Accurate potential energy function and spectroscopic study of the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states of the CP radical*

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This paper calculates the equilibrium internuclear separations, the harmonic frequencies and the potential energy curves of the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states of the CP radical by the highly accurate valence internally contracted multireference configuration interaction method with correlation-consistent basis sets (aug-cc-pV6Z for C atom and aug-cc-pVQZ for P atom). The potential energy curves are all fitted with the analytic potential energy function by the least-square fitting. Employing the analytic potential energy function, we determine the spectroscopic constants (B_e, α_e and $\omega_e\chi_e$) of these states. For the $X^2\Sigma^+$ state, the obtained values of D_e, B_e, α_e, $\omega_e\chi_e$, R_e and ω_e are 5.4831 eV, 0.792119 cm^{-1}, 0.005521 cm^{-1}, 6.89653 cm^{-1}, 0.15683 nm, 12535.11 cm^{-1}, respectively. For the $A^2\Pi$ state, the present values of D_e, B_e, α_e, $\omega_e\chi_e$, R_e and ω_e are 4.586 eV, 0.703333 cm^{-1}, 0.005458 cm^{-1}, 6.03398 cm^{-1}, 0.16613 nm, 1057.89 cm^{-1}, respectively. For the $B^2\Sigma^+$ state, the present values of D_e, B_e, α_e, $\omega_e\chi_e$, R_e and ω_e are 3.506 eV, 0.677561 cm^{-1}, 0.00603298 cm^{-1}, 5.68809 cm^{-1}, 0.1696 nm, 822.554 cm^{-1}, respectively. For these states, the vibrational states with the rotational quantum number J equals zero ($J = 0$) are studied by solving the radial nuclear Schrödinger equation using the Numerov method. For each vibrational state, the vibrational level, the classical turning points, the rotational inertial and the centrifugal distortion constants are calculated. Comparison is made with recent theoretical and experimental results.

Keywords: multi-reference configuration interaction, potential energy curve, molecular constant, spectroscopic parameter

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1. Introduction

The CP radical is an excellent candidate for detection in circumstellar envelopes of stars and in the interstellar medium.[1] In experiment, there are quite a few studies of the properties of CP. As early as 1930, the $B^2\Sigma^+$–$X^2\Sigma^+$ transition of CP was observed in a laboratory by Herzberg.[2] In 1934, the $B^2\Sigma^+$–$X^2\Sigma^+$ system was analysed by Bärwald *et al.*[3] In 1969, the $B^2\Sigma^+$–$A^2\Pi$ transitions were investigated by Chaudhry and Upadhya[4] In 1981, the $A^2\Pi$–$X^2\Sigma^+$ transitions were studied by Tripathi *et al.*[5] In 1987, Fourier transform spectroscopy of the $A^2\Pi$–$X^2\Sigma^+$ system was studied by Ram and Bernath[6] using a high-resolution Fourier transform spectrometer. Some molecular constants for the $X^2\Sigma^+$ and the $A^2\Pi$ states were determined. More recently, interest in the CP radical has been revived as a result of astronomical studies, which has led to the detection of the ground-state CP in the inner, relatively cool layers of the carbon star envelope IRCC10216.[4,7]

In theory, there have been a number of investigations focusing on the potential energy curves (PECs) and the spectroscopic properties of this radical.[8−15] For example, as early as 1970, Murthy N S and Murthy B N[10] constructed the PECs of CP($A^2\Pi$) by the Rydberg–Klein–Rees method. In 1996, de Brouckère and Feller[14] investigated the ground state of CP using a variety of methods. The results include spectroscopic parameters ($\omega_e\chi_e$, α_e, B_e, D_e, R_e and ω_e), rotational transition energies, one-electron properties and so on. In 1997, de Brouckère[15] studied the properties of $CP^-(X^1\Sigma^+)$ using the same methods. The extracted spectroscopic properties from these experimental and theoretical investigations focus mainly on the spectroscopic parameters. Relatively little information is available in the literature of the vibrational properties (vibrational levels, classical turning points, rotational inertial and centrifugal distortion constants), which are very useful in ro-vibrational transition calculations.

