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Structure and analytical potential energy function for the ground state of the BC^x (x=0, −1)*

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In this paper, the electronic states of the ground states and dissociation limits of BC and BC^- are correctly determined based on group theory and atomic and molecular reaction statics. The equilibrium geometries, harmonic frequencies and dissociation energies of the ground state of BC and BC^- are calculated by using density function theory and quadratic CI method including single and double substitutions. The analytical potential energy functions of these states have been fitted with Murrell–Sorbie potential energy function from our ab initio calculation results. The spectroscopic data (α_e, ω_e and $\omega_e\chi_e$) of each state is calculated via the relation between analytical potential energy function and spectroscopic data. All the calculations are in good agreement with the experimental data.

Keywords: ab initio, ground state, potential energy function
PACC: 3110, 3120D, 3130

1. Introduction

The analytical potential energy function (APEF) of two-atom-molecules is the complete description of geometric and electric structure of the molecule, and it is the key to study molecular reaction dynamics.[1−3] For example, to determine the spectroscopic parameters or to perform collision calculations, the APEF of two-atom-molecules is very useful. This kind of APEF is also necessary if one wants to deduce polyatomic molecular APEF by using the many-body expansion method.[4−5]

Nowadays, with modern quantum chemical methods and powerful computers, ab initio calculations can give more and more accurate potential energy curves with serial points, in particular for small molecules.[6]

The simple diatomic BC was first observed by Verhaegen *et al* in 1964,[7] and they also determined its dissociation energy. In 1989 the first spectroscopic study by electron spin resonance[8] confirmed that the ground BC state is $X^4\Sigma^-$ which is in accord with earlier theoretical predictions. Most authors focused their work on optimizing equilibrium geometries and electronic states.[9] However, no APEF of BC has been reported up to now. With the purpose to understand well the structure of BC we have also performed calculations on the anion BC^-. In this work, firstly we deduced the dissociation limits of BC and BC^-, and then using quadratic CI method including single and double substitutions (QCISD) in Gaussian software we optimized equilibrium geometries and calculated single point energy of BC and BC^-. Based on the ab initio results, we deduced the APEFs of them by the Murrell–Sorbie (M-S) potential energy function and least squares fitting method. In order to appreciate reliability of the APEF near the equilibrium position, the spectroscopic parameters had also been calculated and compared with the experimental data.

2. Theoretical details

2.1. Dissociation limits

It is well known that the APEF of different electronic states are different and states dissociating in different channels are different. To deduce molecular APEF, the molecular electronic states and the atomic states after dissociating, i.e. dissociation limits, have

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to be determined first, otherwise we cannot obtain correct potential energy functions. By employing the principles of atomic and molecular reaction statics,[10] we can deduce the molecular dissociation limits step by step.

2.1.1. BC($X^4\Sigma^-$)

The ground state of BC dissociates adiabatically into two ground states of B and C atoms, so its equilibrium configuration is $C_{\infty v}$. According to the group theoretical derivation of molecular electronic states, we resolve the atomic group representations into $C_{\infty v}$ because the BC molecule has $C_{\infty v}$ symmetry. Then the direct products of $C_{\infty v}$ representations of the two atoms are the possible states of the molecule. The ground states of B and C are $^2\mathrm{P_u}$ and $^3\mathrm{P_g}$ respectively, so the possible states of BC corresponding to the dissociation limit are

$$^2\Sigma^-,\quad ^2\Pi,\quad ^2\Delta,\quad ^4\Sigma^+,\quad ^4\Sigma^-,\quad ^4\Pi,\quad ^4\Delta$$

There is $^4\Sigma^-$ state among the possible states, according to the principle of reversibility for the microscopic process, the dissociation limit of BC($X^4\Sigma^-$) is

$$\mathrm{BC}(X^4\Sigma^-) \rightarrow \mathrm{B}(^2\mathrm{P_u}) + \mathrm{C}(^3\mathrm{P_g}). \qquad (1)$$

