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Investigation of analytical potential energy function, harmonic frequency and vibrational levels for the $X^2\Sigma^+$ and $A^2\Pi$ states of CN radical*

Wang Jian-Kun(王建坤)† and Wu Zhen-Sen(吴振森)

School of Science, Xidian University, Xi'an 710071, *China*

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This paper calculates the equilibrium structure and the potential energy functions of the ground state ($X^2\Sigma^+$) and the low lying excited electronic state ($A^2\Pi$) of CN radical are calculated by using CASSCF method. The potential energy curves are obtained by a least square fitting to the modified Murrell–Sorbie function. On the basis of physical theory of potential energy function, harmonic frequency (ω_e) and other spectroscopic constants ($\omega_e\chi_e$, β_e and α_e) are calculated by employing the Rydberg–Klein–Rees method. The theoretical calculation results are in excellent agreement with the experimental and other complicated theoretical calculation data. In addition, the eigenvalues of vibrational levels have been calculated by solving the radial one-dimensional Schrödinger equation of nuclear motion using the algebraic method based on the analytical potential energy function.

Keywords: potential energy function, harmonic frequency, vibrational levels, algebraic method
PACC: 3420

1. Introduction

The CN radical is one of the first species, with the C_2 radical, to be detected in the cometary environment at the end of the nineteenth century. The species of CN radical is also presented in hot flames, in solar and stellar atmospheres and in the heads of comets.[1] The CN radical is of fundamental importance both in laboratory spectroscopy and in astronomy.[2] The spectroscopy of the cyanide radical has been the subject of intense study for decades because of its importance in combustion chemistry, especially in propellant flames and other fields. The two strongest and best- characterized electronic transitions in CN radical are the $B^2\Sigma^+ - X^2\Sigma^+$ violet system and $A^2\Pi - X^2\Sigma^+$ red system.[3] The CN $A^2\Pi - X^2\Sigma^+$ red system is of considerable interest because of its use in determining the nitrogen abundance in stellar atmospheres, comets and red giants. Fluorescence from the CN radical in both the $B^2\Sigma^+$ and $A^2\Pi$ states has been extensively studied as probe of primary photochemical processes in cyanide-containing polyatomic molecules such as NH_3CN.[4] In particular, the low-lying doublet states ($X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$) have been studied in detail mostly from analysis of the intense $A^2\Pi - X^2\Sigma^+$ and of the $B^2\Sigma^+ - X^2\Sigma^+$ emission spectra.[5] The dipole moment and harmonic frequency of the ground state of the CN radical is reported by using multi-reference configuration-interaction calculations (MRCC) approach employed in Ref.[6]. A direct experimental measurement of CN $A \leftarrow X$ electronic–vibrational transition moment for the (2,0) band at 789.5 nm was obtained by He *et al.*[7] Reference [8] reported on the first experimental study of the C (^3P_g) + N (^4S_u) recombination. The potential energy curves of the low-lying states of CN radical were calculated by using *ab initio* configuration interaction methods.[9] Molecular parameters of the low-lying doublet and quartet states of the CN radical were carried out by using time-dependent density-functional theory method.[10] Doubles coupled cluster methods were also used to study the spectroscopic constants of CN radical.[11] Adiabatic and diabatic potential energy surfaces for the interaction of $Ar(^1S_0)$ with the CN molecule in its ground ($X^2\Sigma^+$) and first excited ($A^2\Pi$) electronic states were determined by using MRCC.[12] The experimental potential energy curves for the different electronic states of CN radical were constructed by using the Rydberg-Klein-Rees method and spectroscopic information also were

*Project supported by the National Natural Science Foundation of China (Grant No 60771038).
†E-mail: jkwang@mail.xidian.edu.cn

reported in Ref.[13]. Based on the theory of atomic and molecular statics, this paper derives the reasonable dissociation limit for the ground state ($X^2\Sigma^+$) and the low-lying state ($A^2\Pi$) of CN radical. Using complete-active-space (CAS) self-consistent field (SCF) (CAS SCF) method, we calculate the equilibrium geometries of the ground state ($X^2\Sigma^+$) and the low-lying state ($A^2\Pi$) of CN radical. At the same time, the single point energy scanning calculation is also made at 6-311++G(3d2f)basis set near the equilibrium inter-nuclear separation obtained by the geometry optimization so as to attain the more accurate result. A least squares fitting to the Murrell–Sorbie function is made and other spectroscopic data (α_e, $\omega_e\chi_e$, β_e, T_e) are further computed, which are in good agreement with other theoretical or experimental results. In addition, based on the analytic potential energy function obtained on the CASSCF/6-311++G(3d2f) level, we have also calculated the vibrational levels by using the algebraic method.

