional theory (DFT). Spectroscopic constants i.e.  $T_e$ ,  $R_e$ ,  $w_e$ ,  $w_e x_e$  and some transition lines of  $X^1\Sigma^+$ ,  $A^1\Pi$ ,  $a^3\Pi$  states as well as some other excited states were determined. PECs of these states were also reported. However, limited by the DFT calculation level, the properties of some of these states have not been displayed in detail. For example, the metastable properties of the  $A^1\Pi$

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state have not been illustrated in their PECs and their PEC of the  $^3\Sigma^+$  state is irregular with two potential wells. Their spectroscopic constants also deviated from the experimental data significantly. Taking the ground state as an example, the percentage errors in  $w_e$  and  $w_e x_e$  are all larger than 5%.

In 2006, Yang *et al.* [18] extended their DFT study using a more accurate and reliable *ab initio* electronic structure method (MRCISD+Q) for higher excited states and longer distance. The electronic state structures and the transition properties of the 12 valence and 12 low-lying Rydberg  $\Lambda$ -S states of the BBr molecule were investigated and results reported. Their new calculations solved partial problems existing in the previous DFT study, but spectroscopic constants reported in the work still deviated from the experimental data significantly although the relativistic effect and Davidson modifications were considered in their calculations. In addition, the  $^3\Sigma^+$  state is a repulsive state in their calculations while an irregular curve with two wells in [17]. Therefore, more high level calculations are still needed to understand its PECs and spectroscopic properties more completely.

Here, we calculate the PECs of the ground state and three low-lying excited states at the multi-reference single and double excitation configuration interaction (MRCISD) level. Based on the PECs, we comprehensively determine the spectroscopic constants and ro-vibrational energy levels of these states. In particular, the isotope effects of the ground state are also investigated. Experimental spectroscopic constants and ro-vibrational energy levels in the literature can provide good candidates to test the computational results, we can confirm the accuracy and reliability of our results through comparison with them. Relativistic effects and Davidson modifications used in Ref [18] are discussed and analysed carefully. The spin-orbital coupling effects of the  $a^3\Pi$  state have also been investigated and compared with results in the literature. The analytical potential energy functions (APEFs) of these states have also been fitted.

## 2. Theoretical details

We calculated four low-lying electronic states of the BBr molecule using the complete active space self-consistent-field method (CASSCF) [19,20] which is followed by the MRCISD [21,22] calculations. Dunning's correlation consistent basis sets [23–27] (aug-cc-PVQZ) have been used for both atoms [B:(13s,7p,4d,3f,2g)/[6s,5p,4d,3f,2g]; Br:(22s,17p,13d,3f,2g)/[8s,7p,5d,3f,2g]]. All of the calculations are performed with the MOLPRO 2002.6 program package

[28] running on the Dawning-4000A computer [29] at Ludong University. MOLPRO can use Abelian point group symmetry only. For molecules with degenerate symmetry, an Abelian subgroup must be used. So, for the linear molecule with  $C_{\infty v}$  symmetry, it will be substituted by  $C_{2v}$  symmetry with the order of the irreducible representations as  $a_1/b_1/b_2/a_2$ . In the CASSCF and subsequent MRSDCI calculation, these four states are calculated. Eight molecule orbitals (MOs) are put into active space, including four  $a_1$ , two  $b_1$ , two  $b_2$  symmetry MOs, which correspond to the  $2s2p$  shells of the B atom and  $4s4p$  shells of the Br atom. The rest of the electrons are put into the closed-shell orbits – eight  $a_1$ , three  $b_1$ , three  $b_2$  and one  $a_2$  symmetry MOs. The steps employed in the calculations are 0.05Å for the  $X^1\Sigma^+$ ,  $A^1\Pi$ ,  $^3\Pi$  states and 0.05 bohr for the  $^3\Sigma^+$  state. The smaller step for  $^3\Sigma^+$  state is adopted due to its shallow (about 0.12 eV) and narrow potential well (about 0.2 Å) and density energy points are needed to display the properties of its PEC clearly. However, we note that Yang *et al.* [18] performed MRCISD+Q calculations with aug-cc-PVQZ basis set to study the PECs and spectroscopic constants of the title molecule. But their spectroscopic constants deviate from the experimental data significantly. They attributed this to the error compensation of the MRSDCI method itself, but this is not the case according to our calculations. To check the effect of the MRSDCI/aug-cc-PVQZ calculation for the BBr molecule more widely, we recalculate these states both taking and not taking into account relativistic effects and the Davidson modification and analyse them carefully. For all-electron calculations, the preferred way to consider the relativistic effects is to use the Douglas–Kroll Hamiltonian [30,31]. Therefore, we calculated the relativistic effects in this way. It should be noted that the basis sets aug-cc-PVQZ used in Yang's work are uncontracted, but in the present work are contracted. Calculations using contracted basis sets consume less CPU time than calculations using uncontracted basis sets, and the results using the two kinds of basis sets are only a little different, according to our calculations on the ground state. So, all the calculations in the present work are performed using contracted aug-cc-PVQZ basis sets. Due to the large spin-orbital split values of the  $a^3\Pi$  state mentioned in the literature, spin-orbital coupling (SOC) effects of this state have also been considered in the present work. The SOC calculations are performed using the scheme proposed by Berning *et al.* [32] and implanted in MOLPRO. According to Berning *et al.*, the spin-orbit integral program of MOLPRO is restricted to basis functions with  $l \leq 3$  (f functions) and cannot handle generally contracted basis sets. So, in our spin-orbit coupling calculations, we employ

entirely uncontracted Gaussian-type all-electron basis sets (Dunning's aug-cc-pVQZ) for both B and Br atoms with the *g* functions omitted. The spectroscopic constants and vibrational levels are calculated using the PECs with the aid of module VIBROT in MOLCAS 5.4 program package [33]. The APEFs are fitted in the ORIGIN software [34] with least square fitting method.

### 3. Results and discussion

To get more accurate spectroscopic constants and display the characters of the PECs of the BBr molecule, we calculate four states ( $X^1\Sigma^+$ ,  $^3\Sigma^+$ ,  $A^1\Pi$ ,  $a^3\Pi$ ) of the BBr molecule using a highly accurate *ab initio* method. The calculated PECs of these states are shown in Figure 1. The present calculations at the MRSDCI/aug-cc-PVQZ theoretical level show that the  $^3\Sigma^+$  state is a metastable state formed from the avoided crossing rules. The maximum on the PEC can be seen clearly on Figure 2, obtained by calculating two states of the same symmetry in one MRSDCI calculation. However, the calculations at DFT level [17] gives two irregular potential wells for the  $1^3\Sigma^+$  state, while results at the MRCISD+Q level [18] shows it is a repulsive state because no potential well is found on its PEC. Some more skillful experimental measurements or calculations are needed to understand this state more completely. As for the  $A^1\Pi$  state, metastable properties are not obvious in Zou's [17] study, while both the calculated results in this work and in Yang's study [18] show that it is a metastable state. The present potential barrier is at  $R=2.47$  Å, which is close to 2.43 Å obtained in Yang's study. Moreover, except dissociation energies and bond lengths, all of the other spectroscopic constants reported by Zou [17] and Yang [18] deviate from the experimental data significantly, while ours are close to the experimental values. This fact implies that the dissatisfactory results are not from the method – MRSDCI – itself but from the various modifications. To examine the problem further, we add the relativistic effect and the Davidson modification into our MRSDCI/aug-cc-PVQZ computation to recalculate the ground state as well as three excited states of the title molecule. Parts of the calculated spectroscopic constants are listed in Table 1. From the table, we find that calculations in the present work and in Yang's [18] work give similar equilibrium bond lengths, but the MRSDCI calculations in the present work with no relativistic effect and no Davidson modification give better spectroscopic terms while Yang's [18] work gives better dissociation energies. But generally speaking, for the three spectroscopic constants ( $R_e$ ,  $T_e$ ,  $D_e$ ), the relativistic effect and the

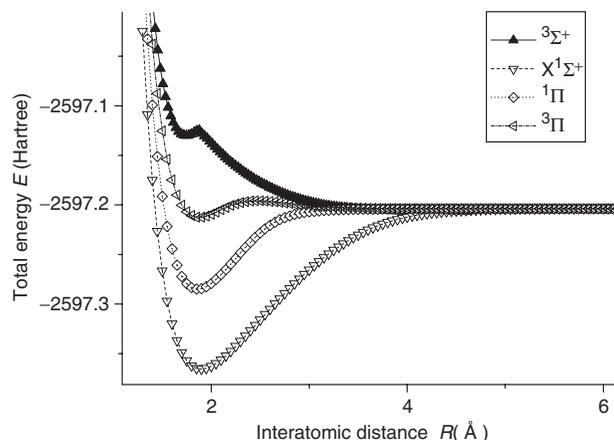


Figure 1. Potential energy curves of the  $X^1\Sigma^+$ ,  $^3\Sigma^+$ ,  $A^1\Pi$ ,  $a^3\Pi$  states, *ab initio* calculation at MRSDCI/aug-cc-PVQZ level.

