



Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Theoretical study on low-lying electronic states of CP radical: Energy levels, Einstein coefficients, Franck-Condon factors and radiative lifetimes

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ARTICLE INFO

Article history:

Received 9 February 2019

Revised 20 March 2019

Accepted 28 March 2019

Available online 29 March 2019

Keywords:

Potential energy curve

Transition dipole moment

Radiative lifetimes

Carbon monophosphide

ABSTRACT

The state-of-the-art *ab initio*-based valence internally contracted multireference configuration-interaction (icMRCI) method, including the Davidson correction, core-valence correction and scalar relativistic correction and the basis-set extrapolation, is used to calculate the potential energy curves (PECs) of the $X^2\Sigma^+$, $B^2\Sigma^+$, $A^2\Pi$, $1^2\Sigma^-$, $1^2\Delta$, $2^2\Delta$, $2^2\Sigma^-$, $1^4\Sigma^+$, $2^4\Sigma^+$, $1^4\Pi$, $1^4\Delta$, $1^4\Sigma^-$, $2^4\Delta$, $2^4\Sigma^-$, $1^6\Sigma^+$ and $2^6\Sigma^+$ electronic states for CP radical. We also calculate the transition dipole moments (TDMs), Einstein coefficients and Franck-Condon factors for nineteen dipole allowed transitions between these sixteen states. The PECs are used to fit spectroscopic parameters, which are in excellent agreement with previous experimental and theoretical ones. The computed Franck-Condon factors also agree quite well with accurate semi-empirical results for the $A^2\Pi-X^2\Sigma^+$ and $B^2\Sigma^+-X^2\Sigma^+$ systems. Such good agreement implies that the results are accurate enough to assist identification of the spectra from astrophysical sources. Large amounts of energy levels and transition data of high accuracy are provided in this work for CP radical of astrophysical interest, where experimental data are still scarce.

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1. Introduction

Phosphorus (P) is of great interest since it is an important element of biological systems. P-bearing molecules may provide important biomarkers in exoplanets. Over the past few years, a few simple P-bearing species had been detected in the circumstellar environments [1–7]. Among these species, carbon monophosphide (CP) is the second P-bearing molecule discovered in the interstellar medium [6]. It was first detected by Guelin et al. [6] in the carbon-rich asymptotic giant branch (AGB) star envelope IRC+10,216, in which Milam et al. [1] also found that CP is primarily the photodissociation product of HCP. Long-wavelength transition spectra had thus been observed for CP. As is known to all, knowledge of molecular parameters, such as energy levels and transition parameters, is vital to analysis of the detected spectra. Available transition parameters of CP radical appear to be extremely limited except for those between the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states.

In the early experimental studies of CP, the $B^2\Sigma^+-X^2\Sigma^+$ system was observed by Herzberg [8], who also, hence, identified the

existence of this radical. Subsequently, Bärwald et al. [9] observed the $B^2\Sigma^+-X^2\Sigma^+$ and $A^2\Pi-X^2\Sigma^+$ systems in the 2900–5000 Å region. Since then, a large number of experimental approaches have been developed to measure the transition spectra of CP radical. Using these techniques, including discharge tube-induced spectroscopy [10,11], Fourier transform spectroscopy [12,13], microwave spectroscopy [14] and millimeter-wave spectroscopy [1], etc., researchers mainly investigated the $B^2\Sigma^+-X^2\Sigma^+$, $A^2\Pi-X^2\Sigma^+$ and $B^2\Sigma^+-A^2\Pi$ systems, as reviewed by Shi et al. [15]. A similar review of the experimental work was given by Abbiche et al. [16], together with some brief comments.

In theory, a number of calculations [15–29] have been carried out to investigate the molecular properties of CP radical. Most studies mainly reported the potential energy curves (PECs) and the spectroscopic parameters of low-lying electronic states for CP radical. Recently, Abbiche et al. [16] gave a comprehensive review of the theoretical work of CP by summarizing the literature before 2014. Among these studies, five groups [20,22,28–30] calculated the radiative transition probabilities for CP radical. Wentink and Spindler [28] calculated the Franck-Condon factors and r-centroids of the $A^2\Pi-X^2\Sigma^+$ system based on the Morse potentials. Murthy et al. [29] employed the Rydberg-Klein-Rees (RKR) potential to compute the Franck-Condon factors and r-centroids of the $B^2\Sigma^+-A^2\Pi$ system. With *ab-initio* multi-reference single- and double-

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Table 1
Dissociation relationships of the thirty-nine electronic states resulting from the lowest four dissociation limits of CP radical.

Dissociation limit	Electronic states	Relative energy (cm ⁻¹)	
		This work ^a	Experiment ^b
C(³ P _g)+P(⁴ S _u)	X ² Σ ⁺ , A ² Π, 1 ⁴ Σ ⁺ , 1 ⁴ Π, 1 ⁶ Σ ⁺ , 1 ⁶ Π,	0.00	0.00
C(¹ D _g)+P(⁴ S _u)	1 ⁴ Σ ⁻ , 2 ⁴ Π, 1 ⁴ Δ	10,104.82	10,192.66
C(³ P _g)+P(² D _u)	B ² Σ ⁺ , 3 ² Σ ⁺ , 1 ² Σ ⁻ , 2 ² Π, 3 ² Π, 4 ² Π, 1 ² Δ, 2 ² Δ, 1 ² Φ 2 ⁴ Σ ⁺ , 3 ⁴ Σ ⁺ , 2 ⁴ Σ ⁻ , 3 ⁴ Π, 4 ⁴ Π, 5 ⁴ Π, 2 ⁴ Δ, 3 ⁴ Δ, 1 ⁴ Φ	11,330.31	11,368.83 ^c
C(³ P _g)+P(² P _u)	4 ² Σ ⁺ , 2 ² Σ ⁻ , 3 ² Σ ⁻ , 5 ² Π, 6 ² Π, 3 ² Δ, 4 ⁴ Σ ⁺ , 3 ⁴ Σ ⁻ , 4 ⁴ Σ ⁻ , 6 ⁴ Π, 7 ⁴ Π, 4 ⁴ Δ	18,839.89	18,735.36 ^d

^a Obtained by the icMRCI+Q/56+CV+DK calculations.

^b Ref. [32].

^c Averaged by the energy levels of the P(²D_{3/2}) and P(²D_{5/2}) states.

