Molecular properties and potential energy function model of BH under external electric field*

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Using the density functional B3P86/cc-PV5Z method, the geometric structure of BH molecule under different external electric fields is optimized, and the bond lengths, dipole moments, vibration frequencies, and other physical properties parameters are obtained. On the basis of setting appropriate parameters, scanning single point energies are obtained by the same method and the potential energy curves under different external fields are also obtained. These results show that the physical property parameters and potential energy curves may change with external electric field, especially in the case of reverse direction electric field. The potential energy function without external electric field is fitted by Morse potential, and the fitting parameters are obtained which are in good agreement with experimental values. In order to obtain the critical dissociation electric parameter, the dipole approximation is adopted to construct a potential model fitting the corresponding potential energy curve of the external electric field. It is found that the fitted critical dissociation electric parameter is consistent with numerical calculation, so that the constructed model is reliable and accurate. These results will provide important theoretical and experimental reference for further studying the molecular spectrum, dynamics, and molecular cooling with Stark effect.

Keywords: BH molecule, potential function model, external electric field

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1. Introduction

Diatomic hydride BH is the most typical neutral polar molecule and an important candidate molecule in molecular AC and DC Stark effect cooling, which has a large permanent electric dipole moment, and will be affected by the electric dipole force under external electric fields. In previous years, there have been abundant studies of the BH molecule. Using the SAC-CI method, the spectrum data of ground state and many low-lying excited states of BH were calculated by Ishida[1] in 2001. Xie *et al.*[2] scanned single-point energy of the ground state ($X^1\Sigma^+$), first excited state ($A^1\pi$), and second excited state ($B^1\Sigma^+$) using the SAC-CI/cc-PVTZ GSUM module, and obtained its molecular potential energy functions and spectroscopic constants in 2005. Zhu *et al.*[3] calculated the single-point energy of ground state ($X^1\Sigma^+$) and two excited states ($B^1\Sigma^+$, $C'\Delta^1$) by the same method and cc-PVDZ basis, and obtained the potential energy functions and spectroscopic constants in the ground state and excited state in 2006. The following year, Zhu *et al.*[4] obtained the spectroscopic constants and potential energy function expression of two excited states $A^3\pi$ and $C'\Delta^1$ using the same method. In 2009, Wang *et al.*[5] used the multi-reference configuration interaction method with aug-cc-PV5Z, and gained the potential energy curves and spectrum constants in the ground state ($X^1\Sigma^+$) and six electronic excited states ($A^3\pi$, $A^1\pi$, $B^1\Sigma^+$, $B^3\Sigma^+$, $b^3\Sigma^-$ and $C'\Delta^1$) of the BH molecule. Zeng *et al.*[6] studied the electron structure of BH under an external electric field by B3LYP/6-311++g** method in 2009. However there has been no study on the potential energy function and critical dissociation electric field of BH under an external electric field.

Due to the effect of the external electric field, the molecular Hamiltonian system energy based on no external electric field increases the interaction Hamiltonian of external electric field and molecular systems, and then the problem becomes more complicated, but in the dipole approximation, the energy of the molecular system can be divided into zero-field potential energy and the interaction potential of the external field with the molecule.[7–10] In this paper we perform the optimum calculating of molecular structures and physical properties by adopting B3P86/cc-PV5Z method, scan the single-point energies by the same method, and obtain potential energy curves of the BH molecule under different external electric fields. The corresponding potential energy curves under external electric fields are fitted by the constructed potential model in the dipole approximation, and the critical dissociation electric parameters are obtained. The critical dissociation electric parameters are compared with numerical calculations and theoretical analyses, further confirming the rationality and reliability of the potential energy function model.

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2. Theoretical details

In the present work, we perform the optimum calculating of the ground state geometry structure and energy of the BH molecule in the zero-field using different methods and basis sets. By comparing the calculations with experimental data and the relevant minimum energy principle,[11] the B3P86 method with cc-PV5Z basis set is elected. Along Z axis (H–B direction) with different external electric fields (−0.04 a.u.–0.04 a.u., the unit a.u. is the abbreviation for atomic unit), we analyze the relations of geometry, dipole moment and the vibration frequency of the BH molecule to the magnitude and direction of the external electric field. Using the same method and basis set, the single-point energies of the BH molecule are scanned under different external fields; afterwards the potential energy curves are obtained through the drawing software. All calculations are carried out using Gaussian03.