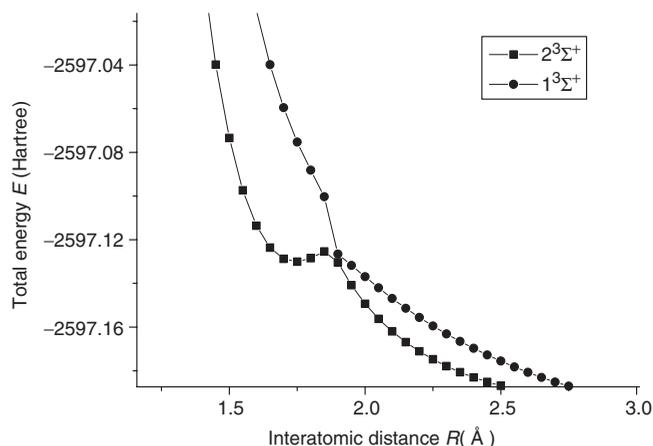


Figure 2. Potential energy curves of two  $^3\Sigma^+$  states, *ab initio* calculation at MRSDCI/aug-cc-PVQZ level.

Davidson modification cannot improve the MRSDCI calculations satisfactorily. For the other spectroscopic constants, the MRSDCI calculations with the relativistic effects make the results worse. To some extent, the Davidson modification compensated this defect but the results are still unsatisfactory. Taking the ground state as an example, the percentage error in  $w_e$ ,  $w_e x_e$  and  $w_e y_e$  are 0.48%, 40.6% and 76.8%, respectively, while in our results they are only 0.15%, 0.14% and 4.1%, respectively. Findings for the excited states are similar. The calculation in Yang's study takes not only the relativistic effect and Davidson modification into account but also the approximation of the frozen-core orbitals. To some degree, the frozen energy counteracts the negative effect caused by the above two experiential modifications, and their calculated spectroscopic constants coincide with the experiment value. But the vibrational frequency  $w_e$  became worse with a

Table 1. Spectroscopic constants of  $X^1\Sigma^+$  state obtained in MRSDCI level with different settings.

		$T_e$ (cm <sup>-1</sup> )	$R_e$ (Å)	$D_e$ (eV)	$w_e$ (cm <sup>-1</sup> )	$w_e x_e$ (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )	$\alpha_e$ (cm <sup>-1</sup> )
$^1\Sigma^+$	Present <sup>1</sup>	0	1.896	4.43	686.25	3.73	0.4848	$0.42 \times 10^{-2}$
	Exp. [12]	0	1.887 <sup>a</sup>	4.58	685.19	3.74	0.4902	$0.42 \times 10^{-2}$
	MRSDCI plus R* <sup>1</sup>	0	1.875	4.83	691.49	2.26	0.4965	$0.33 \times 10^{-2}$
	MRSDCI + Q plus R* <sup>1</sup>	0	1.883	4.80	681.89	2.22	0.4921	$0.23 \times 10^{-2}$
	Yang <i>et al.</i> [18]	0	1.890	4.58	710.40 <sup>d</sup>	3.45	0.5310	
$^1\Pi$	Present <sup>1</sup>	34331	1.876	0.45	636.96	12.52	0.4961	$0.86 \times 10^{-2}$
	Exp. [8]	33935	1.870		637.63	17.58	0.5100	$0.90 \times 10^{-2}$
	MRSDCI plus R* <sup>1</sup>	34011	1.855	0.62	641.55	7.80	0.5074	$0.71 \times 10^{-2}$
	MRSDCI + Q plus R* <sup>1</sup>	33770	1.856	0.64	639.26	8.17	0.5067	$0.72 \times 10^{-2}$
	Yang <i>et al.</i> [18]	35036	1.868	0.41	677.10	25.44	0.5414	
$a^3\Pi_1$	Present <sup>1</sup>	18414	1.861	2.21	761.56	4.56	0.5036	$0.41 \times 10^{-2}$
	Exp. [8]	18851	1.853		757.10	4.80	0.5083	
	MRSDCI plus R* <sup>1</sup>	18765	1.842	2.59	756.40	2.30	0.5140	$0.34 \times 10^{-2}$
	MRSDCI + Q plus R* <sup>1</sup>	17804	1.844	2.53	751.91	2.59	0.5130	$0.35 \times 10^{-2}$
	Yang <i>et al.</i> [18]	19052 <sup>b</sup>	1.853	2.05	792.80	5.91	0.5525	

R\* stands for relativistic effect.

<sup>1</sup>Results calculated in the present work.

percentage error of 3.68%. So, we conclude that the MRSDCI method with aug-cc-PVQZ basis sets can deal with the BBr molecule, while the relativistic effect and the Davidson modification may be improper for this molecule. Therefore all the PECs of the considered states in the present work are calculated at MRSDCI/aug-cc-PVQZ (contracted) level.

Based on the reliable PECs, we determine their intact spectroscopic constants and their ro-vibrational energy levels of these states. Compared with the previous theoretical results, except dissociation energies and bond lengths, all of the other spectroscopic constants obtained in this work are improved. For the ground state, the calculated spectroscopic constants of the four isotopes as well as the experimental data are listed in Table 2. From this table we can find that the spectroscopic constants calculated in this article are in excellent agreement with the experimental data. Taking  $^{11}\text{B}^{79}\text{Br}$  as an example, the percent error in  $w_e$ ,  $w_e x_e$ ,  $w_e y_e$ ,  $B_e$  and  $\alpha_e$  is only 0.15%, 0.14%, 4.1%, 1.1% and 0.9%, respectively. All of the these constants are better than those of other theoretical results. The rotational transition lines of the four isotope molecules together with the experimental data are shown in Table 3. We compare our calculated wavelengths with those of the 151 transition lines reported in Ref. [12], and find that the average deviation is only  $1.096\text{ cm}^{-1}$ , while the largest deviation is  $1.818\text{ cm}^{-1}$ , resulting from the transition between  $v=2, J=35$  and  $v=1, J=36$  of  $^{10}\text{B}^{81}\text{Br}$  isotope. Owing to the length of this article, only part of the ro-vibrational energy levels of the most natural abundant isotope  $^{11}\text{B}^{79}\text{Br}$  is listed in Table 4.

The  $a^3\Pi$  is also a stable bound state. Spin-orbital split for this state is obvious [18], so, the spin-orbital

coupling effect of this state has also been considered in the present work. The calculated spectroscopic constants of the three split states are listed in Table 5. One can see that, except the spectroscopic terms and equilibrium bond lengths, all other spectroscopic constants of the three split states ( $a^3\Pi_{0+}$ ,  $a^3\Pi_1$  and  $a^3\Pi_2$ ) calculated in this work are improved. The calculated split value between the  $a^3\Pi_{0+}$  and  $a^3\Pi_1$  are  $174\text{ cm}^{-1}$  which is much closer to the experimental value  $177\text{ cm}^{-1}$ , while values in Yang's study [18] and Zou's study [17] are  $210\text{ cm}^{-1}$  and  $181\text{ cm}^{-1}$ , respectively. According to our calculation, the difference in the two PECs for the two split states ( $a^3\Pi_{0+}$ ,  $a^3\Pi_0^-$ ) with the total angular momentum  $J=0$  is very small (generally smaller than  $1.0\text{ cm}^{-1}$ ) and we do not distinguish them in further discussion. The spin-orbital coupling effects on the ro-vibrational energy levels are shown in Table 6.