In this paper, the PECs for the $X^2\Sigma^+$, $A^2\Pi$ and

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$B^2\Sigma^+$ states of the CP radical are computed by using the valence internally contracted multi-reference configuration interaction (MRCI)[16] approach with the basis sets aug-cc-pV6Z for C and aug-cc-pVQZ for P. These PECs are all fitted with the Murrel–Sorbie (M–S) function[17] by least-square fitting. Using the obtained analytic potential energy functions, the spectroscopic parameters ($\omega_e\chi_e$, α_e and B_e) are determined. The vibrational states with the rotational quantum number J equal to zero ($J = 0$) are studied by solving the radial nuclear Schrödinger equation. The vibrational levels, the classical turning points, rotational inertial and the centrifugal distortion constants are determined. The results of the present work should be useful in the extraterrestrial and the interstellar medium detection of phosphorus-containing molecules.

2. Summary of calculations

The MRCI method is one of the best approaches available to accurately calculate the potential energy surface (PES) and molecular properties. Compared with other single-reference configuration methods, it provides the best PES. Over the past several years, using this approach, many authors had published lots of papers.[18,19] In this work, the MRCI method and the basis sets,[20,21] aug-cc-pV6Z for C and aug-cc-pVQZ for P, are used. First, the equilibrium structures of the electronic states are optimised. Then, along with the first step, the harmonic frequencies are determined. Finally, the PEC of the states are calculated for the $X^2\Sigma^+$ state over the internuclear distance range from 0.06299 to 0.43299 nm with the interval 0.005 nm and for the $A^2\Pi$ and $B^2\Sigma^+$ states from 0.081759 to 0.477759 nm with the interval 0.002 nm. These PECs are all fitted with the M–S function using the least-square fitting.

These calculations are performed with the Molpro programme package,[1)] in which the Abelian point group is employed. For the CP radical, the calculations are carried out in C_{2v} symmetry with the order of the irreducible representations as $a_1/b_1/b_2/a_2$. Eight molecular orbits (MOs) are put into the active space, including four a_1, two b_1 and two b_2, which correspond to the 2s2p shells of C atom and 3s3p shells of P atom. The rest of the electrons (four a_1, one b_1 and one b_2) are put into the closed-shell orbits.

Based on the accurated potential energy functions (APEFs) obtained here, the force constants, quadratic f_2, cubic f_3 and quadratic f_4 are calculated and, then, the spectroscopic parameters are determined. Finally, by solving the radial nuclear Schrödinger equation with the Numerov method,[22] the vibrational states are studied for the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states. For each vibrational state, the vibrational level, the classical turning points, the rotational inertial and the centrifugal distortion constants are also calculated with $J = 0$.

3. Results and discussion

3.1. The APEFs of the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\ \Sigma^+$ states

In order to obtain more reliable APEF, a number of analytic functions have been tested. We find that the M-S function is the best one. In fact, it is widely used to describe the interaction potential of the diatomic molecules system.[23,24] The M–S function can be written as

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

where $\rho = R - R_e$, R is the internuclear distance of the diatomic molecule, R_e is the equilibrium internuclear distance and is regarded as a fixed parameter in the fitting, D_e is the dissociation energy, which is determined by fitting, a_i ($i = 1, 2, 3, \cdots, n$) are also fitting parameters.

To obtain a satisfactory result, for which the root mean square error (ΔE_{RMSE}) is minimized and the extracted spectroscopic parameters are closest to the experimental ones,[25] we try the fitting from $n = 3$ to $n = 8$. By careful comparison with the experimental data,[25] we find that the favourable spectroscopic constants can be obtained at $n = 3$. In Eq. (1), all the parameters such as D_e, a_1, a_2 and a_3 can be obtained by the fitting. The results are presented in Table 1 together with the R_e and the root mean square error (ΔE_{RMS}) for integrality.