After the potential energy curve is obtained, the potential energy function in zero-field is fitted to Morse function, and the potential parameters are obtained. On this basis, we use the constructed model of molecular potential energy function to fit the potential energy curve under external electric field. By comparing the fitting parameters with numerical calculation data, the rationality and reliability of the model are judged and the critical dissociation electric parameters are obtained.

3. Analytical potential energy function model

At zero-field, the potential energy curve is fitted by Morse potential model. The Morse potential is applied to the three-parameter function of a stable diatomic molecule[12]

$$V(r) = D_e[1 - e^{-a(r-R_e)}]^2, \tag{1}$$

where D_e is the dissociation energy, a is the Morse parameter, R is the inter-nuclear distance, and R_e is its equilibrium distance.

Under an external electric field, the Hamiltonian of molecular system energy will increase the interaction between the external electric field and the molecular system, and H is given as[13,14]

$$H = H_0 + H_{int}, \tag{2}$$

where H_0 is the Hamiltonian at zero-field, and H_{int} is the interaction Hamiltonian between the external electric field and the molecular system. Thus the problem will become more complicated, but under the dipole approximation, the Hamiltonian of external field E and molecular system interaction can be expressed as

$$H_{int} = -\mu \cdot E. \tag{3}$$

Here, μ is the dipole moment and E is the external electric field. Therefore, the molecular potential energy under an external field can be divided into zero-field potential energy and the interaction potential of the external field with the molecule, and the scalar expression is

$$V(r) = D_e(1-y)^2 + br, \tag{4}$$

where $y = e^{-a(r-R_e)}$, $b = -E(q + \alpha E)$ is the related quantity to external electric field (equivalent to the electric field force). When no external electric field exists, the potential energy minimum point is at R_e, D_e is the dissociation energy if zero point vibrational energy is not considered, a is the Morse parameter, r is the nuclear space, q is the dipole charge corresponding to the intrinsic dipole moment, and α is its polarizable parameter, which is the induced dipole moment under an external electric field corresponding to molecular polarization.

4. Results and discussion

4.1. Molecular properties of BH without an external electric field

The BH molecule is a linear diatomic molecule, which belongs to $C_{\infty V}$. The calculated results show that the electronic state is $X^1\Sigma^+$ obtained by different methods and basis sets. The equilibrium geometries and energies from this paper, literature,[6] and experiment[15] are all listed in Table 1. It can be seen from Table 1 that the calculation results obtained with B3P86 method and cc-PV5Z basis set are close to experimental values, and the energy is lowest. Hence, both the structural parameters and potential energy are calculated at the level of B3P86/cc-PV5Z in this paper.

Table 1. Equilibrium structural parameters of BH obtained with different methods.

	B3LYP/6-311g	B3LYP/cc-PV5Z	B3LYP/6-311++g**[6]	B3P86/6-311g	B3P86/cc-PV5Z	B3P86/6-311++g**[6]	Exp.
R_e/nm	0.1242	0.1230	0.12349	0.1247	0.1233	0.124	0.12327
E/a.u.	–25.2901	–25.3016	–25.297561	–25.3862	–25.3962	–25.392416	–

4.2. Molecular properties of BH under different external electric fields

When different external electric fields, namely positive electric field (0 a.u.–0.04 a.u.) and reverse electric field (−0.04 a.u.–0 a.u.), are applied along the Z axis, the optimum calculation of stable geometrical structures of BH is conducted by B3P86/cc-PV5Z. The results indicate that the BH molecular ground state is still $X^1\Sigma^+$ under different external electric fields, its bond

lengths, dipole moments, and vibration frequencies are shown in Table 2. According to Table 2, the calculated values are in accordance with the literature data,[6] the bond length of BH decreases with the increase of the positive electric field, but increases with negative electric field increasing, the dipole moment and vibration frequency increase with the increase of positive electric field, but decrease with reverse electric field increasing. Therefore the positive electric field changes gently, while reverse electric fields change greatly.