Both the  $A^1\Pi$  and  $^3\Sigma^+$  states are metastable. For the  $A^1\Pi$  state, the calculated spectroscopic constants, the previous theoretical results and the experimental data are shown in Table 5. Although the deviation of the  $w_e x_e$  seems to be a little large, the spectroscopic constants in this paper are closer to the experimental data than other theoretical results in the literature. Taking  $w_e$  as an example, the percentage errors in Ref [17] and Ref [18] are 4.2% and 6.2% respectively, but in this work, it is only 0.1%. The deviation of the calculated  $T_e$  from the experimental data is only  $396\text{ cm}^{-1}$  which is much smaller than that of Yang's result  $1101\text{ cm}^{-1}$ . Because the depth of the potential well of the  $A^1\Pi$  state is just  $0.448\text{ eV}$ , we just find two vibrational energy levels of this state, which have been listed in Table 7. There are no experimental data about

Table 2. Spectroscopic constants of the four isotopes  $^{11}\text{B}^{79}\text{Br}$ ,  $^{10}\text{B}^{79}\text{Br}$ ,  $^{10}\text{B}^{81}\text{Br}$ ,  $^{11}\text{B}^{81}\text{Br}$ .

		$^{11}\text{B}^{79}\text{Br}$	$^{10}\text{B}^{79}\text{Br}$	$^{10}\text{B}^{81}\text{Br}$	$^{11}\text{B}^{81}\text{Br}$
$R_e$ (Å)	This work	1.8969	1.8969	1.8969	1.8969
	Exp.	1.8866 <sup>a</sup>	1.8866 <sup>a</sup>	1.8866 <sup>a</sup>	1.8866 <sup>a</sup>
	Yang <i>et al.</i>	1.917 <sup>b</sup> , 1.8894 <sup>c</sup> , 1.890 <sup>d</sup>			
$D_e$ (eV)	This work	4.43	4.43	4.43	4.43
	Exp.	4.06 <sup>c</sup> , 4.53 <sup>f</sup> , 4.32 <sup>c</sup>			
	Yang <i>et al.</i>	4.58 <sup>d</sup>			
$w_e$ (cm <sup>-1</sup> )	This work	686.254	715.589	714.594	685.216
	Exp.	685.189 <sup>e</sup> , 684.310 <sup>f</sup>	714.482 <sup>e</sup>	713.488 <sup>e</sup>	684.153 <sup>e</sup>
	Yang <i>et al.</i>	648.09 <sup>b</sup> , 700.9 <sup>c</sup> , 710.4 <sup>d</sup>			
$w_e x_e$ (cm <sup>-1</sup> )	This work	3.731	4.054	4.042	3.720
	Exp.	3.736 <sup>e</sup>	4.063 <sup>e</sup>	4.051 <sup>e</sup>	3.725 <sup>e</sup>
	Yang <i>et al.</i>	3.37 <sup>b</sup> , 3.45 <sup>d</sup>			
$w_e y_e$ (cm <sup>-1</sup> )	This work	$0.1698 \times 10^{-1}$	$0.1892 \times 10^{-1}$	$0.1885 \times 10^{-1}$	$0.1691 \times 10^{-1}$
	Exp.	$0.1771 \times 10^{-1e}$	$0.2008 \times 10^{-1e}$	$0.2000 \times 10^{-1e}$	$0.1763 \times 10^{-1e}$
$B_e$ (cm <sup>-1</sup> )	This work	0.4848	0.5272	0.5257	0.4834
	Exp.	0.4902 <sup>c</sup>	0.5330 <sup>e</sup>	0.5316 <sup>e</sup>	0.4887 <sup>e</sup>
	Yang <i>et al.</i>	0.531 <sup>d</sup>			
$\alpha_e$ (cm <sup>-1</sup> )	This work	$0.4199 \times 10^{-2}$	$0.4760 \times 10^{-2}$	$0.4740 \times 10^{-2}$	$0.4180 \times 10^{-2}$
	Exp.	$0.4239 \times 10^{-2e}$ , $0.35 \times 10^{-2f}$	$0.4807 \times 10^{-2e}$	$0.4787 \times 10^{-2e}$	$0.4220 \times 10^{-2e}$
$\gamma_e$ (cm <sup>-1</sup> )	This work	$0.2061 \times 10^{-4}$	$0.2422 \times 10^{-4}$	$0.2409 \times 10^{-4}$	$0.2049 \times 10^{-4}$
	Exp.	$0.1993 \times 10^{-4e}$	$0.2357 \times 10^{-4e}$	$0.2344 \times 10^{-4e}$	$0.1981 \times 10^{-4e}$
$\delta_e$ (cm <sup>-1</sup> )	This work	$0.9684 \times 10^{-6}$	$0.1145 \times 10^{-6}$	$0.1139 \times 10^{-6}$	$0.9625 \times 10^{-6}$
	Exp.	$1.0047 \times 10^{-6e}$	$0.1187 \times 10^{-6e}$	$0.1181 \times 10^{-6e}$	$0.9998 \times 10^{-6e}$
$\beta_e$ (cm <sup>-1</sup> )	This work	$0.4409 \times 10^{-8}$	$0.5484 \times 10^{-8}$	$0.5445 \times 10^{-8}$	$0.4375 \times 10^{-8}$
	Exp.	$0.3210 \times 10^{-8e}$	$0.3950 \times 10^{-8e}$	$0.3930 \times 10^{-8e}$	$0.3180 \times 10^{-8e}$

<sup>a</sup>Reference [11].<sup>b</sup>Reference [17].<sup>c</sup>Reference [13].<sup>d</sup>Reference [18].<sup>e</sup>Reference [12].<sup>f</sup>Reference [8].

ro-vibrational spectra on this state. Considering that the spectroscopic constants for this state are very close to the experimental value, we believed that the spectroscopic lines reported here for this state should be good references for the future laboratory research. As for the  $^3\Sigma^+$  state, the depth of the potential well for this state is only 0.12eV. Neither the MOLCAS nor the LEVEL [35] procedure can treat such state well, so no spectroscopic constants have been reported in the present work.

#### 4. Analytical potential energy function

Based on the PECs obtained from the *ab initio* calculations, we fit the APEFs of these four states with the aid of the ORIGIN software. Although some researchers [36,37] emphasize that the metastable states cannot be described well by the Murrell–Sorbie (MS) function [36] and should be described by the modified

Murrell–Sorbie (MMS) function [37], we still fit the four states with both the MS and the MMS functions. The common MS function can be written as

$$V(\rho) = -D_e \left( 1 + \sum_{i=1}^n a_i \rho^i \right) \exp(-a_1 \rho) \quad (1)$$

where  $\rho = R - R_e$ ,  $R$  and  $R_e$  stand for the interatomic distance and the equilibrium bond length, respectively.  $D_e$  is the dissociation energy.  $a_i$  are the fitting parameters. The number of parameter  $a_i$  is different for different molecules. In this work we employ  $n = 9$  for the fitting action of these two states. Usually the parameters  $D_e$  and  $R_e$  are fixed as dissociation energy and equilibrium bond length respectively, but in this work they are treated as fitting parameters equally in order to get the more accurate fitting results.

In 2004, Wang *et al.* [36] proposed the MMS function which can give more accurate descriptions for

Table 3. Transition lines from  $\nu J$  to  $\nu' J'$ , in  $\text{cm}^{-1}$ .

