# Potential energy curves and spectroscopic properties of $X^2\Sigma^+$ and $A^2\Pi$ states of $^{13}C^{14}N$*

Liao Jian-Wen(廖建文)[a] and Yang Chuan-Lu(杨传路)[b]†

[a] *Yibin Vocational and Technical College, Yibin* 644003, *China*

[b] *School of Physics and Optoelectronic Engineering, Ludong University, Yantai* 264025, *China*

(Received 26 September 2013; revised manuscript received 16 December 2013; published online 15 May 2014)

The potential energy curves (PECs) of $X^2\Sigma^+$ and $A^2\Pi$ states of the CN molecule have been calculated with the multi-reference configuration interaction method and the aug-cc-pwCV5Z basis set. Based on the PECs, all of the vibrational and rotational levels of the $^{13}C^{14}N$ molecule are obtained by solving the Schrödinger equation of the molecular nuclear motion. The spectroscopic parameters are determined by fitting the Dunham coefficients with the levels. Both the levels and the spectroscopic parameters are in good qualitative agreement with the experimental data available. The analytical potential energy functions are also deduced from the calculated PECs. The present results can provide a helpful reference for future spectroscopy experiments or dynamical calculations of the molecule.

**Keywords:** multi-reference configuration interaction method (MRCI), potential energy curves, analytical potential energy functions, spectroscopic parameters

**PACS:** 34.20.Cf, 31.50.Df, 33.20.–t **DOI:** 10.1088/1674-1056/23/7/073401

## 1. Introduction

The CN molecule has attracted the attention of researchers for over a century. Recently, its spectroscopic properties have been studied in many theoretical and experimental investigations. Ram *et al.*[1] observed the emission spectrum of the $B^2\Sigma^+$–$X^2\Sigma^+$ system of CN with a high resolution using a Fourier transform spectrometer. A large number of bands involving vibrational levels $v = 0$–15 of both electronic states were obtained and analyzed. The spectroscopic parameters for the two states were also determined. Theoretically, Xiong *et al.*[2] obtained the analytical potential energy function (APEF) and some spectroscopic parameters for the ground state of CN with a method based on the density functional theory and the single reference configuration state. In 2011, Shi *et al.*[3] investigated the ground state and the low-lying excited states of CN with the multi-reference configuration interaction (MRCI) method.[4,5]

The spectroscopy of the isotopic CN molecule has recently received special attention. In 2012, Ram and Bernath[6] measured the high resolution emission spectra of the $A^2\Pi$–$X^2\Sigma^+$ transition of $^{13}C^{14}N$ in the range of 15000–24000 $cm^{-1}$. Colin and Bernath[7] investigated the emission spectra of the $B^2\Sigma^+$–$X^2\Sigma^+$ (violet) system of the $^{12}C^{15}N$ molecule with the same method in the same year. A number of rotational and vibrational levels of the molecule were obtained, and some molecular constants were determined. However, as far as we know, there has been no report on the theoretical investigation for the spectroscopy or the molecular constants of these isotopic molecules.

In the present work, we obtain the potential energy curves (PECs) with high level configuration interaction calculations. The rotational and vibrational energy levels are obtained by solving the Schrödinger equation of nuclear motion based on the *ab initio* PECs. The spectroscopic parameters are determined from the vibrational levels with the Dunham expansion. We fit the PECs into APEFs using the Aguado–Paniagua (AP)[8,9] potential function in order to provide a convenient expression to build an analytical potential energy surface of the polyatomic system or to study the dynamics of the photo dissociation and photo association of the molecule.

## 2. Computational method

### 2.1. Technical details for the calculations of PECs

The MRCI method[4,5] is an accurate and effective method to obtaining a PEC, which has been used for many diatomic molecules.[10–15] Therefore, we use the MRCI method to obtain the accurate PECs for states $X^2\Sigma^+$ and $A^2\Pi$ of the CN molecule. These MRCI calculations are preceded by the complete active space self-consistent field (CASSCF) calculations, in which all the valence molecular orbitals are optimized. In the present CASSCF calculations, 10 occupation orbitals (6, 2, 2, 0) are used and 8 (4, 2, 2, 0) are chosen as

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11174117 and 11374132) and the Program for Scientific Research Innovation Team in Colleges and Universities of Shandong Province, China.