Table 2. Bond lengths, dipole moments, and vibration frequencies under different external electric fields.

E/a.u.	–0.04	–0.03	–0.02	–0.01	0	0.01	0.02	0.03	0.04
R_e/nm	0.1415	0.1337	0.1289	0.1258 (0.12565)	0.1233 (0.12349)	0.1222 (0.12201)	0.1212	0.1206	0.1204
μ/Debye	0.9760	1.2385	1.3938	1.4925	1.5580	1.6024	1.6326	1.6488	1.6538
f/cm^{-1}	1436.4	1793.6	2036.6	2211.2 (2212.059)	2337.2 (2340.569)	2428.8 (2431.141)	2426.1	2424.5	2422.2

4.3. Potential energy function of BH under external electric fields

4.3.1. Potential energy function of BH without external electric field

Without an external electric field, the single-point energy of the BH molecule is scanned by the same method, in which the nucleus distance changes in steps of 0.005 nm, and calculated 50 *ab initio* potential energies. Firstly, the potential energy curve without an external electric field is plotted in Fig. 1 by adopting Origin7.0 software; afterwarda, it is fitted to the Morse potential function and potential parameters are obtained. The parameters, literature data,[6] and experimental data[15] are all given in Table 3, the fitting curve is shown in Fig. 1. It can be seen from the table and figure that the fitting parameters are accordant with experimental data and the relative errors are only 0.02% and 0.08%. These results show that the model can be reliably used to fit the potential energy function under an external electric field.

Table 3. Potential fitting parameters of BH without external electric field.

	Calculation value	Fitting value	Literature value	Exp.
R_e/nm	0.1233	0.1233	0.1254	0.12327
D_e/eV	3.749	3.562	3.74	3.565
a/nm^{-1}	–	13.663	–	–

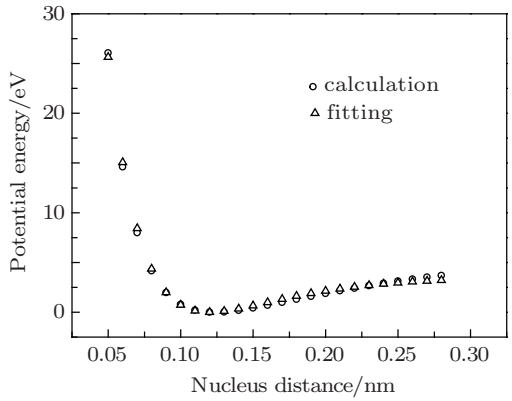


Fig. 1. Potential energy curves without external electric field.

4.3.2. Potential energy functions of BH under different external electric fields

Applying different external electric fields, namely positive electric fields (0.01 a.u.–0.04 a.u.) and reverse electric fields (−0.04 a.u.–0.01 a.u.) along the Z axis, the single-point energies are scanned using the same method. The nucleus distance changes in steps of 0.01 nm, and calculated 55 and 30 *ab initio* potential energies at positive and reverse electric field, respectively. The potential energy curves under external electric fields are all shown in Fig. 2, where the insets exhibit the