2. Computational details

The potential energy plays an important role in the studies such as solution chemistry, atmospheric physics, nebular medium, plasma physics, and gun powder. It describes the molecular structure and molecular spectrum and finds the base of researching the time-dependant process, which matches a definite electronic state of a molecule or radical.[14,15] In order to describe the systematic potential function accurately, the proper dissociation limit of CN radical and conceivable electronic configuration must be determined. The electronic configuration of the ground state ($X^2\Sigma^+$) is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^1 1\Pi^4$, which is similar to that of CO^+ molecule and has A' symmetry. The electronic configuration of the first excited state ($A^2\Pi$) of CN radical is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\Pi^3$. Both the ground state and the first excited state of CN radical are open-shell radical molecules.[6] According to the atomic and molecular reaction statics,[14,15] the possible electronic states can be determined. The ground electronic state of C atom is ^3P_g, and that of N atom is ^4S_u, which belongs to the SU (n) group. CN radical is in $C_{\infty v}$ group. When the C(^3P_g) atom react with N(^4S_u) atom and produce CN molecule, the systematic symmetry decreased. The irreducible representation of SU (n) group can be decomposed into the direct sum of the irreducible representation of $C_{\infty v}$ group. Using direct product and reduction, we can obtain the irreducible representation of $C_{\infty v}$ group, namely the possible electronic states can be determined. The direct sum of irreducible representation of C(^3P_g) resolution into $C_{\infty v}$ group is

$$^3P_g = 3\Sigma_g^- \oplus {}^3\Pi. \tag{1}$$

The ground electronic configuration of N atom is ^4S_u. The irreducible representation of N (^4S_u) decomposition into $C_{\infty v}$ group is $^4\Sigma_u^-$. On the invertible principle of micro-process,[15] the dissociation limit of the ground state ($X^2\Sigma^+$) and low-lying state ($A^2\Pi$) of CN radical respectively are [8,9]

$$\mathrm{CN}(X^2\Sigma^+) \longrightarrow \mathrm{C}(^3P_g) + \mathrm{N}(^4S_u), \tag{2}$$

and

$$\mathrm{CN}(A^2\Pi) \longrightarrow \mathrm{C}(^3P_g) + \mathrm{N}(^4S_u). \tag{3}$$

The calculation method of CAS SCF requests a complete active space multi-configuration SCF (MC-SCF). An MC-SCF calculation is a combination of an SCF computation with a full configuration interaction (CI) involving a subset of the molecular orbits; this subset is known as the active space.[16] The MC-SCF method is a reliable approach to the calculation of low-lying potential energy curves of diatomic molecules.[17] This CAS SCF method provides excellent starting wave functions for all of the low-lying valence states. Additional electron correlation can be added by CI. Thus our CAS SCF calculation is so-called MC SCF method.[17] The inactive and active subspaces are $\{1\sigma, 2\sigma\}$ and $\{3\sigma, 4\sigma, 5\sigma, 6\sigma, 1\Pi, 2\Pi\}$ respectively. Two sets of reference configuration has been employed. The first set of reference configurations include all configurations of the appropriate symmetry which can be formed from 3σ–6σ and 1Π–2Π orbitals. This set allows for proper dissociation into C (^3P_g) + N (^4S_u) atomic states. A second large set of reference configurations is chosen from a CAS SCF with the orbitals with 3σ–6σ, 1Π–2Π and 1δ active.

The basis sets 6-311G, 6-311G(d, p), 6-311 ++ G, 6-311 ++ G(d, p), 6-311G (3df, 3pd), 6-311 ++ G(2df, 2pd), 6-311 ++ G(2df, pd), 6-311G(3df, 2p), 6-311 ++ G(3df, 3pd), 6-311++G(3d2f), cc-PVTZ and AUG-cc-PVTZ employed respectively, the geometry optimization of the ground state ($X^2\Sigma^+$) and the low lying excited electronic state ($A^2\Pi$) of CN radical were carried out using CAS SCF method. The optimization results obtained from the basis sets such as 6-311G, 6-311G(d, p) and 6-311G(3df, 3dp) which

do not contain diffuse functions have considerable discrepancy with the present experimental datum. So these basis sets will not be used in later calculation. Furthermore, we have calculated the dissociation energies for each involved state using the selected basis sets and the calculation results are given in Table 1.