[1)] Werner H J, Knowles P J, Lindh R, Manby F R, Schütz M, Celani P, Korona T, Mitrushenkov A, Rauhut G, Adler T B, Amos R D, Bernhardsson A, Berning A, Cooper D L, Deegan M J O, Dobbyn A J, Eckert F, Goll E, Hampel C, Hetzer G, Hrenar T, Knizia G, Köppl C, Liu Y, Lloyd A W, Mata R A, May A J, McNicholas S J, Meyer W, Mura M E, Nicklass A, Palmieri P, Pflüger K, Pitzer R, Reiher M, Schumann U, Stoll H, Stone A J, Tarroni R, Thorsteinsson T, Wang M and Wolf A 2008 MOLPRO, version 2008.1, a package of *ab initio* programs

Table 1. Parameters of the M–S APEF of CP for the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states.

state	D_e/eV	R_e/nm	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}	$\Delta E_{\rm RMSE}$/kcal·mol^{-1}
$X^2\Sigma^+$	5.4831	0.15683	29.6593441	–423.62182	–1143.6455	0.05787446
$A^2\Pi$	4.586	0.16613	42.9745617	514.704752	2652.92752	0.01568967
$B^2\Sigma^+$	3.506	0.1696	36.5890727	339.280285	2209.58182	0.3391064

In order to evaluate the fitting quality of the APEFs, we have calculated the root mean square error ($\Delta E_{\rm RMS}$) according to the following expression:

$$\Delta E_{\rm RMS} = \sqrt{\frac{1}{N}\left[\sum_{i=1}^{N}(V^i_{\rm APEF} - V^i_{\text{ab initio}})^2\right]}, \quad (2)$$

where $V^i_{\text{ab initio}}$ is the ith energy from the *ab initio* calculation and $V^i_{\rm APEF}$ is the corresponding fitting value, N is the number of fitting points (here $N = 96$ for each state). The present $\Delta E_{\rm RMS}$ are of only 0.05787446 kcal/mol (1 cal = 4.187 J) for the $X^2\Sigma^+$ state, 0.01568967 kcal/mol for the $A^2\Pi$ state and 0.03391064 kcal/mol for the $B^2\Sigma^+$ state. Obviously, these values are superior to the chemical accuracy (1.0 kcal/mol). It shows that the M–S function is very suitable for reproducing the PEC of the CP radical and the fitting is of good quality.

3.2. Spectroscopic constants

Now, we calculate the spectroscopic parameters ($B_{\rm e}$, $\alpha_{\rm e}$ and $\omega_{\rm e}\chi_{\rm e}$) of the radical according to the APEFs tabulated in Table 1. Employing Eq. (1), we can derive the following expressions for the force constants, the quadratic f_2, the cubic f_3 and the quartic f_4 at the equilibrium position:

$$f_2 = D_{\rm e}(a_1^2 - 2a_2), \quad (3)$$

$$f_3 = -6D_{\rm e}(a_3 - a_1a_2 + a_1^3/3), \quad (4)$$

$$f_4 = D_{\rm e}(3a_1^4 - 12a_1^2a_2 + 24a_1a_3). \quad (5)$$

Then, the spectroscopic parameters $B_{\rm e}$, $\alpha_{\rm e}$ and $\omega_{\rm e}\chi_{\rm e}$ can be calculated from the following expressions:

$$B_{\rm e} = \frac{h}{8\pi c\mu R_{\rm e}^2}, \quad (6)$$

$$\alpha_{\rm e} = -\frac{6B_{\rm e}^2}{\omega_{\rm e}}\left(\frac{f_3R_{\rm e}}{3f_2} + 1\right), \quad (7)$$

$$\omega_{\rm e}\chi_{\rm e} = \frac{B_{\rm e}}{8}\left[-\frac{f_4R_{\rm e}^2}{f_2} + 15\left(1 + \frac{\omega_{\rm e}\alpha_{\rm e}}{6B_{\rm e}^2}\right)^2\right]. \quad (8)$$