^d Averaged by the energy levels of the P(²P_{1/2}) and P(²P_{3/2}) states.

excitation configuration interaction (MRD-CI) method, Gu et al. [20] calculated the PECs of thirteen low-lying electronic states and determined the oscillator strengths of the A²Π-X²Σ⁺, B²Σ⁺-X²Σ⁺, B²Σ⁺-A²Π and 1⁴Π-1⁴Σ⁺ systems. Using the CI approach, de Brouckère and Feller [22] obtained the PECs of the A²Π and X²Σ⁺ states, which were used to evaluate the vibrational band origins and Franck-Condon factors of the A²Π-X²Σ⁺ system. In addition, spectroscopic constants from high resolution spectra were used by Ram et al. [13] to calculate the RKR potentials of the A²Π and X²Σ⁺ states. The RKR potentials, together with the transition dipole moments (TDMs) calculated by de Brouckère and Feller [22], were utilized to calculate the Einstein coefficients and oscillator strengths of the A²Π-X²Σ⁺ system.

Much effort has been devoted to the spectroscopic properties of CP radical due to its importance in astrophysics. A large number of spectral bands have been measured for the B²Σ⁺-X²Σ⁺, A²Π-X²Σ⁺ and B²Σ⁺-A²Π systems. The A²Π-X²Σ⁺ and B²Σ⁺-A²Π systems have also been investigated by semi-empirical and *ab initio* methods. Only one group calculated the oscillator strengths of the 1⁴Π-1⁴Σ⁺ system. Except for the 1⁴Π-1⁴Σ⁺ system, the transition properties between quartet or sextet states seem to be unavailable in the literature. Therefore, we determine the radiative transition probabilities between doublet, quartet or sextet states and evaluate the radiative lifetimes for several excited states of CP radical, in order to provide valid theory support for detecting the unobserved band systems either in the laboratory or in astrophysical observations.

In this work, the *ab initio* valence internally contracted multireference configuration-interaction (icMRCI) method, including the Davidson correction, core-valence correction and scalar relativistic correction and the basis-set extrapolation, is adopted to investigate the PECs and the spectroscopic parameters for sixteen low-lying electronic states of CP radical. The theory and methodology are given in Section 2. Transition dipole moments (TDMs) and radiative transition probabilities for dipole allowed transitions are computed and presented in Section 3, along with the radiative lifetimes of vibrational levels for twelve electronic states. In Section 4, some main conclusions are drawn.

2. Theory and methodology

2.1. Dissociation relationships

Details of the lowest four dissociation relationships of thirty-nine Λ-S states for CP radical are displayed in Table 1. We consider fifteen of them in this work, together with the 2⁶Σ⁺ state. The dissociation limits of these fifteen states are the C(³P_g)+P(⁴S_u) for the X²Σ⁺, A²Π, 1⁴Σ⁺, 1⁴Π and 1⁶Σ⁺ states, the C(¹D_g)+P(⁴S_u) for the 1⁴Σ⁻ and 1⁴Δ states, the C(³P_g)+P(²D_u) for the B²Σ⁺, 1²Σ⁻, 1²Δ, 2²Δ, 2⁴Σ⁻ and 2⁴Δ states, and the C(³P_g)+P(²P_u) for the 2²Σ⁻ state, respectively. The dissociation limit of the 2⁶Σ⁺ state

is questionable. According to our calculations, the 2⁶Σ⁺ state most probably correlates to the C(¹S_g)+P(²D_u) or the C(⁵S_g)+P(⁴S_u) dissociation limit, which, however, goes against the Wigner-Witmer rules [31]. As seen in Table 1, the calculated energy separations between each higher dissociation limit and the lowest one agree well with the experimental data [32].

2.2. PECs and TDMs

The PECs of sixteen electronic states of CP radical are calculated using the complete active space self-consistent field (CASSCF) method [33], which is followed by the icMRCI approach with the Davidson correction (icMRCI+Q), as implemented in the MOLPRO 2015 program suite [34] in C_{2v} symmetry. In the CASSCF calculations, the electronic states that have same spin multiplicity and symmetry are averaged using the state-averaging technique. All the CASSCF wave functions are taken as reference for the icMRCI calculations. Nine outermost molecular orbitals (MOs) (5a₁, 2b₁ and 2b₂) are put into the active space, which correspond to the 5-9σ, 2π and 3π MOs. Nine valence electrons of CP are distributed into eleven valence MOs, and the remaining twelve inner electrons are put into six closed-shell MOs (4a₁, 1b₁ and 1b₂).

The potential energy for each internuclear distance is comprised of the reference energy and the correlation energy. Due to the different convergence speeds of the reference energy and the correlation energy, we should extrapolate the reference energy and the correlation energy to the complete basis set (CBS) limit, respectively. The basis-set extrapolation formulas [35,36] are given by

$$E_X^{ref} = E_\infty^{ref} + A^{ref} X^{-\alpha} \quad (1)$$

$$E_X^{cor} = E_\infty^{cor} + A^{cor} X^{-\beta} \quad (2)$$

where E_X^{ref} and E_X^{cor} are the reference and correlation energies, respectively, calculated with the aug-cc-pVXZ (X=5 or 6) basis set. E_∞^{ref} and E_∞^{cor} are the reference and correlation energies, respectively, obtained by the basis set extrapolation. Extrapolated parameters α and β are 3.4 and 2.4 for the reference and correlation energies, respectively [35]. Recently, a new basis-set extrapolation scheme is proposed by Pansini et al. [32,37,38], given by

$$E_X^{ref} = \frac{E_{X_i}^{ref} e^{\beta \tilde{X}_i} - E_{X_j}^{ref} e^{\beta \tilde{X}_j}}{e^{\beta \tilde{X}_i} - e^{\beta \tilde{X}_j}} \quad (3)$$

$$E_X^{cor} = E_{X_j}^{cor} + \frac{\tilde{X}_i^3}{\tilde{X}_j^3 - \tilde{X}_i^3} (E_{X_j}^{cor} - E_{X_i}^{cor}) \quad (4)$$

where \tilde{X}_i and \tilde{X}_j are hierarchical numbers, which are different for the reference and correlation energies. Detailed descriptions can refer to the literature [32,37]. β is a parameter of 1.62 [32]. In this work, The aug-cc-pV5Z (AV5Z) and aug-cc-pV6Z (AV6Z) basis sets

Table 2

Spectroscopic parameters of the ground state $X^2\Sigma^+$ for CP radical extrapolated to the CBS limit by two schemes without consideration of the CV and DK corrections.