Isotopes	$\nu, J-\nu' J'$	Exp. [12]	This work	Isotope	$\nu, J-\nu' J'$	Exp. [12]	This work
$^{11}\text{B}^{79}\text{Br}$	1.3–0.2	680.6490	681.60	$^{11}\text{B}^{81}\text{Br}$	1.4–0.3	680.5664	681.49
$^{11}\text{B}^{79}\text{Br}$	1.2–0.1	679.7027	680.66	$^{11}\text{B}^{81}\text{Br}$	1.3–0.2	679.6251	680.57
$^{11}\text{B}^{79}\text{Br}$	1.3–0.4	673.8193	674.84	$^{11}\text{B}^{81}\text{Br}$	1.2–0.1	678.6769	679.63
$^{11}\text{B}^{79}\text{Br}$	1.6–0.7	670.7624	671.81	$^{11}\text{B}^{81}\text{Br}$	1.1–0.2	674.8030	675.80
$^{11}\text{B}^{79}\text{Br}$	1.5–0.6	671.7925	672.83	$^{11}\text{B}^{81}\text{Br}$	1.2–0.3	673.8165	674.81
$^{11}\text{B}^{79}\text{Br}$	1.10–0–11	666.5767	667.67	$^{11}\text{B}^{81}\text{Br}$	1.4–0.5	671.8121	672.83
$^{11}\text{B}^{79}\text{Br}$	1.13–0.14	663.3510	664.48	$^{11}\text{B}^{81}\text{Br}$	1.5–0.6	670.7927	671.83
$^{11}\text{B}^{79}\text{Br}$	1.14–0.15	662.2573	663.40	$^{11}\text{B}^{81}\text{Br}$	1.9–0.10	666.6532	667.73
$^{11}\text{B}^{79}\text{Br}$	1.16–0.17	660.0523	661.22	$^{11}\text{B}^{81}\text{Br}$	1.12–0.13	663.4607	664.58
$^{11}\text{B}^{79}\text{Br}$	1.17–0.18	658.9363	660.11	$^{11}\text{B}^{81}\text{Br}$	1.13–0.14	662.3797	663.51
$^{11}\text{B}^{79}\text{Br}$	1.18–0.19	657.8134	659.00	$^{11}\text{B}^{81}\text{Br}$	1.15–0.16	660.1980	661.35
$^{11}\text{B}^{79}\text{Br}$	1.20–0.21	655.5419	656.75	$^{11}\text{B}^{81}\text{Br}$	1.16–0.17	659.0929	660.26
$^{11}\text{B}^{79}\text{Br}$	1.31–0.30	703.7542	704.42	$^{11}\text{B}^{81}\text{Br}$	1.18–0.19	656.8600	658.04
$^{11}\text{B}^{79}\text{Br}$	1.9–0.8	686.1721	687.06	$^{11}\text{B}^{81}\text{Br}$	1.19–0.20	655.7361	656.93
$^{11}\text{B}^{79}\text{Br}$	1.13–0.12	689.6895	690.53	$^{11}\text{B}^{81}\text{Br}$	1.20–0.21	654.6009	655.80
$^{11}\text{B}^{79}\text{Br}$	1.17–0.16	693.0626	693.86	$^{11}\text{B}^{81}\text{Br}$	1.32–0.31	703.3621	704.01
$^{11}\text{B}^{79}\text{Br}$	1.41–0.40	710.3008	710.89	$^{11}\text{B}^{81}\text{Br}$	1.38–0.37	707.3351	707.95
$^{11}\text{B}^{79}\text{Br}$	1.36–0.35	707.1395	707.77	$^{11}\text{B}^{81}\text{Br}$	1.43–0.42	710.3954	710.96
$^{11}\text{B}^{79}\text{Br}$	2.15–1.16	653.9881	655.45	$^{11}\text{B}^{81}\text{Br}$	1.42–0.41	709.8014	710.37
$^{11}\text{B}^{79}\text{Br}$	2.12–1.13	657.2339	658.66	$^{11}\text{B}^{81}\text{Br}$	2.8–1.9	660.4840	661.86
$^{11}\text{B}^{79}\text{Br}$	2.10–1.11	659.3548	660.75	$^{11}\text{B}^{81}\text{Br}$	2.7–1.8	661.5153	662.88
$^{11}\text{B}^{79}\text{Br}$	2.8–1.9	661.4478	662.82	$^{11}\text{B}^{81}\text{Br}$	2.5–1.6	663.5510	664.89
$^{11}\text{B}^{79}\text{Br}$	2.7–1.8	662.4852	663.84	$^{11}\text{B}^{81}\text{Br}$	2.4–1.5	664.5554	665.89
$^{11}\text{B}^{79}\text{Br}$	2.6–1.7	663.5088	664.86	$^{11}\text{B}^{81}\text{Br}$	2.5–1.4	674.1616	675.39
$^{11}\text{B}^{79}\text{Br}$	2.3–1.4	666.5369	667.86	$^{11}\text{B}^{81}\text{Br}$	2.6–1.5	675.0741	676.29
$^{11}\text{B}^{79}\text{Br}$	2.3–1.2	673.3087	674.55	$^{11}\text{B}^{81}\text{Br}$	2.9–1.8	677.7741	678.96
$^{11}\text{B}^{79}\text{Br}$	2.7–1.6	676.9919	678.20	$^{11}\text{B}^{81}\text{Br}$	2.11–1.10	679.5209	680.69
$^{11}\text{B}^{79}\text{Br}$	2.8–1.7	677.8996	679.09	$^{11}\text{B}^{81}\text{Br}$	2.12–1.11	680.3897	681.55
$^{11}\text{B}^{79}\text{Br}$	2.10–1.9	679.6692	680.84	$^{11}\text{B}^{81}\text{Br}$	2.14–1.13	682.0907	683.23
$^{11}\text{B}^{79}\text{Br}$	2.11–1.10	680.5488	681.72	$^{11}\text{B}^{81}\text{Br}$	2.23–1.22	689.3196	690.39
$^{11}\text{B}^{79}\text{Br}$	2.14–1.13	683.1179	684.26	$^{11}\text{B}^{81}\text{Br}$	2.28–1.27	693.0388	694.06
$^{11}\text{B}^{79}\text{Br}$	2.22–1.21	689.5981	690.68	$^{11}\text{B}^{81}\text{Br}$	3.6–2.7	655.4059	656.42
$^{11}\text{B}^{79}\text{Br}$	3.8–2.9	654.3095	655.35	$^{11}\text{B}^{81}\text{Br}$	3.3–2.4	658.3889	659.38
$^{11}\text{B}^{79}\text{Br}$	3.7–2.8	655.3361	656.37	$^{11}\text{B}^{81}\text{Br}$	3.2–2.1	664.1598	665.09
$^{11}\text{B}^{79}\text{Br}$	3.8–2.7	670.6201	671.48	$^{11}\text{B}^{81}\text{Br}$	3.9–2.8	670.5089	671.36
$^{11}\text{B}^{79}\text{Br}$	3.11–2.10	673.2409	674.08	$^{11}\text{B}^{81}\text{Br}$	3.12–2.11	673.1017	673.93
$^{11}\text{B}^{79}\text{Br}$	3.12–2.11	674.1040	674.92	$^{11}\text{B}^{81}\text{Br}$	3.13–2.12	673.9499	674.76
$^{11}\text{B}^{79}\text{Br}$	3.15–2.14	676.6263	677.42	$^{11}\text{B}^{81}\text{Br}$	3.14–2.13	674.7857	675.59
$^{11}\text{B}^{79}\text{Br}$	3.20–2.19	680.6701	681.41	$^{11}\text{B}^{81}\text{Br}$	3.17–2.16	677.2593	678.03
$^{11}\text{B}^{79}\text{Br}$	3.32–2.31	689.4637	690.10	$^{11}\text{B}^{81}\text{Br}$	3.20–2.19	679.6431	680.39
$^{11}\text{B}^{79}\text{Br}$	4.3–3.2	658.9240	659.82	$^{11}\text{B}^{81}\text{Br}$	3.21–2.20	680.4298	681.16
$^{11}\text{B}^{79}\text{Br}$	4.4–3.3	659.8458	660.73	$^{11}\text{B}^{81}\text{Br}$	3.24–2.23	682.7157	683.42
$^{11}\text{B}^{79}\text{Br}$	4.8–3.7	663.4395	664.27	$^{11}\text{B}^{81}\text{Br}$	3.25–2.24	683.4542	684.15
$^{11}\text{B}^{79}\text{Br}$	4.20–3.19	673.4092	674.14	$^{11}\text{B}^{81}\text{Br}$	4.9–3.8	663.3386	664.17
$^{11}\text{B}^{79}\text{Br}$	4.25–3.24	677.1891	677.89	$^{11}\text{B}^{81}\text{Br}$	4.13–3.12	666.7564	667.54
$^{11}\text{B}^{79}\text{Br}$	5.6–4.5	654.5888	655.77	$^{11}\text{B}^{81}\text{Br}$	4.18–3.17	670.8335	671.57
$^{11}\text{B}^{79}\text{Br}$	5.9–4.8	657.2224	658.38	$^{11}\text{B}^{81}\text{Br}$	4.21–3.20	673.1766	673.90
$^{11}\text{B}^{79}\text{Br}$	5.13–4.12	660.6172	661.74	$^{11}\text{B}^{81}\text{Br}$	5.10–4.9	657.1243	658.27
$^{11}\text{B}^{79}\text{Br}$	5.14–4.13	661.4432	662.56	$^{11}\text{B}^{81}\text{Br}$	5.12–4.11	658.8235	659.95
$^{11}\text{B}^{79}\text{Br}$	5.16–4.15	663.0766	664.17	$^{11}\text{B}^{81}\text{Br}$	5.18–4.17	663.6988	664.78
$^{11}\text{B}^{79}\text{Br}$	5.17–4.16	663.8786	664.97	$^{11}\text{B}^{81}\text{Br}$	5.27–4.26	670.4404	671.45
$^{11}\text{B}^{79}\text{Br}$	5.28–4.27	672.1397	673.15	$^{11}\text{B}^{81}\text{Br}$	5.28–4.27	671.1476	672.15
$^{11}\text{B}^{79}\text{Br}$	6.15–5.14	655.2251	656.31	$^{11}\text{B}^{81}\text{Br}$	5.22–4.21	666.7810	667.83
$^{11}\text{B}^{79}\text{Br}$	6.25–5.24	662.8875	663.89	$^{11}\text{B}^{81}\text{Br}$	5.29–4.28	671.8475	672.85
$^{10}\text{B}^{79}\text{Br}$	1.41–0.42	654.0157	655.57	$^{11}\text{B}^{81}\text{Br}$	5.30–4.29	672.5394	673.53
$^{10}\text{B}^{79}\text{Br}$	1.40–0.41	655.4401	656.98	$^{11}\text{B}^{81}\text{Br}$	5.45–4.44	681.8121	682.72
$^{10}\text{B}^{79}\text{Br}$	1.34–0.35	663.8233	665.28	$^{11}\text{B}^{81}\text{Br}$	6.21–5.20	658.9620	660.00
$^{10}\text{B}^{79}\text{Br}$	1.29–0.30	670.5710	671.97	$^{11}\text{B}^{81}\text{Br}$	6.43–5.42	673.5117	674.40
$^{10}\text{B}^{79}\text{Br}$	1.27–0.28	673.2110	674.58	$^{11}\text{B}^{81}\text{Br}$	6.17–5.16	655.8704	656.94