†Corresponding author. E-mail: scuycl@gmail.com

© 2014 Chinese Physical Society and IOP Publishing Ltd 

the active space. The basis set aug-cc-pwCV5Z is used. This means that (19s, 13p, 8d, 6f, 4g, 2h) primitive Gaussian functions are contracted to [11s, 10p, 6d, 6f, 4g, 2h] for both C and N atoms. The energies of the PECs are calculated in the range of internuclear distance from 0.8 Å to 5.6 Å with a step of 0.05 Å. The effect of the Davidson correction is included to obtain more accurate PECs. All *ab initio* calculations are performed with the MOLPRO codes.[16]

### 2.2. Vibrational levels and spectroscopic parameters

The rotational and vibrational energy levels are determined by solving the Schrödinger equation of nuclear motion with the *ab initio* PECs, these calculations are carried out with the LEVEL program package.[17] The spectroscopic parameters are determined from the rotational vibrational energy levels with the Dunham expansion[18]

$$T(v,N)=\sum_{m,n}Y_{mn}\left(v+\frac{1}{2}\right)^{m}[N(N+1)]^{n}. \tag{1}$$

Here, $v$ is the vibrational quantum number and $N$ represents the rotational levels. The Dunham coefficients $Y_{mn}$ are calculated using a least-square fitting procedure from the rotational vibrational energy levels, they are related to more familiar spectroscopic constants as follows:

$$\begin{aligned}&Y_{10}\approx\omega_{\rm e},\quad Y_{20}\approx-\omega_{\rm e}\chi_{\rm e},\quad Y_{30}\approx\omega_{\rm e}y_{\rm e},\\&Y_{40}\approx\omega_{\rm e}z_{\rm e},\quad Y_{01}\approx B_{\rm e},\quad Y_{11}\approx-\alpha_{\rm e},\\&Y_{21}\approx\gamma_{\rm e},\quad Y_{02}\approx-D_{\rm rot},\quad Y_{12}\approx-\beta_{\rm e},\end{aligned} \tag{2}$$

where $B_{\rm e}$ is the equilibrium rotational constant, $\alpha_{\rm e}$ is the vibration–rotation coupling constant, $\omega_{\rm e}$ is the harmonic frequency, $\omega_{\rm e}\chi_{\rm e}$, $\omega_{\rm e}y_{\rm e}$, and $\omega_{\rm e}z_{\rm e}$ are the first-anharmonicity constant and the second-anharmonicity constant, $\beta_{\rm e}$ is the first centrifugal distortion constant, and $\gamma_{\rm e}$ is the second rotational constant. It is necessary to point out that equilibrium position $R_{\rm e}$ and dissociation energy $D_{\rm e}$ are obtained from the APEFs, while the other spectroscopic parameters are determined from the ro-vibrational levels with the Dunham expansion for the term values.

### 2.3. The expression for analytical potential energy function

The AP function suggested by Aguado and Paniagua[7,8] can be used to represent the two- and three-body terms of the potential energy surface. Here, we use the two-body term to express the interaction between C and N atoms. The expression is written as

$$V(R)=\frac{c_0\exp(-\beta R)}{R}+\sum_{i=1}^{N}[c_iR\exp(-\alpha R)], \tag{3}$$

where $R$ is the distance between two atoms. In the present work, we truncate the polynomial to a degree of 20 ($N=20$), which will result in 23 parameters ($\alpha$, $\beta$, $c_0$, $c_1,\ldots,a_{20}$) to be determined for the CN molecules with the *ab initio* energies.

The root of mean square (RMS) error can be used to assess quantitatively the quality of the fitting. The RMS can be calculated as

$$\mathrm{RMS}=\frac{1}{N}\sqrt{\sum_{i=1}^{N}(V_{\rm APEF}-V_{ab\ initio})^2}, \tag{4}$$

where $V_{\rm APEF}$ and $V_{ab\ initio}$ are the energies given by the fitting and the *ab initio* calculations, respectively, and $N$ is the number of energy points to be used in the fitting.

## 3. Results and discussion

### 3.1. PECs of $X^2\Sigma^+$ and $A^2\Pi$ states

The PECs of the $X^2\Sigma^+$ and $A^2\Pi$ states of the CN molecule have been obtained with MRCI/aug-cc-pwCV5Z. The *ab initio* energies are listed in Table 1. In order to compare and analyze the PECs conveniently, both of them are also shown in Fig. 1. It is found that the dissociation limits of the PECs are the same and the difference between the two PECs is not large. The $X^2\Sigma^+$ and $A^2\Pi$ states are from the two lower atomic energy levels of $^3$P of the C atom. The difference between the two energy levels is small. Therefore, the difference of the two electronic states is small over the whole range. From the figure, one can find that there are two cross points on the two PECs, which implies that the states can be used as candidates to investigate the diabatic phenomenon. The figure also shows that the two PECs are smooth in the whole considered range and the energy only changes a little, which implies that the present internuclear distance 5.6 Å is large enough to determine the molecular properties.