From Table 1, the equilibrium inter-nuclear distance obtained by cc- PVTZ base set is 0.11158 nm for $X^2\Sigma^+$ state and much lower than the experimental datum[18] 0.11718 nm. In detail, the 6-311++ G(3df, 3pd) base set gives the accurate dissociation energy, but slightly poor equilibrium geometry, and the 6-311++ G(2df, 2pd) base set gives more accurate dissociation energy but poorer equilibrium geometry. By comparing the dissociation energies and equilibrium geometries between theory and experimental or other theoretical values,[4,15,18] we find that the 6-311++G(3d2f) base set is the most suitable one for the $X^2\Sigma^+$ and $A^2\Pi$ states in full active space. So all the later calculations are carried out by the 6-311++G(3d2f) basis set.

Table 1. Comparison of equilibrium geometries (R_e in nm) obtained by OPT calculation and Dissociation energies (D_e in eV) for $X^2\Sigma^+$ and $A^2\Pi$ states of CN radical.

	cc-PVTZ	6-311G(3df,3dp)	6-311++ G(d,p)	6-311++ G(2df,2pd)	6-311++ G(3df, 3pd)	6-311++ G(3d2f)
$R_{e(X^2\Sigma^+)}$/nm	0.11158	0.11267	0. 11482	0.114875	0.11493	0.11796
$R_{e(A^2\Pi)}$/nm	—	0.12763	0.12491	0.12463	0.12342	0.12425
$D_{e(X^2\Sigma^+)}$/eV	8.3248	6.2135	6.6958	7.4526	7.2536	7.3452
$D_{e(A^2\Pi)}$/eV	—	6.8934	5.8634	5.8982	6.1536	6.0618

Eventually the harmonic frequency is derived from the analytic potential energy function fitted with the single point scanning. After comparison with the datum of previous works,[18−20] the calculated results obtained using 6-311++*G*y(3d2f) basis set are in excellent agreement with other experimental or theoretical results. In the Table 1, CAS SCF(62) denotes CAS SCF with orbitals 3σ-6σ and 1Π-2Π active, and CAS SCF(621) denotes CAS SCF with orbitals 3σ-6σ and 1Π, 2Π and 1δ active.

Table 2. Comparison of calculated and experimental equilibrium energy E, dipole moment μ and dissociation energy D_e of CN radical based on CAS SCF/ 6-311++G(3d2f) theoretical level.

Method	Electronic states	R_e/nm	E/Hartree[a)]	μ/deb[b)]	D_e/eV
CAS SCF(62)	$X^2\Sigma^+$	0.11796	–92.36834	1.5008	7.3452
CAS SCF(621)	$X^2\Sigma^+$	0.11823	–92.38624	1.4996	7.3547
Experiment[18]	$X^2\Sigma^+$	0.11718			7.888
CAS SCF(62)	$A^2\Pi$	0.12425	–92.32167	0.1912	6.0618
CAS SCF(621)	$A^2\Pi$	0.12439	–92.34926	0.1902	6.1259
Experiment[20]	$A^2\Pi$	0.12333	–92.32599		6.6137

a) 1hartree=11.05×10^{21} J

b) 1deb=3.34×10^{-30} C·m

From Table 2 it is found that the configurations containing δ orbitals have an inconsiderable effect on the calculation results.

3. Results and discussion

3.1. Calculation of analytical potential energy function and harmonic frequency of CN radical

The single point energy of the ground state ($X^2\Sigma^+$) and the low-lying state ($A^2\Pi$) of CN radical are scanned using CAS SCF/ 6-311++G(3d2f) method, and then a series of single point energy are obtained. During single point energy scanning, all of the parameters except the inter-nuclear distance R between two atoms C and N are kept consistent with that used in the calculation of optimization of molecular structure. Then the series of single point energy are fitted as the following Murrell–Sorbie function[21,22] using the normal equations.

$$V(\rho) = -D_e(1 + \alpha_1\rho + \alpha_2\rho^2 + \alpha_3\rho^3)\exp(-\alpha_1\rho), \quad (4)$$

where D_e is the dissociation energy. The ρ equals to $R - R_e$ in which R is the inter-nuclear distance and R_e is equilibrium inter-nuclear distance. α_1, α_2 and α_3 are fitting coefficients. Fitting results are given in Table 3.