(continued)

Table 3. Continued.

Isotopes	$v, J-v'J'$	Exp. [12]	This work	Isotope	$v, J-v'J'$	Exp. [12]	This work
$^{10}\text{B}^{79}\text{Br}$	1.24–0.25	677.1076	678.44	$^{10}\text{B}^{81}\text{Br}$	1.40–0.41	654.6179	656.16
$^{10}\text{B}^{79}\text{Br}$	1.20–0.21	682.1732	683.46	$^{10}\text{B}^{81}\text{Br}$	1.39–0.40	656.0314	657.56
$^{10}\text{B}^{79}\text{Br}$	1.19–0.20	683.4198	684.69	$^{10}\text{B}^{81}\text{Br}$	1.37–0.38	658.8318	660.33
$^{10}\text{B}^{79}\text{Br}$	1.4–0.3	710.5695	711.54	$^{10}\text{B}^{81}\text{Br}$	1.28–0.29	671.0281	672.40
$^{10}\text{B}^{79}\text{Br}$	2.21–1.22	673.2082	674.82	$^{10}\text{B}^{81}\text{Br}$	1.26–0.27	673.6395	674.99
$^{10}\text{B}^{79}\text{Br}$	2.15–1.16	680.5322	682.05	$^{10}\text{B}^{81}\text{Br}$	1.22–0.23	678.7647	680.07
$^{10}\text{B}^{79}\text{Br}$	2.13–1.14	682.8969	684.39	$^{10}\text{B}^{81}\text{Br}$	1.19–0.20	682.5160	683.78
$^{10}\text{B}^{79}\text{Br}$	2.10–1.11	686.3902	687.85	$^{10}\text{B}^{81}\text{Br}$	1.16–0.17	686.1904	687.42
$^{10}\text{B}^{79}\text{Br}$	2.12–1.11	710.3507	711.54	$^{10}\text{B}^{81}\text{Br}$	1.13–0.14	689.7855	690.97
$^{10}\text{B}^{79}\text{Br}$	3.30–2.31	654.1291	655.46	$^{10}\text{B}^{81}\text{Br}$	1.5–0.4	710.5984	711.56
$^{10}\text{B}^{79}\text{Br}$	3.29–2.30	655.4362	656.76	$^{10}\text{B}^{81}\text{Br}$	2.35–1.36	654.0720	655.89
$^{10}\text{B}^{79}\text{Br}$	3.12–2.13	676.3684	677.49	$^{10}\text{B}^{81}\text{Br}$	2.22–1.23	671.0853	672.70
$^{10}\text{B}^{79}\text{Br}$	3.21–2.20	710.3299	711.06	$^{10}\text{B}^{81}\text{Br}$	2.20–1.21	673.5690	675.16
$^{10}\text{B}^{81}\text{Br}$	3.26–2.27	658.4776	659.76	$^{10}\text{B}^{81}\text{Br}$	2.15–1.16	679.6237	681.15
$^{10}\text{B}^{81}\text{Br}$	3.14–2.15	673.1599	674.30	$^{10}\text{B}^{81}\text{Br}$	2.13–1.14	681.9938	683.49
$^{10}\text{B}^{81}\text{Br}$	3.7–2.8	681.1326	682.19	$^{10}\text{B}^{81}\text{Br}$	2.6–1.5	703.6208	704.87
$^{10}\text{B}^{81}\text{Br}$	3.9–2.10	678.9020	679.98				

Table 4. Ro-vibrational levels for the  $X^1\Sigma^+$  state of the  $^{11}\text{B}^{79}\text{Br}$  isotope, in  $\text{cm}^{-1}$ .

$J$	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$	$v=5$	$v=6$	$v=7$	$v=8$	$v=9$
0	342.26	1021.00	1692.74	2356.92	3013.96	3664.31	4307.71	4944.26	5574.06	6197.17
1	343.22	1021.96	1693.68	2357.86	3014.89	3665.23	4308.63	4945.16	5574.96	6198.06
2	345.15	1023.88	1695.58	2359.74	3016.76	3667.08	4310.46	4946.98	5576.76	6199.85
3	348.05	1026.75	1698.43	2362.56	3019.56	3669.86	4313.21	4949.71	5579.46	6202.53
4	351.91	1030.57	1702.22	2366.33	3023.29	3673.55	4316.88	4953.35	5583.07	6206.11
5	356.74	1035.36	1706.97	2371.03	3027.95	3678.18	4321.46	4957.89	5587.58	6210.57
6	362.53	1041.10	1712.66	2376.67	3033.54	3683.72	4326.96	4963.34	5592.98	6215.93
7	369.29	1047.80	1719.30	2383.26	3040.07	3690.20	4333.38	4969.70	5599.29	6222.19
8	377.01	1055.46	1726.89	2390.78	3047.53	3697.59	4340.71	4976.97	5606.50	6229.34
9	385.70	1064.07	1735.43	2399.25	3055.92	3705.91	4348.96	4985.15	5614.61	6237.37
10	395.35	1073.63	1744.91	2408.65	3065.25	3715.16	4358.12	4994.24	5623.61	6246.31
11	405.96	1084.16	1755.35	2418.99	3075.50	3725.32	4368.20	5004.23	5633.52	6256.13
12	417.54	1095.64	1766.73	2430.27	3086.69	3736.41	4379.20	5015.13	5644.33	6266.85
13	430.08	1108.07	1779.06	2442.49	3098.80	3748.43	4391.11	5026.94	5656.04	6278.46
14	443.59	1121.46	1792.33	2455.65	3111.85	3761.36	4403.93	5039.66	5668.65	6290.96
15	458.06	1135.80	1806.55	469.75	3125.83	3775.22	4417.67	5053.28	5682.15	6304.35
16	473.49	1151.10	1821.72	2484.79	3140.73	3790.00	4432.33	5067.81	5696.56	6318.63
17	489.88	1167.35	1837.83	2500.76	3156.57	3805.70	4447.89	5083.24	5711.86	6333.80
18	507.24	1184.56	1854.89	2517.67	3173.34	3822.32	4464.37	5099.58	5728.06	6349.86
19	525.56	1202.72	1872.89	2535.52	3191.03	3839.87	4481.77	5116.83	5745.16	6366.82