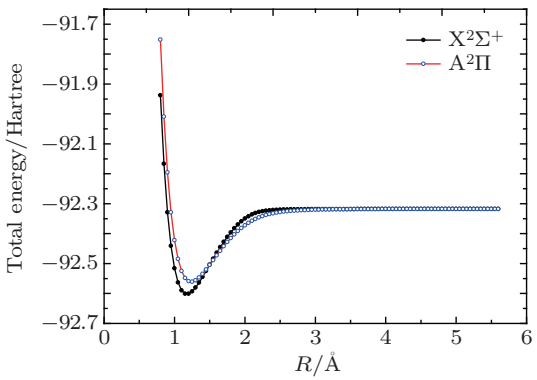



**Fig. 1.** (color online) Potential energy curves for $X^2\Sigma^+$ and $A^2\Pi$ of the CN molecule.

**Table 1.** Total energy points of PECs ($R$ in Å, energy in Hartree. For the sake of brevity, only one of the *ab initio* energies is listed when $R$>2.0).

| $R$ | Total energy | | $R$ | Total energy | |
|---|---|---|---|---|---|
| | $X^2\Sigma^+$ | $A^2\Pi$ | | $X^2\Sigma^+$ | $A^2\Pi$ |
| 0.80 | –91.93811861 | –91.75224603 | 2.70 | –92.31897136 | –92.3235538 |
| 0.85 | –92.16683661 | –92.00948479 | 2.80 | –92.31875047 | –92.32214839 |
| 0.90 | –92.32885276 | –92.19580245 | 2.90 | –92.31860094 | –92.32112843 |
| 0.95 | –92.44100929 | –92.32890235 | 3.00 | –92.31848725 | –92.32037464 |
| 1.00 | –92.51595042 | –92.42187137 | 3.10 | –92.31839268 | –92.31980784 |
| 1.05 | –92.56302353 | –92.48465759 | 3.20 | –92.31830928 | –92.31937492 |
| 1.10 | –92.58943586 | –92.52484311 | 3.30 | –92.31823376 | –92.31903949 |
| 1.15 | –92.60066037 | –92.54819323 | 3.40 | –92.31816478 | –92.31877656 |
| 1.20 | –92.60086252 | –92.55910020 | 3.50 | –92.31810183 | –92.31856831 |
| 1.25 | –92.59321609 | –92.56091673 | 3.60 | –92.31804460 | –92.31840186 |
| 1.30 | –92.58013828 | –92.55620379 | 3.70 | –92.31799283 | –92.31826776 |
| 1.35 | –92.56346574 | –92.54691604 | 3.80 | –92.31794623 | –92.31815888 |
| 1.40 | –92.54458725 | –92.53454166 | 3.90 | –92.31790444 | –92.31806983 |
| 1.45 | –92.52454466 | –92.52020864 | 4.00 | –92.31786709 | –92.31799649 |
| 1.50 | –92.50411187 | –92.50476674 | 4.10 | –92.31783379 | –92.31793569 |
| 1.55 | –92.48385308 | –92.48885243 | 4.20 | –92.31780419 | –92.31788502 |
| 1.60 | –92.46417619 | –92.47293552 | 4.30 | –92.31777793 | –92.31784255 |
| 1.65 | –92.44536931 | –92.45736426 | 4.40 | –92.31775466 | –92.31780679 |
| 1.70 | –92.42763442 | –92.44239275 | 4.50 | –92.31773411 | –92.31777657 |
| 1.75 | –92.41111415 | –92.42820538 | 4.60 | –92.31771598 | –92.31775094 |
| 1.80 | –92.39591401 | –92.41493408 | 4.70 | –92.31770002 | –92.31772915 |
| 1.85 | –92.38211955 | –92.40266981 | 4.80 | –92.31768604 | –92.31771061 |
| 1.90 | –92.36980651 | –92.39146919 | 4.90 | –92.31767378 | –92.31769478 |
| 1.95 | –92.35904031 | –92.38135774 | 5.00 | –92.31766312 | –92.31768129 |
| 2.00 | –92.34986353 | –92.37233177 | 5.10 | –92.31765381 | –92.31766975 |
| 2.10 | –92.33620996 | –92.35739573 | 5.20 | –92.31764576 | –92.31765992 |
| 2.20 | –92.32800890 | –92.34619747 | 5.30 | –92.31763876 | –92.31765151 |
| 2.30 | –92.32354308 | –92.33808193 | 5.40 | –92.31763268 | –92.31764428 |
| 2.40 | –92.32120656 | –92.33233913 | 5.50 | –92.31762743 | –92.3176381 |
| 2.50 | –92.31998626 | –92.32832551 | 5.60 | –92.31762287 | –92.31763265 |
| 2.60 | –92.31933553 | –92.32552416 | | | |