Table 3. The constants of the analytical potential energy function and spectroscopic constants for the $X^2\Sigma^+$ and $A^2\Pi$ states of CN radical.

States	T_e/cm^{-1}	D_e/eV	α_1/nm^{-1}	α_2/nm^{-2}	α_3/nm^{-3}	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	Data source
$X^2\Sigma^+$	0.00	7.3452	56.86	868.8	4526	2142.7	15.2	1.865	0.015	CAS SCF(62)
	0.00	7.8880	53.12	766.3	5369					Reference [15]
	0.00	7.1700				2027	12.6	1.862	0.0169	Reference [4]
						2067.7	12.93	1.893	0.0172	Reference [19]
$A^2\Pi$	10018	6.0618	53.89	818.37	5956	1791.8	12.7	1.701	0.0169	CAS SCF(62)
		6.6137				1792	12.4	1.697	0.0167	Reference [15]
	9736	5.9800				1792	12.4	1.697	0.0167	Reference [4]
						1814.4	12.88	1.717	0.0175	Reference [15]

The potential energy curves showed in the Figs.1 and 2 with the minimum energy point demonstrate that the ground state ($X^2\Sigma^+$) and first excited state ($A^2\Pi$) can exist stably.

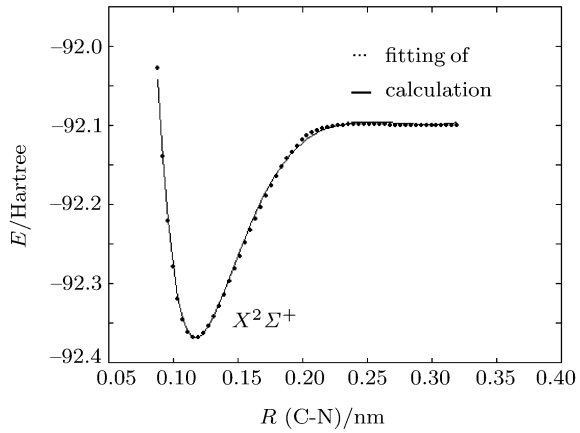


Fig.1. The potential energy curve of the ground state ($X^2\Sigma^+$) of CN radical.

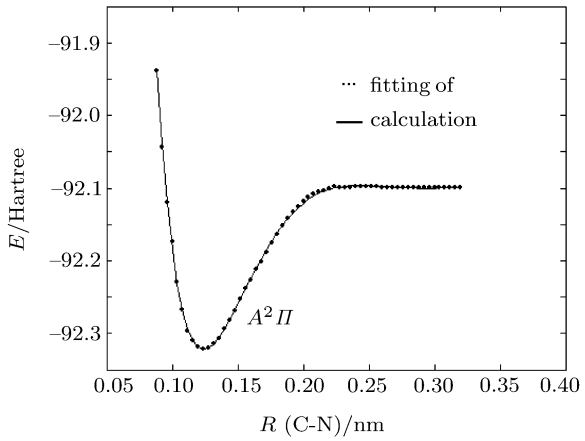


Fig.2. The potential energy curve of the first excited state ($A^2\Pi$) of CN radical.

The calculation results of spectroscopic constants are given in Table 3 employing the analytical energy function for the $X^2\Sigma^+$ and $A^2\Pi$ states of CN radical. From Table 3, we can easily see that the computed dissociation energy is in agreement with the experimental or other theoretical values[4,15,19] within 0.5428 eV for the $X^2\Sigma^+$ state, and within 0.5519 eV for $A^2\Pi$ state respectively. The computed equilibrium inter-nuclear distance is in accord with the experimental data[15] within 0.00078 nm for the $X^2\Sigma^+$ state, and 0.00088 nm for the $A^2\Pi$ state at the present CASSCF(62)/6-311++G(3d2f) level of theory in full active space respectively. Comparison of the theoretical determinations of the dissociation energies and the equilibrium inter-nuclear distances with the previous theoretical results[4] clearly shows that the present work represents an improvement in agreement between theories and experiments.