2.1.2. $\mathrm{BC}^-(X^3\Pi)$

The possible dissociation limits channels of BC^- are:

$$\mathrm{BC}^- \rightarrow \mathrm{B} + \mathrm{C}^-, \qquad (2)$$

$$\mathrm{BC}^- \rightarrow \mathrm{B}^- + \mathrm{C}. \qquad (3)$$

The orbital electronegativities of B and C are 2.04 and 2.55[11] respectively. The greater the orbital electronegativities are, the more powerful attraction to electron is, when chemical bond is formed. So it can be seen that channel (2) is better than channel (3) of the possible dissociation limits channels of BC^-. Ground electronic state of B is $^2\mathrm{P_g}$, and ground electronic state of C^- is $^4\mathrm{S_u}$. According to the principle of reversibility for the microscopic process of atomic and molecular statics, the dissociation limit of $\mathrm{BC}^-(X^3\Pi)$ is

$$\mathrm{BC}^-(X^3\Pi) \rightarrow \mathrm{B}(^2\mathrm{P_g}) + \mathrm{C}^-(^4\mathrm{S_u}). \qquad (4)$$

3. Results and discussion

3.1. Structure parameters of BC($X^4\Sigma^-$) and $\mathrm{BC}^-(X^3\Pi)$

Ab initio methods have been extensively used to study the structures and spectra of atom and molecule. For BC, it is well known from previous ab initio studies that the ground state is $X^4\Sigma^-$, with a $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^1(1\pi)^2$ occupation scheme. The ground state of BC^- is $X^3\Pi$. Therefore we focus exclusively on these states. We know that the Hartree–Fock and semi-empirical methods are inadequate because of overlooking the electronic correlation effects.[12] Density function theory (DFT) calculation was carried out by using Becke–Lee–Yang–Parr's three-parameter hybrid functional (referred to as B3LYP) method and QCISD. By employing 6-311++G(2df, 2pd) basis sets we optimized the structures of BC($X^4\Sigma^-$) and $\mathrm{BC}^-(X^3\Pi)$ (Tables 1 and 2). After comparing and analysing, it can be seen that the results of QCISD are closer to experimental data,[13] so we computed more features of BC($X^4\Sigma^-$) and $\mathrm{BC}^-(X^3\Pi)$ using the QCISD method.

Table 1. Data of geometry optimization of BC ($X^4\Sigma^-$).

method	electric state	R_e/nm	E/eV	μ/Debye	ω_e/cm^{-1}
B3LYP	$X^4\Sigma^-$	0.1482	–62.685	1.299	1299.8
QCISD (T)	$X^4\Sigma^-$	0.1488	–62 .521	2.615	1166.6
Expt	$X^4\Sigma^-$	0.1491			1172

Table 2. Data of geometry optimization of $\mathrm{BC}^-(X^3\Pi)$.

method	electric state	R_e/nm	E/eV	μ/Debye	ω_e/cm^{-1}
B3LYP	$X^3\Pi$	0.1425	–62.763	1.7415	1349.6
QCISD (T)	$X^3\Pi$	0.1441	–62.587	1.2365	1299.8
MRCI[13]	$X^3\Pi$	0.1445			1301.4

3.2. APEF

In order to describe the APEF of diatomic molecules, a number of functions have been proposed. Among them, the M-S potential energy function is a better one. It can describe the interaction potential energies of neutral and ionic diatomic molecules well, and has been used for many molecules.[14] Now, we try to use it to describe BC($X^4\Sigma^-$) and BC^-($X^3\Pi$) molecule. The common M-S function is

$$V(\rho) = -D_e(1 + \sum_{i=1}^{n} a_i\rho^i)\exp(-a_1\rho), \qquad (5)$$

where $\rho = R - R_e$, R and R_e are the interatomic distance and the equilibrium bond length respectively, D_e is the dissociation energy. The parameters a_i and D_e are determined by fitting. In this paper they are all deduced from the computational data with ab initio method.