3.2.1. The $X^2\Sigma^+$ state of CP

Table 2 tabulates the spectroscopic parameters ($D_{\rm e}$, $B_{\rm e}$, $\alpha_{\rm e}$, $\omega_{\rm e}\chi_{\rm e}$, $R_{\rm e}$ and $\omega_{\rm e}$) of the CP($X^2\Sigma^+$) radical together with the available experiments and other theories. For this state, the earlier work was done by Brouckèrey and Feller,[14] who calculated the PECs using four kinds of methods and a series of correlation-consistent basis sets. By fitting, they determined the spectroscopic parameters, $\omega_{\rm e}\chi_{\rm e}$, $\alpha_{\rm e}$, $B_{\rm e}$, $R_{\rm e}$ and $\omega_{\rm e}$. By comparison with the experimental values,[25] we find that their favourable results were

Table 2. Spectroscopic parameters from available measurements and theories for the $X^2\Sigma^+$ state.

source	$D_{\rm e}$/eV	$R_{\rm e}$/nm	$\omega_{\rm e}$/cm^{-1}	$B_{\rm e}$/cm^{-1}	$\alpha_{\rm e}$/cm^{-1}	$\omega_{\rm e}\chi_{\rm e}$/cm^{-1}
this work	5.4831	0.15683	1235.11	0.792119	0.005521	6.89653
exp.[1]	—	0.15619	1239.79	0.798867	0.005969	6.83376
exp.[3]	—	0.15621	1239.67	—	—	6.86
exp.[6]	—	0.15619	1239.80	0.798869	0.005971	6.8402
exp.[25]	5.3566	0.1562	1239.67	0.7986	0.00597	6.86
theory[14]						
aVDZ	—	0.15979	1200.9	0.7634	0.00559	6.67
aVQZ	—	0.15654	1270.0	0.7954	0.00590	9.11
theory[26]						
SCF	2.17	0.1516	—	—	—	—
SDCI	4.08	0.1543	—	—	—	—
SDQ	4.71	0.1558	—	—	—	—
theory[27]	—	0.15895	1243	—	—	–

obtained by using the MRCI method at two basis sets, aug-cc-pVDZ and aug-cc-pVQZ. For the aug-cc-pVDZ basis set, the deviations of their R_e, ω_e, B_e, α_e and $\omega_e\chi_e$ from the experimental ones[25] are 2.3%, 3.1%, 4.4%, 6.4% and 2.8%, respectively. For the aug-cc-pVQZ basis set, the deviations of their R_e, ω_e, B_e, α_e and $\omega_e\chi_e$ from the experimental ones[25] are 0.2 %, 2.4%, 0.3%, 1.1% and 32.8%, respectively. Obviously, their results are much poorer than the present result.

Later, McLean *et al.*[26] evaluated the D_e and the R_e using three approaches, which included single configuration self-consistent field (SCF), singles and doubles configuration-interaction (SDCI) and singles and doubles with quadruples correction (SDQ). In their calculation, the Slater-type basis sets were used. Compared with the experimental values,[25] their favourable results were derived using the SDQ method, and the deviation of D_e from the experimental one[25] is 11.9%. While, in our theory, the deviation of D_e from the same experimental one is only 2.36%. Obviously, the present D_e is more accurate.

Recently, Gu *et al.*[27] investigated the R_e and the ω_e of 13 electronic states of the CP radical by *ab initio* multi-reference single- and double-excitation (MRD-CI) calculations. Only two spectroscopic constants, R_e and ω_e, were evaluated in their investigations. Although their ω_e is equivalent to the present one, their R_e deviates greatly from the experiment value,[25] and the deviation is up to 1.76%.

According to the above discussion and comparison in Tables 2, we believe that the spectroscopic parameters we obtained are more accurate and complete than previous theoretical investigations. For example, for the CP($X^2\Sigma^+$) state, the values of D_e, R_e, ω_e, B_e and $\omega_e\chi_e$ deviate from the experimental values[25] only by 2.36%, 0.4%, 0.38%, 0.81% and 0.53%, respectively. As to the α_e, the difference between our result and the experimental value[25] is only 0.000449 cm^{-1}. Although it is equivalent to 7.52%, such deviations are indeed not large since the α_e is a very small quantity.