3.2. Calculation of vibrational levels of the $X^2\Sigma^+$ state of CN radical based on the analytical potential energy function

The vibrational energy levels (E_v in cm^{-1}) are obtained by solving the radial one-dimensional Schrödinger equation of nuclear motion.

$$\left[-\frac{\hbar}{2\mu}\frac{d^2}{d_r^2}+\frac{\hbar^2}{2\mu r^2}J(J+1)+V(r)\right]\Psi_{\upsilon,J}(r) = E_{\upsilon,J}\,\Psi_{\upsilon,J}(r). \quad (5)$$

In this equation $V(r)$ denotes analytical potential energy function. The υ and J denote vibrational quantum number and rotational quantum number separately. When J equals to 0, E_v is eigenvalue of vibrational energy and it can be expressed as follow-

ing equation[23] which is inferred using the algebraic method.

$$\begin{aligned} E_{\rm v} = {} & \omega_0 + (\omega_{\rm e} + \omega_{\rm eo})(v+1/2) \\ & - \omega_{\rm e}X_{\rm e}(v+1/2)^2 + \omega_{\rm e}Y_{\rm e}(v+1/2)^3 \\ & + \omega_{\rm e}Z_{\rm e}(v+1/2)^4 + \omega_{\rm e}t_{\rm e}(v+1/2)^5 \\ & + \omega_{\rm e}s_{\rm e}(v+1/2)^6 + \omega_{\rm e}r_{\rm e}(v+1/2)^7 + \ldots . \end{aligned} \quad (6)$$

Compared with the Herzberg[14] empirical vibrational energy levels expression, $\omega_{\rm o}$ and $\omega_{\rm eo}$ are the new terms. The $\omega_{\rm o}$ is the null order vibrational spectroscopic constant of $(\nu + \frac{1}{2})$ term and $\omega_{\rm eo}$ is the correction term of first harmonic spectroscopic constant of $(\nu + \frac{1}{2})$ term. Both of the $\omega_{\rm o}$ and $\omega_{\rm eo}$ are small quantities but play important roles in calculation of vibrational energy levels:

$$\begin{aligned} \omega_{\rm o} = {} & -\frac{7}{16\omega_{\rm e}}b_3^2f_3^2 + \frac{3}{8}b_4f_4 - \frac{1107}{256\omega_{\rm e}}b_5^2f_5^2 \\ & - \frac{945}{128\omega_{\rm e}}b_4b_6f_4f_6 - \frac{1155}{128\omega_{\rm e}}b_3b_7f_3f_7 \\ & - \frac{180675}{2048\omega_{\rm e}}b_7^2f_7^2 - \frac{89775}{512\omega_{\rm e}}b_6b_8f_6f_8 \\ & + \frac{315}{128}b_8f_8 \end{aligned} \quad (7)$$

$$\begin{aligned} \omega_{\rm eo} = {} & -\frac{95}{8\omega_{\rm e}}b_3b_5f_3f_5 - \frac{67}{16\omega_{\rm e}}b_4^2f_4^2 + \frac{25}{8}b_6f_6 \\ & - \frac{19277}{256\omega_{\rm e}}b_6^2f_6^2 - \frac{22029}{128\omega_{\rm e}}b_5b_7f_5f_7 \\ & - \frac{10521}{64\omega_{\rm e}}b_4b_8f_4f_8 - \frac{5450499}{2048\omega_{\rm e}}b_8^2f_8^2. \end{aligned} \quad (8)$$

In Eqs.(7) and (8) expansion coefficients b_n have the definite expression. Vibrational force constants $f_{(n)}$ can be obtained by the potential variational method.[23]

According to the definition of the nth-order matrix $f_{(n)}$ of vibrational force constants,[14]

$$f_{(n)} = \left(\frac{{\rm d}^{(n)}V(R)}{{\rm d}R^{(n)}}\right)_{R_{\rm e}} \quad n = 2, 3, 4, \ldots, \quad (9)$$

where $f_{(n)}$ is the nth-order matrix of vibrational force constants which is closely connected with the vibrational spectroscopic constants such as (ω_0, $\omega_{\rm e} + \omega_{\rm eo}$, $\omega_{\rm e}X_{\rm e}$, $\omega_{\rm e}Y_{\rm e}, \ldots$). $V(R)$ is the potential energy function.

Based on the analytical potential function, the vibrational force constants can be obtained using the potential variational method, and then the vibrational spectroscopic constants can be calculated after the calculation of vibrational force constants. The eigenvalues of vibrational levels are compared with that of Ref.[13].