MRCI+Q	D_e/cm^{-1}	T_e/cm^{-1}	$R_e/\text{\AA}$	ω_e/cm^{-1}	$\omega_e x_e/\text{cm}^{-1}$	$\omega_e y_e/\text{cm}^{-1}$	B_e/cm^{-1}	$10^3 \alpha_e/\text{cm}^{-1}$
AV5Z	43,373.2	0.00	1.5690	1213.8	0.0383	0.844	0.7913	5.21
AV6Z	43,558.2	0.00	1.5679	1215.7	0.1910	0.815	0.7922	5.17
56 ^a	43,989.1	0.00	1.5663	1219.2	0.4845	0.760	0.7936	5.12
56 ^b	43,884.6	0.00	1.5670	1217.8	0.4104	0.763	0.7930	5.10
Experiment ^c	43,203.88 ^d	0.00	1.5620	1239.80	6.83377	0.0013769	0.79887	5.96933

^a Obtained from the basis-set extrapolation scheme given by Truhlar [35,36].

^b Obtained from the basis-set extrapolation scheme given by Pansini et al. [32,37,38].

^c Ref. [13].

^d Ref. [42].

of Dunning [39–41] are both employed to extrapolate the potential energy to the CBS limit. The obtained energy is expressed as “56” for convenient description. The spectroscopic parameters of the ground state obtained by these two extrapolation schemes are presented in Table 2. As clearly seen, these two sets of results are very close to each other. In view of good agreement of these two results, the use of earlier Eqs. (1) and (2) is justified for the CP molecular system studied in this work.

Core-valence (CV) correlation correction is taken into account by the icMRCI method with the cc-pCV5Z basis set [43]. Scalar relativistic correction is calculated at the icMRCI/cc-pV5Z-DK [44] level of theory, with consideration of the third-order Douglas-Kroll-Hess (DKH3) Hamiltonian approximation [45,46] (denoted as DK). Similar treatments can be found in Ref. [15,47]. Finally, we calculate the potential energy for each internuclear distance at the icMRCI+Q/56+CV+DK level of theory.

Utilizing the obtained PECs, the vibrational levels and the inertial rotation constants are obtained by the LEVEL program [48]. They are then used to fit the spectroscopic parameters. The electronic transition dipole moments (TDMs) are calculated by the valence icMRCI method with the AV6Z basis set, as applied in the MOLPRO 2015 program suite.

2.3. Transition probabilities

The obtained PECs are introduced in the nuclear radial Schrödinger equation to calculate the vibrational wave functions $\psi_{v'}(r)$. Radiative transition probabilities such as the square of electronic-vibrational transition moment $(R_e^{v'v''})^2$, the Einstein coefficients $A_{v'v''}$ and the Franck-Condon factors $q_{v'v''}$ from vibrational levels v' in the upper electronic state to those v'' in the lower electronic state are expressed in terms of the vibrational wave function and the TDMs $R_e(r)$ [49,50]

$$(R_e^{v'v''})^2 = \left[\int_0^\infty \psi_{v'}(r) R_e(r) \psi_{v''}(r) dr \right]^2 \quad (5)$$

$$A_{v'v''} = 2.026 \times 10^{-6} \sigma_{v'v''}^3 \frac{2 - \delta_{0,\Lambda'+\Lambda''}}{2 - \delta_{0,\Lambda'}} (R_e^{v'v''})^2 \quad (6)$$

$$q_{v'v''} = \left(\int \psi_{v'}(r) \psi_{v''}(r) dr \right)^2 \quad (7)$$

where $\sigma_{v'v''}$ is the wavenumber of a band system, Λ' and Λ'' are the projections of electronic orbital angular momentum on the internuclear axis for upper and lower electronic levels, respectively. The total Einstein coefficients of a certain vibrational level v' in the upper electronic state are obtained by summing all the Einstein coefficients from v' to all possible vibrational levels v'' in the lower electronic states. The radiative lifetimes of this vibrational level $\tau_{v'}$ is determined as the reciprocal of its total Einstein coef-

ficients, given by

$$\tau_{v'} = \frac{1}{\sum_{v''=0}^{v''_{\max}} A_{v'v''}} \quad (8)$$

3. Results and discussion

3.1. Electronic structures

For clarity, Fig. 1 provides the PECs of sixteen electronic states for CP versus the internuclear distance up to 4.0 Å. The PECs for long-range regions (up to 10 Å) are given in the supplemental material. Vibrational levels G_v and internal rotation constants B_v for each electronic state are determined by solving the radial Schrödinger equation over the obtained PECs. Some G_v and B_v ($v \leq 24$ whenever available) are listed in the supplement material. The calculated spectroscopic parameters are given in Table 3, together with their comparison with previous computations and experimental determinations. For the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states, a very good agreement of their spectroscopic parameters with available experimental data is noticeable. Hence, similar accuracy is assumed for the other unobserved electronic states. The obtained spectroscopic parameters considered here are in an overall agreement with those recently calculated by Shi et al. [15] and Abbiche et al. [16]. In addition, T_e and G_v are utilized to compute the band positions, which are then used to identify the spectral ranges of different band systems, given in the supplemental material.

Table 4 lists the dominant electron configurations for each electronic state near its equilibrium internuclear distance. The representations of different electron orbitals can refer to Fig. 155 of Ref. [51] and some explanations for different orbitals can be found in its corresponding chapter. The ground $X^2\Sigma^+$ state of the CP radical is mainly characterized by the electron configuration $5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta\beta}7\sigma^{\alpha}3\pi^08\sigma^0$ (88.6%) around the equilibrium internuclear distance. The other electron configuration $5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta\beta}7\sigma^{\alpha}3\pi^{\alpha}8\sigma^0$ (9.9%) is insignificant. Hence, we think that the multireference characterization of the ground state is not obvious. The $A^2\Pi$ state is obtained after promotion of one electron from the ground state, i.e. $2\pi^{\beta} \rightarrow 7\sigma^{\beta}$. For the $B^2\Sigma^+$, $1^2\Sigma^-$, $1^2\Delta$, $2^2\Delta$, $2^2\Sigma^-$, $1^4\Sigma^+$, $1^4\Delta$ and $1^4\Sigma^-$ states, they have similar electron compositions and are dominantly described by a $2\pi \rightarrow 3\pi$ excitation, explicit α or β excitations from the 2π to the 3π MO are clearly presented in Table 4. The $1^4\Pi$, $2^4\Sigma^+$, $2^4\Delta$, $2^4\Sigma^-$ and $1^6\Sigma^+$ states are double excitations from the ground state. For example, the $2^4\Sigma^+$, $2^4\Delta$, $2^4\Sigma^-$ and $1^6\Sigma^+$ states correspond to simultaneous two electron excitations of the 2π MO to the 3π MO, differing only in the α or β promotions. The $1^4\Pi$ state is mainly described by the $2\pi^{\alpha\beta} \rightarrow 7\sigma^{\beta}3\pi^{\alpha}$ electron excitations. For the $2^6\Sigma^+$ state, it is formed by three electron excitations from the ground state with the $5\sigma^{\alpha\beta}6\sigma^{\alpha}2\pi^{\alpha\alpha}7\sigma^{\alpha\beta}3\pi^{\alpha\alpha}8\sigma^0$ (62.5%) configuration. It is worth noting that the electron configurations