3.2.2. The $A^2\Pi$ and $B^2\Sigma^+$ states of CP

Table 3 presents the D_e, B_e, α_e, $\omega_e\chi_e$, R_e and ω_e of the CP($A^2\Pi$) and the CP($B^2\Sigma^+$) from available experiments and theories. For the $A^2\Pi$ state, only three groups of calculations can be found in the literature. These calculations are performed by McLean *et al.*[26] in 1992, Gu *et al.*[27] in 1994 and de Brouckèrey and Feller[28] in 1998, respectively. In 1992, McLean *et al.*[26] evaluated the R_e of this state using the SCF and the SDCI methods with the Slater-type basis sets. In 1994, Gu *et al.*[27] investigated the R_e and the ω_e with similarity method used in the $X^2\Sigma^+$ state of this radical. Only limited spectroscopic parameters were evaluated in these investigations.[26,27] In 1998, Brouckèrey and Feller[28] calculated the PECs using the MRCI and the MRCI+Q methods combined with the correlation-consistent basis sets, aug-cc-pVnZ (n = D, T and Q). By comparison with the available experiments,[1,6,25]

Table 3. Spectroscopic parameters from available measurements and theories for the $A^2\Pi$ and the $B^2\Sigma^+$ states.

source	D_e/eV	R_e/nm	ω_e/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}
$A^2\Pi$						
this work	4.586	0.16613	1057.89	0.703333	0.005458	6.03398
Exp[1]	—	0.16544	1062.47	0.712087	0.005620	6.03277
Exp[3]	—	0.16710	1061.99	—	—	6.035
Exp[6]	—	0.16544	1062.48	0.71208	0.005616	6.0376
Exp[25]	—	0.1653	1061.99	0.7135	0.0058	6.035
theory[26]						
SCF	—	0.1619	—	—	—	—
SDCI	—	0.1639	—	—	—	—
theory[27]	—	0.16724	1062	—	—	—
theory[28]	—	0.16552	1009.9	0.7114	0.0096	6.06
$B^2\Sigma^+$						
this work	3.506	0.1692	822.554	0.677561	0.0060329	5.68809
Exp[3]	—	0.16892	836.32	—	—	5.917
Exp[25]	—	0.16894	836.32	0.6829	0.00628	5.917
theory[27]	—	0.17178	832.0	—	—	—

we find that their favourable results were obtained at the MRCI +Q/aug-cc-pVQZ level of theory. Though their R_e, B_e and $\omega_e\chi_e$ are slightly superior to the present ones, their ω_e is too small and their α_e is too large when compared with the present results.

Spectroscopic investigations on the CP($B^2\Sigma^+$) are sparse. Only one group of calculations reported by Gu *et al.*[27] in 1994 has been found. They studied the R_e and the ω_e of this state by using the MRD-CI method and the atomic orbital basis set. Although their ω_e is slightly superior to the present, their spectroscopic constants are not complete.

From the above discussion, one can see that the spectroscopic parameters R_e and ω_e, which are directly obtained from the *ab initio* calculations, are in excellent agreement with the measurements.[1,6,25] The spectroscopic parameters, B_e, α_e and $\omega_e\chi_e$, which are obtained from the APEF fitted here, also agree well with the experiments.[1,6,25] These show that the present APEFs of the CP($A^2\Pi$) and the CP($B^2\Sigma^+$) are credible and can be used to carry out the vibrational calculations. At the same time, the present spectroscopic properties are more complete and accurate as a whole compared with previous theoretical investigations.[14,26,27]

3.3. The vibrational properties

In the adiabatic approximation, the radial nuclear Schrödinger equation can be written as