### 3.2. Vibrational and rotational energy levels and spectroscopic properties

Based on the obtained PECs, we solve the one-dimensional Schrödinger equation of nuclear motion with the LEVEL8.0 program package.[17] The results are presented in Table 2. For the sake of brevity, we collect the vibrational levels but omit the rotational levels in the table. We find 50 vibrational levels for the ground state $X^2\Sigma^+$, while there are 53 levels for the excited $A^2\Pi$ state of the $^{13}C^{14}N$ molecule. Here we only list the lower 10 levels for the two states in Table 2. It is found that the present computed vibrational levels and rotational constants are both in agreement with the available experimental data in the literature.[6] To show the difference clearly, we present the energy differences between the present computed levels and the experimental ones in Fig. 2. One can find from the figure that the difference increases approximately linearly with the increase of the quantum number of the level. However, the change of the percent error is small, and the largest percent error is only 0.62% for both electronic states. This implies that the predicted levels are reliable and can be used as a helpful reference for future theoretical or experimental investigations.

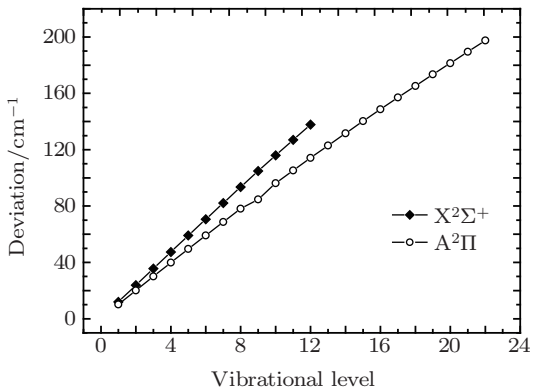



**Fig. 2.** The differences between the present computed vibrational levels and the experimental values.

**Table 2.** Vibrational levels and rotational constants for the $X^2\Sigma^+$ and $A^2\Pi$ states of $^{13}C^{14}N$ (in units of $cm^{-1}$, the zero point energy is excluded).

| State | $v$ | $T_v$ | | $B_v$ | |
|---|---|---|---|---|---|
| | | Present | Expt.[6] | Present | Expt.[6] |
| $X^2\Sigma^+$ | 1 | 1988.1 | 2000.085149 | 1.8016544911 | 1.796343167(28) |
| | 2 | 3951.1 | 3974.971257 | 1.7853672634 | 1.779944756(28) |
| | 3 | 5889.0 | 5924.620803 | 1.7690289413 | 1.763494605(28) |
| | 4 | 7801.6 | 7848.994889 | 1.7526381730 | 1.746990597(28) |
| | 5 | 9689.0 | 9748.054730 | 1.7362145172 | 1.730430474(28) |
| | 6 | 11551.2 | 11621.76177 | 1.7196946816 | 1.713811608(38) |
| | 7 | 13388.0 | 13470.07384 | 1.7031463765 | 1.697131426(34) |
| | 8 | 15199.4 | 15292.94401 | 1.6865521143 | 1.680386763(34) |
| | 9 | 16985.5 | 17090.32410 | 1.6698730575 | 1.663574505(35) |
| | 10 | 18746.2 | 18862.16082 | 1.6531022075 | 1.6466892(39) |
| $A^2\Pi$ | 1 | 1740.6 | 1750.705549 | 1.6108783338 | 1.62018706(13) |
| | 2 | 3456.8 | 3476.908402 | 1.5947078432 | 1.60393531(17) |
| | 3 | 5148.6 | 5178.593093 | 1.5784911446 | 1.58763390(15) |
| | 4 | 6815.9 | 6855.745329 | 1.5622306859 | 1.57129018(26) |
| | 5 | 8458.8 | 8508.356759 | 1.5459293256 | 1.55490792(58) |
| | 6 | 10077.2 | 10136.41428 | 1.5295384024 | 1.5384619(26) |
| | 7 | 11671.3 | 11739.90376 | 1.5131444632 | 1.5219892(17) |
| | 8 | 13240.7 | 13318.8484 | 1.4966655666 | 1.5056222(45) |
| | 9 | 14785.6 | 14870.31956 | 1.4801213051 | 1.477061(72) |
| | 10 | 16305.9 | 16402.16389 | 1.4634888257 | 1.4721124(97) |