the metastable state of diatomic molecules. Zhang *et al.* [38] used it to fit four metastable states of  $\text{B}_2^{++}$  molecule successfully. The function can be written as

$$V = C/r + \left( \sum_{i=0}^n b_i r^i \right) \exp(-kr) \quad (2)$$

where  $C$ ,  $b_j$  and  $k$  are parameters to be determined,  $r$  is the interatomic distance.

To judge the quality of the fitting results, we calculate their Root Mean Square (RMS) error. The RMS function can be expressed as

$$\text{RMS} = \frac{1}{m} \sqrt{\sum_{i=1}^m (V_{MS}(i) - V_{ab-initio}(i))^2} \quad (3)$$

where  $V_{ab-initio}(i)$  is the  $i$ th energy of the *ab initio* calculation and  $V_{MS}(i)$  is the corresponding fitting value.

Table 5. Spectroscopic constants of  $A^1\Pi$ ,  $a^3\Pi_{0+}$ ,  $a^3\Pi_1$ , and  $a^3\Pi_2$  states, in  $\text{cm}^{-1}$ .

	$A^1\Pi$ state		$a^3\Pi_{0+}$		$a^3\Pi_1$		$a^3\Pi_2$
	Theo.	Exp. [8]	Theo.	Exp. [8]	Theo.	Exp. [8]	Theo.
$T_e$	34331 35036 <sup>b</sup> 33608 <sup>a</sup>	33935	18240 19052 <sup>b</sup> 18729 <sup>a</sup>	18674	18414 19262 <sup>b</sup> 18910 <sup>a</sup>	18851	18587 19497 <sup>b</sup>
$R_e$ (Å)	1.876 1.869 <sup>a</sup> 1.868 <sup>b</sup>	1.87	1.863		1.861 1.856 <sup>a</sup> 1.853 <sup>b</sup>	1.853	1.860
$D_e$ (eV)	0.45 0.41 <sup>b</sup>	–	2.20 2.08 <sup>b</sup>		2.21 2.05 <sup>b</sup>		2.23 2.03 <sup>b</sup>
$D_0$ (eV)	–	–	2.15		2.17		2.19
$w_e$ ( $\text{cm}^{-1}$ )	636.97 610.77 <sup>a</sup> 677.1 <sup>b</sup>	637.63	758.43 735.2 <sup>a</sup> 796.7 <sup>b</sup>	759.80	761.56 731.5 <sup>a</sup> 792.8 <sup>b</sup>	757.1	764.83 788.3 <sup>b</sup>
$w_e x_e$ ( $\text{cm}^{-1}$ )	12.52 20.39 <sup>a</sup> 25.44 <sup>b</sup>	17.58	4.50 5.47 <sup>a</sup> 5.87 <sup>b</sup>	4.80 <sup>c</sup>	4.56 5.55 <sup>a</sup> 5.91 <sup>b</sup>		4.65 5.89 <sup>b</sup>
$w_e y_e$ ( $\text{cm}^{-1}$ )	0.00	–	$0.16 \times 10^{-1}$		$0.15 \times 10^{-1}$		$0.12 \times 10^{-1}$
$B_e$ ( $\text{cm}^{-1}$ )	0.50 0.54 <sup>b</sup>	0.51	0.50 0.55 <sup>b</sup>	0.50	0.50 0.55 <sup>b</sup>	0.51	0.50 0.55 <sup>b</sup>
$\alpha_e$ ( $\text{cm}^{-1}$ )	$0.86 \times 10^{-2}$	$0.9 \times 10^{-2}$	$0.41 \times 10^{-2}$		$0.41 \times 10^{-2}$		$0.41 \times 10^{-2}$
$\gamma_e$ ( $\text{cm}^{-1}$ )	0.00	–	$0.17 \times 10^{-4}$		$0.17 \times 10^{-4}$		$0.18 \times 10^{-4}$
$\delta_e$ ( $\text{cm}^{-1}$ )	$0.12 \times 10^{-5}$	–	$0.88 \times 10^{-6}$		$0.88 \times 10^{-6}$		$0.88 \times 10^{-6}$
$\beta_e$ ( $\text{cm}^{-1}$ )	$0.98 \times 10^{-7}$	–	$0.58 \times 10^{-8}$		$0.59 \times 10^{-8}$		$0.60 \times 10^{-8}$

<sup>a</sup>Reference [17].<sup>b</sup>Reference [18].<sup>c</sup>No spin-orbital coupling.Table 6. Ro-vibrational levels for  $a^3\Pi_{0+}$ ,  $a^3\Pi_1$ ,  $a^3\Pi_2$  states, in  $\text{cm}^{-1}$ .

$J$	$a^3\Pi_{0+}$				$a^3\Pi_1$				$a^3\Pi_2$			
	$v=0$	$v=1$	$v=2$	$v=3$	$v=0$	$v=1$	$v=2$	$v=3$	$v=0$	$v=1$	$v=2$	$v=3$
0	379.07	1128.59	1867.27	2597.90	379.84	1132.35	1875.18	2608.84	380.73	1136.33	1883.25	2619.89
1	380.07	1129.58	1868.25	2598.88	380.85	1133.35	1876.16	2609.82	381.74	1137.32	1884.24	2620.87
2	382.07	1131.57	1870.23	2600.83	382.85	1135.34	1878.13	2611.77	383.75	1139.31	1886.21	2622.83
3	385.08	1134.55	1873.18	2603.76	385.86	1138.32	1881.09	2614.71	386.76	1142.30	1889.18	2625.77
4	389.09	1138.52	1877.12	2607.67	389.87	1142.30	1885.04	2618.62	390.78	1146.28	1893.13	2629.68
5	394.09	1143.49	1882.05	2612.55	394.89	1147.28	1889.97	2623.51	395.80	1151.26	1898.06	2634.58
6	400.10	1149.45	1887.96	2618.41	400.91	1153.24	1895.89	2629.38	401.82	1157.24	1903.99	2640.46
7	407.12	1156.41	1894.85	2625.25	407.93	1160.21	1902.79	2636.22	408.85	1164.21	1910.90	2647.31
8	415.13	1164.36	1902.74	2633.06	415.95	1168.16	1910.68	2644.04	416.89	1172.17	1918.80	2655.14
9	424.14	1173.30	1911.60	2641.85	424.98	1177.11	1919.56	2652.84	425.92	1181.13	1927.68	2663.95
10	434.16	1183.23	1921.45	2651.61	435.00	1187.06	1929.42	2662.62	435.96	1191.08	1937.55	2673.74
11	445.17	1194.16	1932.28	2662.35	446.03	1198.00	1940.26	2673.37	447.01	1202.03	1948.41	2684.51
12	457.19	1206.08	1944.10	2674.06	458.06	1209.93	1952.09	2685.10	459.05	1213.98	1960.25	2696.26
13	470.20	1218.99	1956.90	2686.75	471.09	1222.85	1964.91	2697.81	472.1	1226.91	1973.08	2708.98
14	484.22	1232.89	1970.69	2700.42	485.13	1236.77	1978.71	2711.49	486.15	1240.85	1986.90	2722.68
15	499.23	1247.79	1985.45	2715.06	500.16	1251.68	1993.49	2726.15	501.21	1255.77	2001.70	2737.36
16	515.25	1263.67	2001.20	2730.67	516.20	1267.58	2009.26	2741.78	517.26	1271.69	2017.48	2753.01
17	532.26	1280.55	2017.94	2747.26	533.23	1284.48	2026.01	2758.39	534.32	1288.60	2034.25	2769.64
18	550.27	1298.42	2035.65	2764.82	551.27	1302.36	2043.74	2775.97	552.38	1306.51	2052.01	2787.25
19	569.28	1317.27	2054.35	2783.35	570.30	1321.24	2062.46	2794.53	571.44	1325.4	2070.75	2805.83

For the MS function, the calculated RMS values for these four states  $X^1\Sigma^+$ ,  $a^3\Pi$ ,  $A^1\Pi$ ,  $^3\Sigma^+$  are  $1.3\text{ cm}^{-1}$ ,  $3.6\text{ cm}^{-1}$ ,  $2.84\text{ cm}^{-1}$  and  $81.15\text{ cm}^{-1}$ , respectively. The large RMS value of the  $^3\Sigma^+$  state indicated that the MS function is unable to describe PEC with

Table 7. Ro-vibrational levels for the  $A^1\Pi$  states, in  $\text{cm}^{-1}$ .