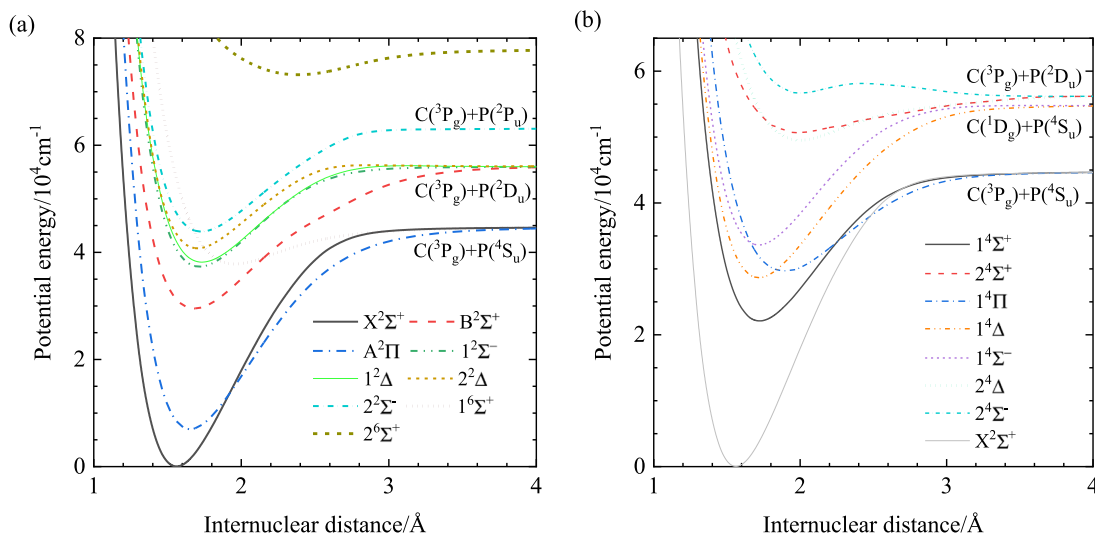


Fig. 1. The computed PECs of (a) the $X^2\Sigma^+$, $B^2\Sigma^+$, $A^2\Pi$, $1^2\Sigma^-$, $1^2\Delta$, $2^2\Delta$, $2^2\Sigma^-$, $1^6\Sigma^+$ and $2^6\Sigma^+$ states (b) the $1^4\Sigma^+$, $2^4\Sigma^+$, $1^4\Pi$, $1^4\Delta$, $1^4\Sigma^-$, $2^4\Delta$ and $2^4\Sigma^-$ states for CP calculated by the icMRCI+Q/56+CV+DK level of theory.

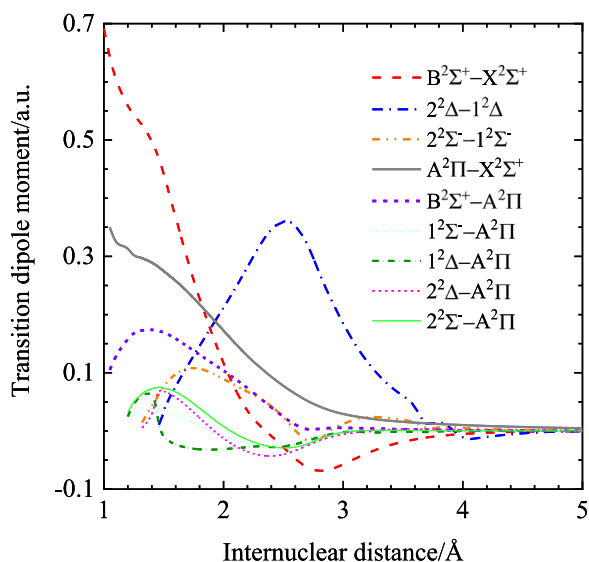


Fig. 2. The calculated TDMs versus the internuclear distance for nine band transition systems between the $X^2\Sigma^+$, $B^2\Sigma^+$, $A^2\Pi$, $1^2\Sigma^-$, $2^2\Sigma^-$, $1^2\Delta$ and $2^2\Delta$ states.

discussed here are the leading compositions of the corresponding electronic states.

3.2. Electric dipole transitions between doublet states

In order to clearly show the transitions for the $2^2\Sigma^- - 1^2\Sigma^-$ and $2^2\Delta - 1^2\Delta$ systems, the detailed electron configurations are presented in Table 4. As clearly shown, the main electron transition for these two systems is $2\pi^\alpha 3\pi^\beta \rightarrow 2\pi^\beta 3\pi^\alpha$ promotion. The TDMs between doublet states are given in Fig. 2. The TDMs of the $1^2\Sigma^- - A^2\Pi$, $1^2\Delta - A^2\Pi$, $2^2\Delta - A^2\Pi$ and $2^2\Sigma^- - A^2\Pi$ systems are very similar, which is consistent with the $1^2\Sigma^-$, $1^2\Delta$, $2^2\Delta$ and $2^2\Sigma^-$ states having similar electron compositions, differing only in the coupling of the angular momentum.