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{\hbar^2}{2\mu r^2}J(J+1)+V(r)\right]\Psi_{\nu,J}(r) = E_{\nu,J}\Psi_{\nu,J}(r), \tag{9}$$

where $V(r)$ is the rotationless APEF, which is tabulated in Table 2, r is the internuclear distance of the C and P atom, μ is the reduced mass of the CP radical, ν and J are the vibrational and the rotational quantum numbers, respectively. The rotational sub-level of a given vibrational level is represented by the following equation:

$$\begin{aligned} E_{\nu,J} = {} & G(\nu)+B_\nu[J(J+1)]-D_\nu[J(J+1)]^2 \\ & +H_\nu[J(J+1)]^3+L_\nu[J(J+1)]^4 \\ & +M_\nu[J(J+1)]^5+N_\nu[J(J+1)]^6 \\ & +O_\nu[J(J+1)]^7, \end{aligned} \tag{10}$$

where $G(\nu)$ is the vibrational level, B_ν is the rotational inertial constant, D_ν, H_ν, L_ν, M_ν, N_ν and O_ν are the centrifugal distortion constants. By solving Eq. (9) with the Numerov method, we have obtained the vibrational states for the three states when the rotational quantum number J is equal to zero ($J = 0$). For the $X^2\Sigma^+$ state, 60 vibrational states are predicted. For the $A^2\Pi$ state, 43 vibrational states are predicted. And for the $B^2\Sigma^+$ state, 29 vibrational states are predicted when $J = 0$. Here, Due to the restriction on length, we only tabulate the vibrational levels, the classical turning points and the rotational inertial constants of the first 26 vibrational states of the CP($X^2\Sigma^+$) in Table 4, and also only present the six centrifugal distortion constants of the first 26 vibrational states of the CP($X^2\Sigma^+$) in Table 5.

Table 4. Comparison of vibrational levels and classical turning points with available experiments when $J = 0$.

ν	$G(\nu)/\mathrm{cm}^{-1}$		$R_{\min}$/nm		$R_{\max}$/nm		B_ν/cm^{-1}
	this work	exp.[1]	this work	exp.[1]	this work	exp.[1]	this work
0	625.36	618.2003	0.151374	0.15087	0.162589	0.16211	0.703479
1	1866.36	1844.3276	0.147791	0.14731	0.167311	0.16687	0.698809
2	3094.01	3056.7749	0.145466	0.14501	0.170792	0.17308	0.694103
3	4308.24	4255.5341	0.143659	0.14322	0.173775	0.17339	0.689361
4	5509.00	5440.5969	0.142152	0.14174	0.176476	0.17610	0.684581
5	6696.22	6611.9549	0.140848	0.14046	0.178993	0.17863	0.679763
6	7869.82		0.139694		0.181382		0.674906
7	9029.74		0.138654		0.183678		0.670009
8	10175.91		0.137706		0.185905		0.665070
9	11308.25		0.136834		0.188079		0.660088
10	12426.68		0.136027		0.190214		0.655062
11	13531.14		0.135274		0.192320		0.649991
12	14621.54		0.134569		0.194406		0.644874
13	15697.80		0.133906		0.196479		0.639708

Table 4 *Continued*

ν	$G(\nu)/\mathrm{cm}^{-1}$		$R_{\min}/\mathrm{nm}$		$R_{\max}/\mathrm{nm}$		B_ν/cm^{-1}
	this work	exp.[1]	this work	exp.[1]	this work	exp.[1]	this work
14	16759.83		0.133281		0.198545		0.634493
15	17807.55		0.132689		0.200611		0.629227
16	18840.87		0.132127		0.202680		0.623908
17	19859.70		0.131593		0.204758		0.618535
18	20863.95		0.131085		0.206851		0.613105
19	21853.51		0.130600		0.208962		0.607616
20	22838.28		0.130131		0.211118		0.602067
21	23788.16		0.129692		0.213259		0.596455
22	24733.05		0.129267		0.215455		0.590777
23	25662.82		0.128859		0.217691		0.585032
24	26577.37		0.128468		0.219972		0.579216
25	27467.58		0.128095		0.222282		0.573326

Table 5. The centrifugal distortion constants of the first 26 vibrational states for the CP($X^2\Sigma^+$) when $J = 0$ at the MRCI/aug-cc-pV6Z for C and aug-cc-pVQZ for P level of theory.