$J$	$v=0$	$v=1$	$J$	$v=0$	$v=1$
0	315.35	927.27	10	369.44	980.41
1	316.33	928.24	11	380.25	991.04
2	318.30	930.17	12	392.05	1002.63
3	321.25	933.07	13	404.82	1015.18
4	325.19	936.94	14	418.58	1028.70
5	330.10	941.77	15	433.32	1043.18
6	336.00	947.57	16	449.04	1058.62
7	342.89	954.33	17	465.74	1075.02
8	350.76	962.06	18	483.42	1092.39
9	359.61	970.76	19	502.07	1110.72

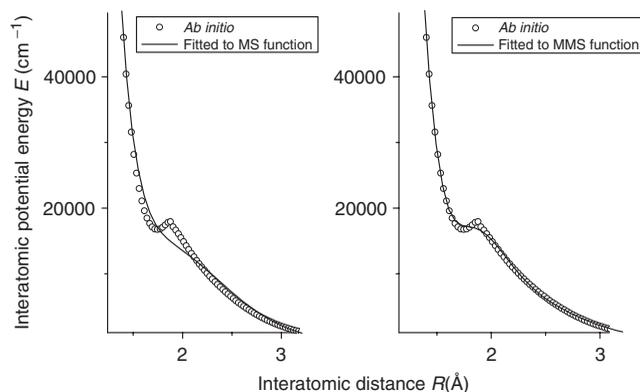


Figure 3. Potential energy curves of the  $^3\Sigma^+$  states for the *ab initio* calculation at MRSDCI/aug-cc-PVQZ level and the fitted MS and MMS function.

such a shallow and narrow well. As for the MMS function, the calculated RMS values of these four states are  $3.83\text{ cm}^{-1}$ ,  $15.16\text{ cm}^{-1}$ ,  $1.34\text{ cm}^{-1}$  and  $50.1\text{ cm}^{-1}$ , respectively. Obviously, the MMS function cannot reproduce the PEC of the  $^3\Sigma^+$  state either, because its RMS value is still  $50.1\text{ cm}^{-1}$ . The fitted PECs of the  $^3\Sigma^+$  state calculated with the two different functions and the *ab initio* ones are shown in Figure 3. The figure clearly shows the impropriety of the two functions in fitting the PEC of the  $^3\Sigma^+$  state. So, more complicated function is still needed for such metastable state. For the two bound states  $X^1\Sigma^+$  and  $a^3\Pi$ , the MS function can give more satisfactory results (the RMS values are  $1.3\text{ cm}^{-1}$ ,  $3.6\text{ cm}^{-1}$ ) than those of the MMS function (the RMS values are  $3.83\text{ cm}^{-1}$  and  $15.16\text{ cm}^{-1}$ ). But for the metastable state  $A^1\Pi$ , the MS function can also give acceptable fitting results, however, the MMS function do give more accurate fitting results. For the sake of simplicity, only the fitting parameters given relatively better results are listed in Table 8. Their fitting PECs and the *ab initio* ones are shown in Figures 4–6.

## 5. Conclusions

In the present work, PECs for four low-lying states ( $X^1\Sigma^+$ ,  $^3\Sigma^+$ ,  $A^1\Pi$ ,  $a^3\Pi$ ) of the BBr molecule are calculated using the MRSDCI method with aug-cc-PVQZ basis sets. For the  $A^1\Pi$  state, its metastable property is confirmed. As for the  $^3\Sigma^+$  state, the present PEC shows that it is a metastable state forming from the avoided crossing rule. Except the dissociation energies, all of the other spectroscopic constants as well as the ro-vibrational spectra lines are in good agreement with the available experimental data. The satisfactory results indicate that the present computational level is effective for the title molecule

Table 8. Parameters for fitting functions.

MS function	$a^3\Pi$	$X^1\Sigma^+$	MMS function	$A^1\Pi$
$D_e$ ( $\text{cm}^{-1}$ )	17891.57136	35711.09625	$C$ ( $\text{cm}^{-1} * \text{\AA}$ )	-40.51797
$R_e$ ( $\text{\AA}$ )	1.86506	1.89657	$b_1$ ( $\text{cm}^{-1} * \text{\AA}^{-1}$ ) $* 10^8$	377.27010
$a_1$ ( $\text{\AA}^{-1}$ )	2.89365	1.90925	$b_2$ ( $\text{cm}^{-1} * \text{\AA}^{-2}$ ) $* 10^8$	-2231.67600
$a_2$ ( $\text{\AA}^{-2}$ )	-0.50724	-0.08415	$b_3$ ( $\text{cm}^{-1} * \text{\AA}^{-3}$ ) $* 10^8$	5396.07040
$a_3$ ( $\text{\AA}^{-3}$ )	-2.57888	0.59325	$b_4$ ( $\text{cm}^{-1} * \text{\AA}^{-4}$ ) $* 10^8$	-7061.59830
$a_4$ ( $\text{\AA}^{-4}$ )	-2.49191	-0.37994	$b_5$ ( $\text{cm}^{-1} * \text{\AA}^{-5}$ ) $* 10^8$	5513.40740
$a_5$ ( $\text{\AA}^{-5}$ )	2.60482	-0.02373	$b_6$ ( $\text{cm}^{-1} * \text{\AA}^{-6}$ ) $* 10^8$	-2637.44310
$a_6$ ( $\text{\AA}^{-6}$ )	2.12208	-0.12013	$b_7$ ( $\text{cm}^{-1} * \text{\AA}^{-7}$ ) $* 10^8$	755.31680
$a_7$ ( $\text{\AA}^{-7}$ )	-2.52526	0.12425	$b_8$ ( $\text{cm}^{-1} * \text{\AA}^{-8}$ ) $* 10^8$	-118.53909
$a_8$ ( $\text{\AA}^{-8}$ )	0.79210	-0.03487	$b_9$ ( $\text{cm}^{-1} * \text{\AA}^{-9}$ ) $* 10^8$	7.85136
$a_9$ ( $\text{\AA}^{-9}$ )	-0.08055	0.00312	$k$ ( $\text{\AA}^{-1}$ )	6.02160
RMS ( $\text{cm}^{-1}$ )	3.60	1.30	RMS ( $\text{cm}^{-1}$ )	1.34

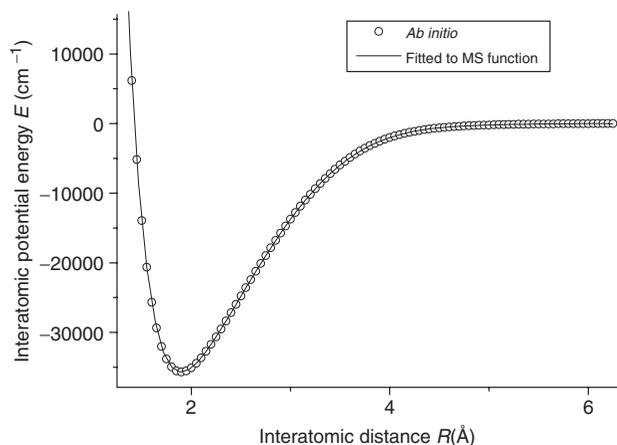


Figure 4. Potential energy curves of the  $X^1\Sigma$  states for the *ab initio* calculation at MRSDCI/aug-cc-PVQZ level and the fitted MS function.