The $A^2\Pi - X^2\Sigma^+$ system is analogous to the red system of CN. First observation of this system was conducted by Ram and Bernath [12], later extended to new bands involving $v=0-4$ of

both states. The PECs of the $A^2\Pi$ and $X^2\Sigma^+$ states and the Franck-Condon factors for this system were also computed by Ram et al. [13] using their fitting molecular constants. Utilizing our calculated PECs and TDMs, we determine the Einstein coefficients and the Franck-Condon factors for this system by the LEVEL program [48]. As shown in Table 5, Our calculated Franck-Condon factors agree very well with the semi-empirical results of Ram et al. [13] and the ab initio results of de Brouckère and Feller [22]. Detailed comparisons show that our theoretical results are closer to the semi-empirical values than those calculated by de Brouckère and Feller [22] due to the larger basis set used in this work, along with the CV and DK corrections. Using the T_e and G_v of the $X^2\Sigma^+$ and $A^2\Pi$ states, we evaluate the vibrational band origins of the $A^2\Pi - X^2\Sigma^+$ system, which shows that transitions in the infrared region between low-lying vibrational levels of both states are most likely occurring, which is consistent with the experimental observation [12,13]. The $A^2\Pi$ state is the first excited state that has dipole allowed transition. The estimated radiative lifetimes of some low-lying vibrational levels for the $A^2\Pi$ state are presented in Table 12.

For the $B^2\Sigma^+ - A^2\Pi$ system, Bärwald et al. [9] first observed the $B^2\Sigma^+ - A^2\Pi$ system in the 4390–4660 Å spectral region and identified the rotational constants of this system based on head-origin separations. In order to obtain more information about this system, Chaudhry and Upashya [10] photographed the bands of this system, but only the (0, 0) band with its two sub-bands were photographed with sufficient intensity. About ten years later, Tripathi et al. [11] reinvestigated the $B^2\Sigma^+ - A^2\Pi$ system, photographed the rotational structures in the (0, 0) and (1, 1) bands and determined the accurate spectroscopic constants. Since then, no further experimental work seems to be available on this band system. In our calculations, the vibrational wavefunctions between the $A^2\Pi$ and $B^2\Sigma^+$ states are non-orthogonal. Therefore, large radiative transition probabilities should lie in and near the diagonal matrix elements. Some of them are collected in Table 5. As for the observed (0,0) and (1,1) bands, our calculated Einstein coefficients are larger than other low-lying vibrational bands, which is also consistent with the fact that they were first observed experimentally. The calculated Einstein coefficients are smaller than those computed by Gu et al. [20], but their relative variation between transitions from one band to another band is similar. Similar finding was also presented by Ram et al. [13] for the $A^2\Pi - X^2\Sigma^+$ system. Our results

Table 3

Spectroscopic parameters of sixteen low-lying electronic states for CP radical calculated at the icMRCI+Q/56+CV+DK level of theory.

State		D_e/cm^{-1}	T_e/cm^{-1}	$R_e/\text{Å}$	ω_e/cm^{-1}	$\omega_e X_e/\text{cm}^{-1}$	$10^2 \omega_e Y_e/\text{cm}^{-1}$	B_e/cm^{-1}	$10^3 \alpha_e/\text{cm}^{-1}$
$X^2\Sigma^+$	This work	43,991.3	0.0	1.5602	1238.3	6.595	2.681	0.7966	5.88
	Exp. [42]	43,203.88	0.0	1.5622	1239.67	6.86		0.7986	5.97
	Exp. [13]		0.0	1.5620	1239.80	6.83377	0.13769	0.79887	5.96933
	Cal. [17]			1.5732	1223.4				
	Cal. [21]	43,649.09	0.0	1.5697	1239.7	8.78	2	0.7910	5.83
	Cal. [23]			1.56	1284			0.80124	
	Cal. [24]			1.563	1258				
	Cal. [25]			1.5722	1224.5	6.76		0.703	
	Cal. [27]			1.5737				0.78654	
	Cal. [15]	43,704.8	0.0	1.5642	1238.7	6.807	0.699	0.79652	5.92
Cal. [16]		0.0	1.5590	1250.8	6.84		0.80214	6.05	
$A^2\Pi$	This work	37,016.3	6975.3	1.6529	1065.9	5.970	2.178	0.7134	5.59
	Exp. [42]	36,229.60	6974.05	1.653	1061.99	6.035		0.7135	5.8
	Exp. [13]	36,348.97±1399.78		1.6544	1062.47	6.03277	0.897	0.71209	5.6203
	Cal. [22]		6729.5	1.6542	1064.8				
	Cal. [25]		6637.94	1.6646	1050.7	5.98	0.789		
	Cal. [15]	36,688.5	7016.17	1.6562	1063.42	6.041	0.975	0.71000	5.39
Cal. [16]			1.6510	1070.5	6.07		0.71481	5.61	
$1^4\Sigma^+$	This work	21,914.1	22,091.3	1.7220	892.0	6.279	2.155	0.6572	6.08
	Cal. [20]		19,405.69	1.7549	891				
	Cal. [15]	21,924.6	21,780.22	1.7157	876.7	0.820	77.6	0.65709	8.03
Cal. [16]			1.7204	896.4	6.42		0.65844	6.16	
$1^4\Delta$	This work	25,443.1	28,653.0	1.7167	890.5	7.016	6.79	0.6613	6.48
	Cal. [20]		27,761.59	1.7478	882				
	Cal. [15]	25,536.3	28,353.5	1.7201	887.61	6.499	2.635	0.65874	6.36
Cal. [16]			1.7151	893.3	6.36		0.66283	6.37	
$B^2\Sigma^+$	This work	25,810.2	29,511.4	1.6874	834.8	5.060	12.73	0.6802	5.82
	Exp. [42]	25,466.14	29,100.4	1.6894	836.32	5.917		0.6829	6.28
	Cal. [20]		28,753.65	1.7178	832				
	Cal. [15]	25,768.6	29,280.77	1.6895	837.87	5.023	14.94	0.68276	6.07
$1^4\Pi$	This work	14,281.6	29,716.4	1.8865	623.7	4.226	50.81	0.5434	3.96
	Cal. [20]		27,245.40	1.9119	675				
	Cal. [15]	14,469.58	29,235.34	1.8797	672.95	5.282	4.487	0.55158	5.78
Cal. [16]			1.8722	681.1	4.77		0.55613	6.43	
$1^4\Sigma^-$	This work	20,392.0	33,618.6	1.7162	876.9	7.033	3.54	0.6615	6.71
	Cal. [20]		33,133.24	1.7435	841				
	Cal. [15]	20,541.32	33,347.85	1.7190	877.22	6.961	0.013	0.65953	6.70
$1^2\Sigma^-$	This work	18,594.6	37,311.9	1.7158	875.6	7.535	1.425	0.6620	6.99
	Cal. [20]		38,496.83	1.7499	798				
	Cal. [15]	18,580.59	37,057.63	1.7212	866.89	6.919	0.339	0.65784	6.86
$1^6\Sigma^+$	This work	7001.8	37,814.3	1.9555	607.4	10.08	19.86	0.5081	6.48
	Cal. [16]			1.9722	565.5	5.32		0.50098	10.24
$1^2\Delta$	This work	17,227.0	38,164.4	1.7389	845.6	5.958	5.205	0.6490	6.50
	Cal. [20]		38,964.63	1.7725	783				
	Cal. [15]	17,136.05	37,913.36	1.7369	845.96	6.041	15.03	0.64600	6.17
$2^2\Delta$	This work	15,042.0	40,746.9	1.7027	864.0	8.542	0.595	0.6721	8.06
	Cal. [15]	14,426.03	40,623.00	1.7076	860.88	8.009	24.61	0.66837	7.74
$2^2\Sigma^-$	This work	18,972.1	43,859.2	1.7272	823.0	7.038	0.204	0.6533	7.59
	Cal. [15]	18,548.33	43,873.86	1.7312	821.45	7.510	5.701	0.65039	7.62
$2^4\Delta$	This work	5995.5	49,493.4	1.9928	571.6	13.69	3.819	0.4865	5.41
	Cal. [15]	5837.03	49,211.92	2.0008	520.62	8.110	34.11	0.48694	7.95
$2^4\Sigma^+$	This work	5034.3	50,664.7	1.9544	501.0	18.025	382.7	0.4952	13.6
$2^4\Sigma^-$	This work	1473.6	56,675.7	1.9992	533.2	4.094	575.7	0.4863	10.0
	Cal. [15]	1686.50	56,271.32	2.0066	491.4	8.733	156.6	0.48351	7.67
$2^6\Sigma^+$	This work	4697.9	73,159.7	2.3850	369.5	2.221	20.71	0.3406	0.76
	Cal. [15]	4520.74	72,212.64	2.3853	357.32	1.868	62.11	0.34259	1.10