Table 4. Vibrational energy levels ($E_{\rm V}$ in cm^{-1}) for the $X^2\Sigma^+$ state of CN radical.

v	E_v	Reference [13]	v	$E_{\rm v}$
0	1027.4	1031.0	16	30576.4
1	3063.1	3073.4	17	32213.5
2	5073.1	5089.7	18	33826.4
3	7057.6	7079.7	19	35414.9
4	9016.6	9043.6	20	36979.1
5	10950.1	10981.3	21	38519.1
6	12858.6	12892.9	22	40034.7
7	14741.8	14778.2	23	41525.8
8	16599.9		24	42992.4
9	18433.2		25	44434.3
10	20241.7		26	45851.3
11	22025.5		27	47243.3
12	23784.5		28	48610.2
13	25519.1		29	49951.3
14	27229.3		30	51266.8
15	28915.0		31	52556.1

4. Summary

The equilibrium structure of the ground state ($X^2\Sigma^+$) and the low lying excited electronic state ($A^2\Pi$) of CN radical are calculated using CASSCF/ 6-311++G(3d2f) method and analytical potential energy functions are fitted. On the basis of physical theory of potential energy functions, harmonic frequency and other spectroscopic constants are calculated by employing the Rydberg–Klein–Rees method. The theoretical calculation results are in excellent agreement with the experimental and other complicated theoretical calculation results which means that calculation method presented in this paper is reasonable and feasible. In addition the eigenvalues of vibrational levels of the ground state ($X^2\Sigma^+$) of CN radical are derived using the algebraic method based on the analytical potential energy function.

The harmonic frequency of higher-excited states of CN radical will be calculated using CASSCF/ 6-311++G(3d2f) method, so the rationality and accuracy of this method will be tested in our further calculations.

References

[1] Robert J, Fallon T, Joseph, Vanderlice D and Robert D C 1962 *J. Chem. Phys.* **37** 1096

[2] Davies P B and Hamilton P A 1982 *J. Chem. Phys.* **76** 2127

[3] Guthrie J A, Bowen T S, Anderson W R, Kotlar A J and Bunte S W 1997 *Army Research Laboratory* ARL-TR-1381 p4

[4] Peter K J and Werner H J 1988 *J. Chem. Phys.* **89** 7334

[5] Haruhiko ITO and Yasushi OZAKI 1985 *J. Chem. Phys.* **98** 81

[6] Ajitha D and Kimihiko H 2001 *Chem. Phys. Lett.* **347** 121

[7] He G, Tokue I and Glen M R 1998 *J. Chem. Phys.* **109** 6312

[8] Washida N, Kley D, Becker K H and Groth W 1975 *J. Chem.Phys.* **63** 4230

[9] Henry F, Schaefer T and Heil G 1971 *J. Chem. Phys.* **54** 2574

[10] Guan J, Casida M E and Salahub D R 2000 *J. Molec. Struct.* **527** 229

[11] Peris G, Rajadell F and Li X J 1998 *Molec. Phys.* **94** 235

[12] Millard H, Alexander and Xin Y 2000 *J. Chem. Phys.* **112** 781

[13] Reddy R R and Nazeer A Y 2003 *Astrophys. Space Sci.* **286** 419

[14] Zhu Z H and Yu H G 1997 *Molecular Structure and Molecular Potential Function* (Beijing: Science Press) p110 (in Chinese)

[15] Zhu Z H 1996 *Atomic and Molecular Reaction Statics* (Beijing: Science Press) p39 (in Chinese)

[16] Murrell N J, Carter S and Farantos S C 1984 *Molecular Potential Energy Functions* (New York: Edmundsbury) p151

[17] Anwar B G, Larry C A and Paul R C 1999 *J. Chem. Phys.* **110** 7650

[18] Bernath P F 2002 *Molecular Spectroscopy* (Ontario: University of Waterloo Press) p9

[19] Foresman J B and Frisch E 1996 *Exploring Chemistry with Electronic Structure Methods* 2nd ed (Gaussian Inc., Pittsburgh, PA) p253

[20] Gene A, Capelle and Steven N S 1976 *IEEE J. Quantum Electronics* **12** 417

[21] Liu G Y, Sun W G and Feng H 2003 *Science in China* (Series G) **33** 439

[22] Yu B H, Shi D H, Sun J F, Zhu Z L, Liu Y F and Yang X D 2007 *Chin. Phys.* **16** 2371

[23] Sun W G, Hou S L, Feng H and Ren W Y 2002 *J. Mol. Spectrosc.* **215** 93