To understand the molecular properties, we determine the spectroscopic parameters with the Dunham expression and the computational vibrational levels (the same levels as those in Ref. [6] are used in the fitting process). The fitting results and the experimental values are collected in Table 3. The obtained spectroscopic parameters for both electronic states are in good agreement with the experimental values,[6] which again shows the accuracy of the present calculations. The $R_e'$s of the two states are close to both the experimental values[6] and the recent theoretical values obtained by Shi *et al.*[3] The present obtained dissociation energy $D_e$ for the ground state $X^2\Sigma^+$ is 62400.8 $cm^{-1}$, which is in agreement with the experimental value $62104.4 \pm 483.9$ $cm^{-1}$.[19] This implies that the theoretical level MRCI/aug-cc-pwCV5Z can give accurate results for both the spectroscopic and the energy properties of the CN molecule.

**Table 3.** Spectroscopic parameters for the $X^2\Sigma^+$ and $A^2\Pi$ states of $^{13}C^{14}N$ (in units of $cm^{-1}$).

| $v$ | $X^2\Sigma^+$ | | $A^2\Pi$ | |
|---|---|---|---|---|
| | Present | Expt.[6] | Present | Expt.[6] |
| $R_e$ | 1.1757 | 1.171822 | 1.2365 | 1.23303836 |
| | | 1.1753[a)] | 1.2363[a)] | |
| $D_e$ | 62400.8 | $62104.4 \pm 483.9$[b)] | 53449.9 | / |
| $\omega_e$ | 2013.2250 | 2025.2509 | 1765.8466 | 1775.21504 |
| $\omega_e\chi_e$ | 12.5376 | 12.57330 | 12.399975 | 12.24736 |
| $\omega_e y_e$ | –0.005686 | –0.00572 | –0.001772 | –0.001734 |
| $\omega_e z_e$ | –0.00002538 | –0.0000530 | –0.0006918 | / |

[a)] Theoretical value obtained by MRCI in Ref. [3]; [b)] from Ref. [19], where it is in units of eV.

### 3.3. Analytical potential energy functions

To make the PECs more convenient for further applications (for example, the investigation of photoassociation transition or the construction of APEF for a polyatomic system), we construct APEFs for the two states with the AP potential. The fitted parameters and the RMS are presented in Table 4. The RMSs are only 13.0 $cm^{-1}$ and 1.8 $cm^{-1}$ for the two states, respectively. This implies that the fitting process is of high quality and the present APEFs can accurately reproduce the interaction energy between C and N atoms. The satisfactory fitting results also suggest that the AP potential is effective when accurately reproducing both long-range and short-range PECs. We also calculate the ro-vibrational levels with the APEFs and compare the results with those from the *ab initio* PECs. It is found that some of the levels obtained by the two methods are close to each other, and the largest difference approximately

equals the RMS.

**Table 4.** Fitted parameters and RMSs of the analytical potential energy functions for the $X^2\Sigma^+$ and $A^2\Pi$ states of CN.