are considered to be more accurate since we use a higher level of theory, with the CBS extrapolation, the CV and DK corrections.

With regard to the $B^2\Sigma^+-X^2\Sigma^+$ system, only one experimental study was conducted by Bärwald et al. [9] to investigate its transition properties, but many bands including $v'=0-10$, $v''=0-9$, were recorded. The vibrational band origins of this system are calculated to compare with those determined experimentally [9]. A deviation of 400 cm^{-1} is observed, which can be explained by the difference of also about 400 cm^{-1} between our calculated T_e of the

$B^2\Sigma^+$ state and the corresponding experimental value [42]. This deviation is commonly observed for these quantities (T_e or D_e) using such a large level of theory. Our calculated Franck-Condon factors of the $B^2\Sigma^+-X^2\Sigma^+$ system are listed in Table 5, which match well with those determined using the Morse potential [28]. Such a good agreement verifies the accuracy of our calculated transition data.

The other doublet transition systems presented in this work have not been observed in the experiments. The TDMs of the

Table 4

Main electron configurations of sixteen electronic states for CP radical around their corresponding equilibrium internuclear distances.

State	Main Electron Configuration ^a	State	Main Electron Configuration ^a	State	Main Electron Configuration ^a
$X^2\Sigma^+$	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^08\sigma^0(0.886)$	$2^2\Delta$	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^08\sigma^0(0.520)$	$2^4\Delta$	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^{\alpha\alpha}8\sigma^0(0.689)$
	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^{\alpha}8\sigma^0(0.099)$		$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^{\alpha}8\sigma^0(0.380)$		$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\beta\alpha}7\sigma^{\alpha}3\pi^{\alpha\alpha}8\sigma^0(0.299)$
$B^2\Sigma^+$	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^08\sigma^0(0.503)$	$A^2\Pi$	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^08\sigma^0(0.912)$	$2^4\Sigma^-$	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^{\alpha\alpha}8\sigma^0(0.511)$
	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^{\alpha}8\sigma^0(0.446)$		$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^{\alpha}8\sigma^0(0.638)$		$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\alpha}7\sigma^{\alpha}3\pi^{\alpha\alpha}8\sigma^0(0.363)$
$1^2\Sigma^-$	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^{\alpha}8\sigma^0(0.606)$	$1^4\Sigma^+$	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\beta\alpha}7\sigma^{\alpha}3\pi^{\alpha\alpha}8\sigma^0(0.145)$	$2^4\Sigma^+$	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\beta\alpha}7\sigma^{\alpha}3\pi^{\alpha\alpha}8\sigma^0(0.684)$
	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^08\sigma^0(0.236)$		$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^{\alpha}8\sigma^0(0.645)$		$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^{\alpha\alpha}8\sigma^0(0.308)$
$2^2\Sigma^-$	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^08\sigma^0(0.596)$	$1^4\Delta$	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^{\alpha\alpha}8\sigma^0(0.099)$	$1^6\Sigma^+$	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\alpha}7\sigma^{\alpha}3\pi^{\alpha\alpha}8\sigma^0(0.886)$
	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^{\alpha}8\sigma^0(0.237)$		$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^{\alpha}8\sigma^0(0.643)$		$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\alpha}7\sigma^{\alpha}3\pi^{\alpha\alpha}8\sigma^0(0.886)$
$1^2\Delta$	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^{\alpha}8\sigma^0(0.527)$	$1^4\Sigma^-$	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^{\alpha\alpha}8\sigma^0(0.080)$	$2^6\Sigma^+$	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\alpha}7\sigma^{\alpha}3\pi^{\alpha\alpha}8\sigma^0(0.625)$
	$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^08\sigma^0(0.373)$		$5\sigma^{\alpha\beta}6\sigma^{\alpha\beta}2\pi^{\alpha\beta}7\sigma^{\alpha}3\pi^{\alpha}8\sigma^0(0.915)$		

^a Values in parentheses are CSF-squared coefficients related to the electron configuration. The core configuration of each electronic state is $1\sigma^22\sigma^23\sigma^24\sigma^21\pi^4$.

Table 5Einstein coefficients (s^{-1}) and Franck-Condon factors of the $A^2\Pi-X^2\Sigma^+$, $B^2\Sigma^+-X^2\Sigma^+$ and $B^2\Sigma^+-A^2\Pi$ systems for CP radical.