ν	$D_\nu(\times10^{-6})/\mathrm{cm}^{-1}$	$H_\nu(\times10^{-12})/\mathrm{cm}^{-1}$	$L_\nu(\times10^{-17})/\mathrm{cm}^{-1}$	$M_\nu(\times10^{-23})/\mathrm{cm}^{-1}$	$N_\nu(\times10^{-28})/\mathrm{cm}^{-1}$	$O_\nu(\times10^{-33})/\mathrm{cm}^{-1}$
0	0.896766	0.050719	–0.210692	–0.475862	–0.269577	–0.122104
1	0.902538	0.027299	–0.223081	–0.541766	–0.308907	–0.146116
2	0.908509	0.002438	–0.236494	–0.615172	–0.353837	–0.174290
3	0.914688	-0.023968	–0.251032	–0.697015	–0.405164	–0.207356
4	0.921086	-0.052036	–0.266805	–0.788356	–0.463865	–0.246203
5	0.927715	-0.081887	–0.283940	–0.890404	–0.531084	–0.291889
6	0.934588	-0.113659	–0.302575	–1.004541	–0.608160	–0.345698
7	0.941718	-0.147501	–0.322867	–1.132356	–0.696664	–0.409139
8	0.949119	-0.183575	–0.344992	–1.275671	–0.798448	–0.484100
9	0.956806	-0.222060	-0.369147	-1.436588	-0.915695	-0.572775
10	0.964796	–0.263155	–0.395554	–1.617530	–1.050990	–0.677906
11	0.973107	–0.307075	–0.424464	–1.821307	–1.207399	–0.802709
12	0.981758	–0.354062	–0.456162	–2.051175	–1.388575	–0.951311
13	0.990770	–0.404380	–0.490970	–2.310925	–1.598876	–1.128631
14	1.000164	–0.458323	–0.529254	–2.604980	–1.843528	–1.340885
15	1.009966	–0.516219	–0.571433	–2.938517	–2.128799	–1.595219
16	1.020201	–0.578429	–0.617984	–3.317615	–2.462260	–1.901032
17	1.030897	–0.645361	–0.669455	–3.749431	–2.853077	–2.270014
18	1.042086	–0.717466	–0.726473	–4.242425	–3.312384	–2.716396
19	1.053801	–0.795253	–0.789766	–4.806627	–3.853782	–3.259052
20	1.066080	–0.879293	–0.860170	–5.453982	–4.493908	–3.919855
21	1.078962	–0.970228	–0.938660	–6.198762	–5.253274	–4.728026
22	1.092492	–1.068786	–1.026367	–7.058091	–6.157235	–5.720899
23	1.106719	–1.175789	–1.124617	–8.052608	–7.237325	–6.945885
24	1.121695	–1.292175	–1.234961	–9.207300	–8.532933	–8.464352
25	1.137481	–1.419010	–1.359230	–10.05525	–10.093567	–10.035588

Only one group[1] has reported the vibrational levels and the classical turning points of the CP ($X^2\Sigma^+$) radical so far. In order to conveniently compare them with the present result, we also tabulate them in Table 4. As a whole, the present results are in good accord with the experiments. For example, the largest deviation of the $G(\nu)$ from the experimental data[1] does not exceed 1.26% and the largest deviation of the classical turning points from the experiments[1] is also within 0.27%. These show

that the present results are accurate.

Unfortunately, no experiments and theories can be found in the literature about the vibrational levels and the classical turning points when the vibrational level is higher than 5, and no rotational inertial constants and centrifugal distortion constants have been reported. Thus, we cannot make any direct comparison. However, according to the high-quality fitting of the APEF, the excellent agreement between the present spectroscopic parameters and the measurements, and the good accord of vibrational levels and classical turning points between theory and experiment,[1] we believe that the results collected in Tables 4 and 5 should be accurate. Therefore, we can conclude that the APEF tabulated in Table 1 can describe the interaction potential of these three electronic states of the CP radical.