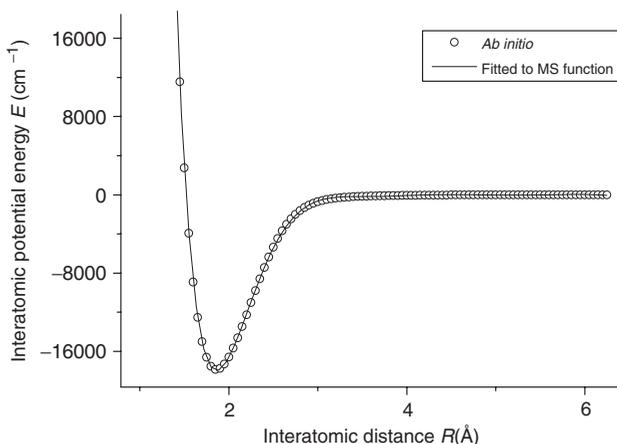


Figure 5. Potential energy curves of the  $a^3\Pi$  states for the *ab initio* calculation at MRSDCI/aug-cc-PVQZ level and the fitted MS function.

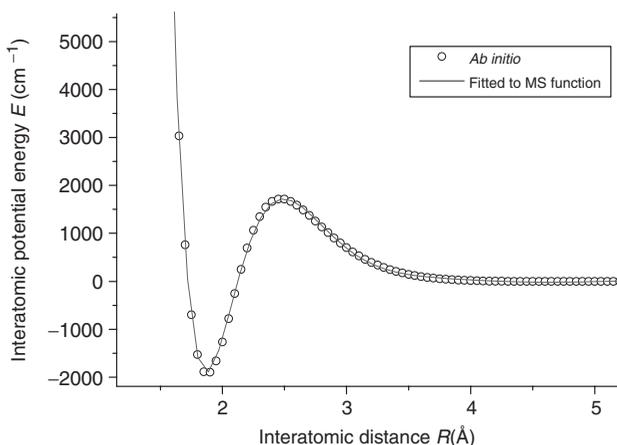


Figure 6. Potential energy curves of the  $A^1\Pi$  states for the *ab initio* calculation at MRSDCI/aug-cc-PVQZ level and the fitted MMS function.

and that the relativistic effect and Davidson modification may be unsuitable for the BBr molecule. Moreover, for the unmeasured ro-vibrational states of the  $A^1\Pi$  and three split  $^3\Pi$  states, our predictions could provide reasonably guidelines for laboratory research. It is also found that the MS function can perfectly reproduce the PECs of the two bound states  $X^1\Sigma^+$  and  $a^3\Pi$ , and the modified MS function proposed by Wang *et al.* can treat the metastable state- $A^1\Pi$  better, for its calculated RMS value is just  $1.34\text{ cm}^{-1}$ . However, the potential well of the  $^3\Sigma^+$  state is too shallow and narrow to be fitted with any functions; even the MMS function cannot give satisfactory results. A more complicated function is needed to deal with such metastable states.

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### References

- [1] P. Jensen and P.R. Bunker, *Computational Molecular Spectroscopy* (J. Wiley and Sons, New York, 2000), ISBN 978-0-471-48998-6.
- [2] J.F. Harrison, *Chem. Rev.* **100**, 679 (2000).
- [3] J.F. Harrison, *J. Phys. Chem.* **100**, 3513 (1996).
- [4] Chuan-Lu Yang, Yu-Jun Huang, Xin Zhang, *et al.*, *J. Mol. Struct. (Theochem)* **625**, 289 (2003).
- [5] Chuan-Lu Yang, Feng Gao, Xiao-Yan Zhang, *et al.*, *J. Chem. Phys.* **123**, 204308 (2005).
- [6] R.H. Burton, R.A. Gottscho, and G. Smolinsky, *Dry Etching for Microelectronics* (Elsevier, New York, 1984).
- [7] E. Miescher and M. Wehrli, *Helv. Phys. Acta* **6**, 256 (1933).
- [8] K.P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- [9] C. Destoky, H. Bredohl, and I. Dubois, *J. Mol. Spectrosc.* **134**, 314 (1989).
- [10] C. Destoky, I. Dubois, and H. Bredohl, *J. Mol. Spectrosc.* **136**, 216 (1989).
- [11] M. Nomoto, T. Okabayashi, and T. Klaus, *J. Mol. Struct.* **413**, 471 (1997).
- [12] N.T. Hunt, W.Y. Fan, Z. Liu, *et al.*, *J. Mol. Spectrosc.* **191**, 326 (1998).
- [13] J.M.L. Martin and A. Sundermann, *J. Chem. Phys.* **114**, 3408 (2001).
- [14] M. Dolg, U. Wedig, H. Stoll, *et al.*, *J. Chem. Phys.* **86**, 866 (1987).
- [15] W. Müller, J. Flesch, and W. Meyer, *J. Chem. Phys.* **80**, 3297 (1984).
- [16] G. Menconi and D.J. Tozer, *Chem. Phys. Lett.* **360**, 38 (2002).

- [17] Wenli Zou, Meirong Lin, Xinzheng Yang, *et al.*, Chem. Phys. Lett. **369**, 214 (2003).
- [18] Xinzheng Yang and J.E. Boggs, J. Chem. Phys. **124**, 194307 (2006).
- [19] H.-J. Werner and P. J. Knowles, J. Chem. Phys. **82**, 5053 (1985).
- [20] P.J. Knowles and H.-J. Werner, Chem. Phys. Lett. **115**, 259 (1985).
- [21] H.J. Werner and P.J. Knowles, J. Chem. Phys. **89**, 5803 (1988).
- [22] P.J. Knowles and H.J. Werner, Chem. Phys. Lett. **145**, 514 (1988).
- [23] D.E. Woon and T.H. Dunning Jr., J. Chem. Phys. **98**, 1358 (1993).
- [24] R.A. Kendall, T.H. Dunning Jr and R.J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
- [25] T.H. Dunning Jr, J. Chem. Phys. **90**, 1007 (1989).
- [26] K.A. Peterson, D.E. Woon, and T.H. Dunning Jr., J. Chem. Phys. **100**, 7410 (1994).
- [27] A. Wilson, T. van Mourik, and T.H. Dunning Jr., J. Mol. Struct. **388**, 339 (1997).
- [28] MOLPRO is a package of *ab initio* programs designed by H.-J. Werner and P.J. Knowles.
- [29] Dawning-4000A is a large parallel computer containing 134 CPUs (AMD Opteron 64-bit 1.8GHZ) in Ludong University. It is based on TURBO LINUX8.0 and implements with MOLPRO 2002, Gaussian 03, MOLCAS 5.0, and so on.
- [30] A. Berning, M. Schweizer, H.-J. Werner, *et al.*, Mol. Phys. **98**, 1823 (2000).
- [31] M. Douglas and N. M. Kroll, Ann. Phys. NY **82**, 89 (1974).
- [32] B.A. Hess, Phys. Rev. A **33**, 3742 (1986).
- [33] K. Anderson, M.R.A. Blomberg, M.P. Fülscher, *et al.*, MOLCAS (version 5.4 at Ludong University, Sweden, 2003).
- [34] Origin is a professional data analysis and graphing software for scientists and engineers, <http://www.originlab.com>.
- [35] R.J. Le Roy, LEVEL 7.4: A computer program for solving the radial Schrödinger equation for bound and quasibound levels, University of Waterloo Chemical Physics Research Report, CP-642R3 (2001).
- [36] J.N. Murrell and K.S. Sorbie, J. Chem. Soc. Faraday Trans. **2**, 1552 (1974).
- [37] F.H. Wang, C.L. Yang, and Z.H. Zhu, J. Mol. Struct. **684**, 9 (2004).
- [38] Xiao-Yan Zhang, Chuan-Lu Yang, Feng Gao, *et al.*, Chin. Phys. **15**, 1981 (2006).