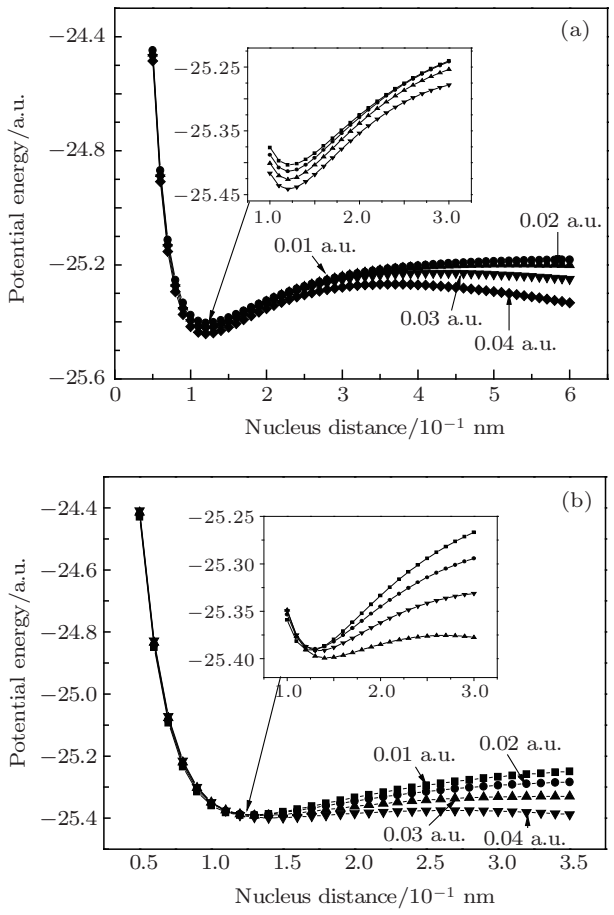


Fig. 2. Plots of potential energy versus nucleus distance under different external electric fields.

curves of potential energy near equilibrium bond length. According to Fig. 2, the dissociation energy declines slowly and the equilibrium nuclear distance changes gently with the gradual increase of positive electric field, but as reverse electric field increases, the dissociation energy decreases sharply and equilibrium nuclear distance increases gently. The potential energy curve has a stable minimum and an unstable maximum point, similar to the volcano state,[12,16] the barrier decreases between minimum and maximum points and equilibrium bond length increases. When a critical electric field is reached, the stable point of the potential energy curve disappears, the barrier tends to be 0 and the molecule dissociates, which explains the fact that the dissociation energy decreases as external electric field increases, but decreases obviously in reverse electric field, that is to say, the molecule will more easily dissociate. These analyses are consistent with the variety of physical properties. Therefore the critical dissociation electric parameters should be identified from the reverse electric field.

In order to find the critical dissociation electric field from numerical calculation, the molecular structure of the reverse electric field (-0.05 a.u. and -0.06 a.u.) is optimized. When the reverse electric field arrives at -0.06 a.u., the optimization will not be carried out any more, so it must make a new start of optimization as the reverse electric field decreases slightly. The results show that the optimization will not be carried out any more if the reverse electric field is more than -0.056 a.u. Through scanning the single energies of the reverse electric field (-0.05 a.u, -0.055 a.u., and -0.056 a.u.), the potential energy curves are obtained as shown in Fig. 3. It can also be seen from the figure that the stable point disappears when the reverse electric field reaches -0.056 a.u., which shows that the molecule dissociates. Consequently, the critical dissociation field of the BH molecule is -0.056 a.u., the corresponding dissociation bond length is 0.1773 nm, and dipole moment is 4.9745 Debye.

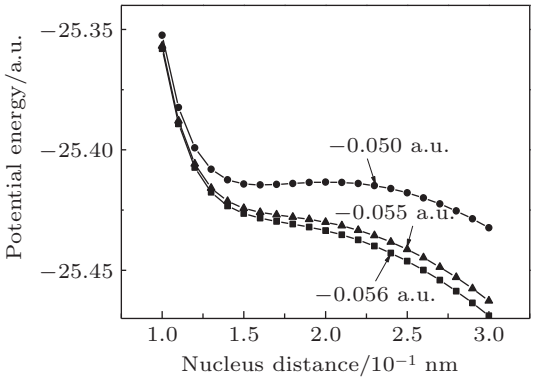


Fig. 3. Potential energy curves under critical dissociation fields.

4.3.3. Potential model fitting parameters of BH in reverse electric field

Using the constructed model, the different potential curves in reverse external electric fields are fitted, and then the parameters of potential energy function analytical expression are obtained as listed in Table 4, where D_e and a are the parameters for the case of no external field and b is the parameter under external field.

Table 4. Potential fitting parameters of BH under different external fields.