$A^2\Pi-X^2\Sigma^+$						$B^2\Sigma^+-X^2\Sigma^+$					$B^2\Sigma^+-A^2\Pi$			
v'	v''	EC ^a	FC ^b	FC ^c	FC ^d	v'	v''	EC	FC	FC ^e	v'	v''	EC	FC
0	0	1.34E+04	0.2806	0.2835	0.3498	0	0	7.23E+05	0.1121	0.1186	0	0	8.50E+05	0.8208
0	1	8.82E+03	0.3845	0.3907	0.3961	0	1	1.16E+06	0.2446	0.2385	0	1	9.19E+04	0.1379
0	2	2.07E+03	0.2260	0.2310	0.1870	0	2	9.30E+05	0.2685	0.2534	0	2	1.13E+04	0.0230
0	3	1.97E+02	0.0752	0.0768	0.0534	0	3	4.87E+05	0.1948	0.1890	1	0	2.37E+05	0.1542
0	4	5.60E+00	0.0155	0.0158	0.0120	0	4	1.84E+05	0.1033	0.1108	1	1	5.70E+05	0.5404
1	0	3.05E+04	0.3200	0.3240	0.3092	0	5	5.30E+04	0.0422	0.0542	1	2	1.46E+05	0.2176
1	1	9.77E+02	0.0178	0.0188	0.0044	1	0	1.97E+06	0.2333	0.2562	1	3	3.14E+04	0.0618
1	2	3.52E+03	0.1344	0.1352	0.2015	1	1	9.45E+05	0.1512	0.1494	1	4	2.79E+03	0.0083
1	3	3.14E+03	0.2794	0.2845	0.3047	1	2	1.72E+04	0.0039	0.0051	2	0	2.01E+04	0.0081
1	4	6.23E+02	0.1702	0.1743	0.1394	1	3	2.13E+05	0.0617	0.0447	2	1	4.20E+05	0.2772
2	0	3.51E+04	0.2096	0.2134	0.1718	1	4	4.21E+05	0.1692	0.1336	2	2	3.49E+05	0.3204
2	1	6.89E+03	0.0680	0.0672	0.0932	1	5	3.14E+05	0.1768	0.1568	2	3	1.68E+05	0.2482
2	2	8.53E+03	0.1446	0.1478	0.1402	2	0	2.73E+06	0.2524	0.2755	2	4	5.52E+04	0.1072
2	3	1.22E+02	0.0044	0.0041	0.0196	2	1	4.93E+04	0.0063	0.0024	2	5	6.91E+03	0.0198
2	4	2.65E+03	0.1955	0.1988	0.2566	2	2	5.93E+05	0.0964	0.1018	3	1	6.59E+04	0.0277
3	0	2.80E+04	0.1041	0.1070	0.0948	2	3	4.95E+05	0.1093	0.1102	3	2	5.42E+05	0.3581
3	1	2.97E+04	0.1686	0.1700	0.1755	2	4	1.94E+04	0.0060	0.0137	3	3	1.80E+05	0.1583
3	2	2.45E+02	0.0020	0.0024	0.0002	2	5	1.10E+05	0.0445	0.0171	3	4	1.65E+05	0.2426
3	3	9.50E+03	0.1475	0.1489	0.1695	3	0	2.57E+06	0.1868	0.1941	3	5	8.00E+04	0.1523
3	4	9.95E+02	0.0277	0.0285	0.0109	3	1	4.41E+05	0.0414	0.0715	3	6	1.35E+04	0.0376
4	0	1.78E+04	0.0441	0.0455	0.0455	3	2	8.83E+05	0.1118	0.1090	3	7	1.77E+03	0.0066
4	1	4.39E+04	0.1574	0.1601	0.1494	3	3	6.18E+02	0.0000	0.0004	4	2	1.41E+05	0.0624
4	2	1.01E+04	0.0548	0.0541	0.0656	3	4	4.07E+05	0.0910	0.0816	4	3	5.93E+05	0.3924
4	3	7.15E+03	0.0596	0.0618	0.0460	3	5	2.52E+05	0.0771	0.0831	4	4	6.75E+04	0.0535
4	4	4.85E+03	0.0697	0.0695	0.1088	4	0	1.86E+06	0.1079	0.0997	4	5	1.42E+05	0.2071

^a EC refers to Einstein coefficient.

^b FC denotes as Franck-Condon factor.

^c Ref. [13].

^d Ref. [22].

^e Ref. [28].

$1^2\Sigma^-A^2\Pi$, $1^2\Delta-A^2\Pi$, $2^2\Delta-A^2\Pi$ and $2^2\Sigma^-A^2\Pi$ systems are very similar and are not large enough, but because of the large energy separations of the $1^2\Sigma^-$, $1^2\Delta$, $2^2\Delta$ and $2^2\Sigma^-$ states relative to the $A^2\Pi$ state, there are many strong transitions for these four band systems. As shown in Tables 6 and 7, relatively large Einstein coefficients of these four systems are of the order of $10^4 s^{-1}$, which is commonly thought to be strong enough to be detected experimentally. Hence, these four systems are expected to be observed in appropriate spectroscopic experiments.

Contrary to the $1^2\Sigma^-A^2\Pi$, $1^2\Delta-A^2\Pi$, $2^2\Delta-A^2\Pi$ and $2^2\Sigma^-A^2\Pi$ systems, the TDMs of the $2^2\Delta-1^2\Delta$ and $2^2\Sigma^-1^2\Sigma^-$ systems are relatively large in the Franck-Condon region, whereas the energy separation between the $2^2\Delta$ and $1^2\Delta$ states (or the $2^2\Sigma^-$ and $1^2\Sigma^-$ states) is small. As presented in Table 7, the calculated transition probabilities are relatively small. In order to observe the emission bands for these two systems, much efforts should be devoted to the experimental techniques.

3.3. Electric dipole transitions between quartet states

To our knowledge, quartet states of CP radical have not been observed experimentally so far. There have been several theoretical studies that aim at obtaining the PECs and the spectroscopic constants of quartet states [15,16,20]. Only Gu et al. [20] calculated the transition probabilities of the $1^4\Pi-1^4\Sigma^+$ system. Other dipole allowed transitions between quartet states appear to be unavailable in the literature, which motivates us to study further.

Fig. 3 displays the TDMs of the transition systems between quartet states. The trends of the $2^4\Sigma^+-1^4\Sigma^+$, $2^4\Delta-1^4\Delta$ and $2^4\Sigma^-1^4\Sigma^-$ are similar, just as the explanation of the $1^2\Sigma^-A^2\Pi$, $1^2\Delta-A^2\Pi$, $2^2\Delta-A^2\Pi$ and $2^2\Sigma^-A^2\Pi$ systems. As for the TDMs of these quartet transition systems, there are no experimental transition intensities, hence, it is difficult to judge the accuracy of any TDMs. The highest level of ab initio level, icMRCI+Q/AV6Z, is therefore used to compute the TDMs of these transition systems. Then,

Table 6Einstein coefficients (s^{-1}) and Franck-Condon factors of the $1^2\Sigma^- - A^2\Pi$, $1^2\Delta - A^2\Pi$ and $2^2\Delta - A^2\Pi$ systems for CP radical.