Usually, the fitted potential energy curve (PEC) is in agreement with the *ab initio* data when n equals 3, and no obvious improvement when n augments further. This fact leads to a 4-parameter M-S function as

$$V = -D_e(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho). \qquad (6)$$

Based on the relation between spectroscopic parameters and APEF, we can calculate the spectroscopic parameters. Furthermore, the precision and credibility of the APEF can be examined by comparing the calculated spectroscopic parameters with experimental counterparts directly. First of all, the force parameters can be determined from the parameters of M-S potential energy function

$$f_2 = D_e(a_1^2 - 2a_2), \qquad (7)$$

$$f_3 = 6D_e\left(a_1a_2 - a_3 - \frac{a_1^3}{3}\right), \qquad (8)$$

$$f_4 = D_e(3a_1^4 - 12a_1^2a_2 + 24a_1a_2), \qquad (9)$$

where f_2, f_3, f_4 are quadratic, cubic and quartic force parameters respectively. Then the spectroscopic parameters are

$$B_e = \frac{h}{8\pi\mu cR_e^2}, \qquad (10)$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(\frac{f_3R_e}{3f_2} + 1\right), \qquad (11)$$

$$\omega_e\chi_e = \frac{B_e}{8}\left(-\frac{f_4R_e^2}{f_2} + 15\left(1 + \frac{\omega_e a_e}{6B_e^2}\right)^2\right), \qquad (12)$$

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2\mu c^2}}. \qquad (13)$$

Using the M-S potential energy function and least squares fitting method, we get the APEFs and parameters of M-S function. Based on the fitted APEFs and Eqs.(5)–(13), we can calculate the spectroscopic parameters of these states. All the calculation results are collected in Tables 3–5.

The potential energy curves (PECs) of BC($X^4\Sigma^-$) and BC^-($X^3\Pi$) are computed at QCISD / 6-311++G (2df, 2pd) level. The increasing step of calculation is 0.01nm, and we computed 70 scattered potential energy points in total. In addition, we performed optimization calculation to find the equilibrium distance and minimum energy. Therefore the PEC is composed of 70 potential energy points. These calculations give the dissociation energy of BC($X^4\Sigma^-$) 4.158eV, which is close to the experimental value 4.597eV. While the dissociation energy of BC^-($X^3\Pi$) is 5.588eV.

Table 3. Calculated data of BC($X^4\Sigma^-$) and BC^-($X^3\Pi$): dissociation energy D_e(eV), parameters of MS functions a_1 ($10nm^{-1}$), a_2 (10^2nm^{-2}), a_3(10^3nm^{-3}), and force parameters f_2($10^2aJ{\cdot}nm^{-2}$), f_3($10^3aJ{\cdot}nm^{-3}$), f_4($10^4aJ{\cdot}nm^{-4}$).

Molecule	D_e	a_1	a_2	a_3	f_2	f_3	f_4
BC	4.158	2.745	0.409	0.567	4.678	–25.294	113.505
BC^-	5.588	3.496	2.767	1.019	5.981	–29.992	114.341

Note: $1aJ=10^{-18}J$.

Table 4. Data of BC($X^4\Sigma^-$): energies E (hartrees), harmonic frequencies and anharmonic corrections ω_e (cm^{-1}), $\omega_e\chi_e$ (cm^{-1}), rotational vibrational couplings a_e ($cm^{-1)}$), bond lengths r_e (nm), dissociation energies D_e (eV), and dipole moment $\mu(D)$.

	$-E$	ω_e	$\omega_e\chi_e$	$a_e(10^{-2})$	r_e	D_e	μ
QCISD	62.4	1166.6	9.06	1.550	0.1488	4.158	2.615
RHF-CCSD(T)[9]	62.5	1147.9	10.2		0.1502		
Expt		1172	10.3		0.1491	4.597	

Table 5. Data of $BC^-(X^3\Pi)$: energies E (hartrees), harmonic frequencies and anharmonic corrections ω_e (cm^{-1}), $\omega_e\chi_e$ (cm^{-1}), rotational vibrational couplings a_e ($cm^{-1)}$), bond lengths r_e (nm), dissociation energies D_e (eV), and dipole moment $\mu(D)$.