E/a.u.	–0.01	–0.02	–0.03	–0.04	–0.05	–0.055	–0.056
b/eV·nm^{-1}	–1.313	–5.101	–7.652	–12.858	–18.547	–22.457	–23.617

In order to calculate the critical parameters, $z = b/2aD_e$ is introduced. According to the potential energy extremum condition, the critical dissociation bond length can be obtained as

$$R_c = R_e + 1/a \ln 2 = R_e + 0.6931/a. \quad (5)$$

Due to the fact that the BH molecule is a heteronuclear diatomic molecule, the molecular polarization is ignored in external fields, then $\alpha = 0$, the critical dissociation field E_c can be obtained by dissociation conditions as

$$E_c = aD_e/2q. \quad (6)$$

The critical dissociation electric field and bond length are calculated by the above two formulas under different external electric fields. The results indicate that when the external electric field is -0.056 a.u., the critical dissociation electric field E_c and bond length R_c are -0.057 a.u. and 0.1739 nm, respectively, which are close to numerical calculations, with the relative errors being only 1.79% and 1.91%. These results show that the constructed model is reasonable and reliable.

5. Conclusions

The optimum calculation of BH molecular geometries and physical property parameters is conducted by B3P86/cc-PV5Z method under different external electric fields, at the same time single-point energy is scanned with the same method and basis set. The results show that the equilibrium bond lengths, dipole moments, and vibration frequencies are all changed with an external electric field, and the changed amplitudes of reverse electric fields are larger than those of positive electric fields. The barrier of the potential energy curve between minimum and maximum point decreases and equilibrium bond length increases. The potential energy curves without an external electric field are fitted using the Morse model, and potential parameters are obtained which are in good agree-

ment with experimental values. The different reverse electric potential energy curves are fitted by the constructed potential model under external electric fields, and the corresponding fitting parameters are obtained. On the basis of the above data, the calculated critical dissociation electric field parameters are compared with numerical calculations, with the relative errors being only 1.79% and 1.91%, which explains the fact that the constructed model is reasonable and reliable. These results will provide important theoretical and experimental reference for further investigating molecular spectrum, dynamics, and Stark effect cooling.

References

[1] Ishida M, Toyota K, Ehara K and Nakatsuji H 2001 *Chem. Phys. Lett.* **347** 493

[2] Xie A D, Shi D H, Zhu Z L and Zhu Z H 2005 *Acta Phys. Chim. Sin.* **21** 658 (in Chinese)

[3] Zhu Z L, Ma H and Sun J F 2006 *J. Atom. Mol. Phys.* **6** 1092 (in Chinese)

[4] Zhu Z L, Sun J F, Shi D H and Zhu Z H 2007 *J. Mol. Struct. (Theochem)* **802** 7

[5] Wang X Q, Yang C L, Su T and Wang M S 2009 *Acta Phys. Sin.* **58** 6873 (in Chinese)

[6] Zeng F J, Linghu R F and Yang M 2009 *J. Kaili University* **27** 28

[7] Xu G L, Liu X F, Xie H X, Zhan X Z and Liu Y F 2010 *Chin. Phys. B* **19** 113201

[8] Xu G L, Liu X F, Yuan W, Zhan X Z and Liu Y F 2012 *Chin. Phys. B* **21** 053101

[9] Huang D H, Wang F H, Wan M J and Jiang G 2013 *Acta Phys. Sin.* **62** 013104 (in Chinese)

[10] Xu M, Linghu R F, Li Y F, Yang X D and Wang X L 2012 *Acta Phys. Sin.* **61** 093102 (in Chinese)

[11] Zhu Z H 1996 *Atomic and Molecular Reaction Statics* (Beijing: Science Press) (in Chinese)

[12] Zhu Z H and Yu H G 1997 *Molecular Structure and Potential Energy Function* (Beijing: Science Press) (in Chinese)

[13] Xu G L, Zhu Z H, Ma M Z and Xie A D 2005 *Acta Phys. Sin.* **54** 3087 (in Chinese)

[14] Chaudhuri R K, Mudholkar A, Freed K F, Martin C H and Sun H 1997 *J. Chem. Phys.* **106** 9252

[15] Huber K P and Herzberg G 1978 *Molecular Spectra and Molecular Structure IV: Constants of Diatomic Molecules* (New York: Van Nostrand Reinhold Company)

[16] Ran M, Gao T, Huang P and Zhu Z H 2004 *Chin. J. Chem. Phys.* **14** 28 (in Chinese)