4. Conclusions

In this paper, the MRCI approach combined with the large correlation-consistent basis sets in the valence range is used to investigate the equilibrium internuclear separations, the harmonic frequencies and the PECs of the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states of the CP radical. The PECs are all fitted with the M–S function. Based on the APEFs obtained, the spectroscopic parameters are evaluated. By numerically solving the radial nuclear Schrödinger equation with $J = 0$, we determine the vibrational states, the rotational inertial and the centrifugal distortion constants. By comparison with the available experiments, we find that the obtained vibrational propertises are both reliable and accurate. These results can be used as a reference for future investigations of the CP radical.

References

[1] Ram R S, Tam S and Bernath P F 1992 *J. Mol. Spectrosc.* **152** 89

[2] Herzberg G 1930 *Nature* **126** 131

[3] Bärwald H, Herzberg G and Herzberg L 1934 *Ann. Phys.* **20** 569

[4] Chaudhry A K and Upadhya K N 1969 *Ind. J. Phys.* **43** 83

[5] Tripathi R, Rai S B and Upadhya K N 1981 *Pramana* **17** 249

[6] Ram R S and Bernath P F 1987 *J. Mol. Spectosc.* **122** 282

[7] Saito S, Yamamoto S, Kawaguchi K, Ohishi M, Suzuki H, Ishikawa S I and Kaifu N 1989 *Astrophys. J.* **341** 1114

[8] Singh P D and Pathak A N 1969 *Ind. J. Pure Appl. Phys.* **7** 132

[9] Wentink T and Spindler R J 1970 *J. Quant. Spectrosc. Radiat. Transfer.* **10** 609

[10] Murthy N S and Murthy B N 1970 *J. Phys.* B **3** L15

[11] Murthy N S, Gowda L S and Murthy B N 1976 *Pramana* **6** 25

[12] Rohlfing C M and AlmlÖf J 1988 *Chem. Phys. Lett.* **147** 258

[13] Richman K W, Shi Z G and Mccullough E A 1987 *Chem. Phys. Lett.* **141** 186

[14] de Brouckère G and Feller D 1996 *J. Phys.* B **29** 5283

[15] de Brouckère G 1997 *J. Phys.* B **30** 1847

[16] Knowles P J and Werner H J 1988 *Chem. Phys. Lett.* **145** 514

[17] Shi D H, Zhang J P, Sun J F, Liu Y F and Zhu Z L 2009 *Acta Phys. Sin.* **58** 2369 (in Chinese)

[18] Gao F, Yang C L, Hu Z Y and Wang M S 2007 *Chin. Phys.* **16** 3668

[19] Chen H J, Cheng X L, Tang H Y, Wang Q W and Su X F 2010 *Acta. Phys. Sin.* **59** 4556 (in Chinese)

[20] Peterson K A, Woon D E and Dunning T H 1994 *J. Chem. Phys.* **100** 7410

[21] Woon D E and Dunning T H 1993 *J. Chem. Phys.* **98** 1358

[22] González J L M Q and Thompson D 1997 *Comput. Phys.* **11** 514

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

[24] Zhang X N, Shi D H, Zhang J P, Zhu Z L and Sun J F 2010 *Chin. Phys.* B **19** 053401

[25] Huber K P and Herzberg G 1979 *Molecular Spectra and Molecular Structure* IV *Constants of Diatomic Molecules* (New York: van Nostrand Reinhold Company) p420

[26] McLean A D, Liu B and Chandler G S 1992 *J. Chem. Phys.* **97** 8459

[27] Gu J P, Buenker R J and Hirsch G 1994 *Chem. Phys.* **185** 39

[28] de Brouckèrey G and Feller D 1998 *J. Phys.* B **31** 5053