	$-E$	ω_e	$\omega_e\chi_e$	$a_e(10^{-2})$	r_e	D_e	μ
QCISD	62.4	1299.8	8.44	1.32	0.1441	5.588	1.236
MRCI[13]		1301.4	9.82	1.55	0.1445		

The result of calculation of $BC(X^4\Sigma^-)$ can be seen in Table 4: ω_e and r_e are in excellent agreement with the experimental values, and are much better than those of RHF-CCSD(T). As there are no experimental single point energy data available, we compared our result with the calculated results of RHF-CCSD(T), and the two results are almost the same. D_e is computed in this work as well, which is close to the experimental data.

For $BC^-(X^3\Pi)$, there are no experimental data available so we compared our work with the results of MRCI calculation. It can be seen in Table 5 that ω_e and r_e are almost the same. $\omega_e\chi_e$ and a_e are smaller than their results, but provides useful reference for future experiment.

3.3. Potential energy curves of $BC(X^4\Sigma^-)$ and $BC^-(X^3\Pi)$

Figures 1, 2 are PECs of $BC(X^4\Sigma^-)$ and $BC^-(X^3\Pi)$ respectively. The scattered points are theoretically calculated, and the real lines are fitted PECs of these points. We can see from these figures that the dissociation energies and equilibrium bond lengths of fitting are in excellent agreement with calculated ones and the APEFs are in good agreement with ab initio values on the whole. It shows that the M-S function can precisely describe the potential energy of $BC(X^4\Sigma^-)$ and $BC^-(X^3\Pi)$.

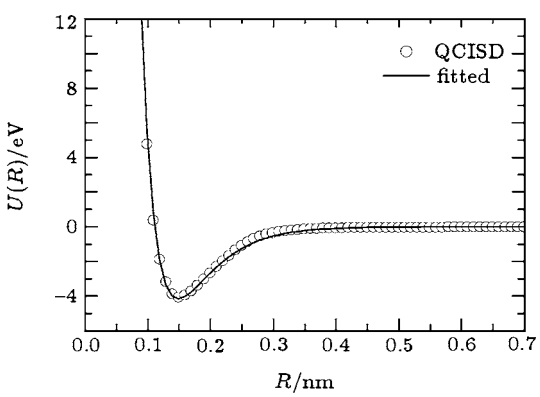


Fig.1. PEC of $BC(X^4\Sigma^-)$.

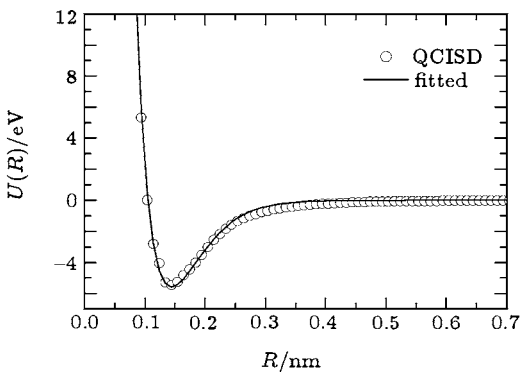


Fig.2. PEC of $BC^-(X^3\Pi)$.

4. Conclusion

In this work, the ground electronic structure of the carbide BC and the corresponding anion BC^- have been investigated. Optimization of the geometry structure of BC and BC^- are performed by using B3LYP and QCISD method. Then the energy of BC and BC^- are scanned at QCISD/6-311++G(2df, 2pd) level. The APEFs of these states are obtained by using the M-S potential energy function and least squares fitting method from our ab initio calculation results; finally spectroscopic data (α_e, ω_e and $\omega_e\chi_e$) of each state have been obtained. All these calculation results can be used to study their reactive dynamics features.

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