| | $X^2\Sigma^+$ | $A^2\Pi$ |
|---|---|---|
| $\alpha$ | $0.110426590303\times10^{1}$ | $0.136820325815\times10^{1}$ |
| $\beta$ | $0.487640203842\times10^{1}$ | $0.393148992308\times10^{1}$ |
| $c_0$ | $0.711449538760\times10^{7}$ | $0.491738893578\times10^{7}$ |
| $c_1$ | $0.119249302895\times10^{5}$ | $0.100244710760\times10^{4}$ |
| $c_2$ | $-0.174512945975\times10^{7}$ | $-0.698404721359\times10^{6}$ |
| $c_3$ | $0.942331901618\times10^{8}$ | $0.364835845678\times10^{8}$ |
| $c_4$ | $-0.261799765939\times10^{10}$ | $-0.126016447974\times10^{10}$ |
| $c_5$ | $0.409341029597\times10^{11}$ | $0.236651366715\times10^{11}$ |
| $c_6$ | $-0.364837077473\times10^{12}$ | $-0.258327918784\times10^{12}$ |
| $c_7$ | $0.162673826799\times10^{13}$ | $0.145823038387\times10^{13}$ |
| $c_8$ | $-0.134467708245\times10^{12}$ | $-0.224328094792\times10^{13}$ |
| $c_9$ | $-0.378106628805\times10^{14}$ | $-0.212738946191\times10^{14}$ |
| $c_{10}$ | $0.199474992937\times10^{15}$ | $0.145515104489\times10^{15}$ |
| $c_{11}$ | $-0.485608190830\times10^{15}$ | $-0.403694386386\times10^{15}$ |
| $c_{12}$ | $0.601530135843\times10^{15}$ | $0.569583948487\times10^{15}$ |
| $c_{13}$ | $-0.547334177526\times10^{15}$ | $-0.579762121620\times10^{15}$ |
| $c_{14}$ | $0.116822605736\times10^{16}$ | $0.116852297739\times10^{16}$ |
| $c_{15}$ | $-0.195357053122\times10^{16}$ | $-0.195341011814\times10^{16}$ |
| $c_{16}$ | $0.107627000013\times10^{16}$ | $0.107634493263\times10^{16}$ |
| $c_{17}$ | $-0.161067557213\times10^{14}$ | $-0.160754539923\times10^{14}$ |
| $c_{18}$ | $0.653796571030\times10^{14}$ | $0.653915955415\times10^{14}$ |
| $c_{19}$ | $0.591335632917\times10^{11}$ | $0.636233682522\times10^{11}$ |
| $c_{20}$ | $-0.850182252060\times10^{11}$ | $-0.839239759587\times10^{11}$ |
| RMS/cm$^{-1}$ | 13.0 | 1.8 |

## 4. Conclusion

In summary, PECs of $X^2\Sigma^+$ and $A^2\Pi$ states of the CN molecule have been obtained at MRCI/aug-cc-pwCV5Z basis set theoretical level. The rotational and vibrational levels and the spectroscopic parameters are determined. It is found that the computational vibrational levels for the $X^2\Sigma^+$ and $A^2\Pi$ states of the $^{13}C^{14}N$ molecule are in good agreement with the experimental ones. In addition, all of the calculated spectroscopic parameters are in accordance with the experimental data. The AP potential can accurately reproduce the present short-range PECs. The accurate APEFs can be conveniently used in future investigations.

## References


[1] Ram R S, Davis S P and Wallace L 2006 *J. Mol. Spectrosc.* **237** 225
[2] Xiong B K, Wang L, Wang D C, Zhang D L, Dai Q R and Shi D H 2007 *J. Zhengzhou University* **3** 71
[3] Shi D H, Li W T and Sun J F 2011 *J. Quant. Spectrosc. Rad. Trans.* **112** 2335
[4] Werner H J and Knowles P J 1988 *J. Chem. Phys.* **89** 5803
[5] Knowles P J and Werner H J 1988 *Chem. Phys. Lett.* **145** 514
[6] Ram R S and Bernath P F 2012 *J. Mol. Spectrosc.* **274** 22
[7] Colin R and Bernath P F 2012 *J. Mol. Spectros.* **273** 30
[8] Aguado A, Tablero C and Paniagua M 1998 *Comp. Phys. Comm.* **108** 259
[9] Aguado A, Tablero C and Paniagua M 2001 *Comp. Phys. Comm.* **134** 97
[10] Cao Y B, Yang C L, Wang M S and Ma X G 2013 *Chin. Phys. B* **22** 123401
[11] Shi D H, Wang J M and Sun J F 2010 *Chin. Phys. B* **19** 113404
[12] Wang X Q, Yang C L, Su T and Wang M S 2009 *Acta Phys. Sin.* **58** 6873 (in Chinese)
[13] Bai F J, Yang C L, Qian Q and Zhang L 2009 *Chin. Phys. B* **18** 549
[14] Gao F, Yang C L and Zhang X Y 2007 *Acta Phys. Sin.* **56** 2547 (in Chinese)
[15] Qian Q, Yang C L, Gao F and Zhang X Y 2007 *Acta Phys. Sin.* **56** 4420 (in Chinese)
[16] Werner H J, Knowles R J and Lindh R 2010 MOLPRO, version 2010. 1, see http://www.molpro.net
[17] Le Roy R J 2007 LEVEL 8.0
[18] Dunham J L 1932 *Phys. Rev.* **41** 721
[19] Huber K P and Herzberg G 1979 *Molecular Spectra and Molecular Structure IV* (New York: Van Nostrand Reinhold Company)