$1^2\Sigma^- - A^2\Pi$				$1^2\Delta - A^2\Pi$				$2^2\Delta - A^2\Pi$			
ν'	ν''	EC ^a	FC ^b	ν'	ν''	EC	FC	ν'	ν''	EC	FC
0	0	2.53E+04	0.6155	0	0	2.38E+04	0.4647	0	0	1.11E+05	0.7294
0	1	4.30E+03	0.2905	0	1	1.85E+04	0.3545	0	1	1.16E+04	0.2132
1	0	2.26E+04	0.2810	0	2	6.30E+03	0.1295	0	2	4.41E+02	0.0365
1	1	6.21E+03	0.1633	0	3	1.28E+03	0.0299	1	0	6.38E+04	0.2176
1	2	4.49E+03	0.3457	1	0	1.75E+04	0.3349	1	1	4.66E+04	0.3355
2	0	1.02E+04	0.0718	1	1	1.14E+03	0.0260	1	2	1.48E+04	0.3130
2	1	2.36E+04	0.3198	1	2	1.51E+04	0.2820	1	3	8.96E+02	0.0971
2	2	3.60E+02	0.0090	1	3	1.16E+04	0.2316	2	0	1.74E+04	0.0334
2	3	3.05E+03	0.2709	1	4	3.84E+03	0.0864	2	1	8.61E+04	0.3252
3	0	3.11E+03	0.0135	2	0	6.62E+03	0.1333	2	2	1.28E+04	0.0984
3	1	2.01E+04	0.1546	2	1	1.28E+04	0.2409	2	3	1.28E+04	0.3109
3	2	1.58E+04	0.2344	2	2	2.12E+03	0.0298	2	4	1.11E+03	0.1632
3	3	4.71E+02	0.0192	2	3	6.40E+03	0.1191	3	0	2.94E+03	0.0034
3	3	1.51E+03	0.1533	2	4	1.30E+04	0.2525	3	1	4.36E+04	0.0932
4	1	9.46E+03	0.0444	2	5	6.90E+03	0.2004	3	2	7.79E+04	0.3276
4	2	2.48E+04	0.2083	2	6	1.85E+03	0.0473	3	3	8.79E+02	0.0053
4	3	7.29E+03	0.1183	3	0	1.65E+03	0.0391	3	4	8.40E+03	0.2370
4	4	2.06E+03	0.0874	3	1	1.11E+04	0.2138	3	5	1.00E+03	0.2137
5	1	3.12E+03	0.0095	3	2	4.18E+03	0.0829	4	0	3.32E+02	0.0003
5	2	1.71E+04	0.0876	3	3	8.01E+03	0.1217	4	1	1.17E+04	0.0152
5	3	2.32E+04	0.2139	3	4	8.21E+02	0.0167	4	2	6.79E+04	0.1622
5	4	1.84E+03	0.0320	3	5	1.06E+04	0.2004	4	3	5.39E+04	0.2528
5	5	3.00E+03	0.1428	3	6	9.37E+03	0.1979	4	4	1.00E+03	0.0166
6	2	7.58E+03	0.0251	3	7	3.46E+03	0.0855	4	5	4.15E+03	0.1343

^a EC refers to Einstein coefficient.^b FC denotes as Franck-Condon factor.**Table 7**Einstein coefficients (s^{-1}) and Franck-Condon factors of the $2^2\Delta - 1^2\Delta$, $2^2\Sigma^- - A^2\Pi$ and $2^2\Sigma^- - 1^2\Sigma^-$ systems for CP radical.

$2^2\Delta - 1^2\Delta$				$2^2\Sigma^- - A^2\Pi$				$2^2\Sigma^- - 1^2\Sigma^-$			
ν'	ν''	EC ^a	FC ^b	ν'	ν''	EC	FC	ν'	ν''	EC	FC
0	0	5.30E+02	0.8961	0	0	3.20E+05	0.5137	0	0	6.71E+03	0.9686
0	1	1.50E+00	0.0791	0	1	1.28E+05	0.3317	0	1	5.68E+01	0.0152
1	0	4.72E+02	0.0871	0	2	2.38E+04	0.1098	1	0	1.89E+02	0.0154
1	1	6.36E+02	0.7480	0	3	2.64E+03	0.0243	1	1	7.06E+03	0.9357
1	2	4.55E+00	0.1266	1	0	2.93E+05	0.3246	1	2	1.32E+02	0.0322
2	0	3.69E+01	0.0008	1	1	3.17E+04	0.0553	2	1	4.61E+02	0.0329
2	1	1.04E+03	0.1553	1	2	1.08E+05	0.2970	2	2	7.31E+03	0.8983
2	2	7.63E+02	0.6373	1	3	4.25E+04	0.2110	2	3	2.32E+02	0.0512
2	3	9.09E+00	0.1530	1	4	7.45E+03	0.0752	3	2	8.17E+02	0.0526
3	1	1.01E+02	0.0017	2	0	1.40E+05	0.1115	3	3	7.48E+03	0.8568
3	2	1.73E+03	0.2097	2	1	2.37E+05	0.2798	3	4	3.55E+02	0.0716
3	3	9.22E+02	0.5549	2	2	6.80E+03	0.0155	4	3	1.25E+03	0.0737
3	4	1.48E+01	0.1648	2	3	4.94E+04	0.1456	4	4	7.54E+03	0.8118
4	2	1.86E+02	0.0023	2	4	4.51E+04	0.2430	4	5	5.04E+02	0.0935
4	3	2.55E+03	0.2529	2	5	1.22E+04	0.1371	5	4	1.78E+03	0.0961
4	4	1.12E+03	0.4941	2	6	1.52E+03	0.0442	5	5	7.53E+03	0.7633
4	5	2.10E+01	0.1670	3	0	4.62E+04	0.0276	5	6	6.80E+02	0.1167
5	2	3.97E+00	0.0002	3	1	2.43E+05	0.2054	6	4	1.50E+01	0.0030
5	3	2.77E+02	0.0025	3	2	9.98E+04	0.1269	6	5	2.38E+03	0.1193
5	4	3.52E+03	0.2878	3	3	5.18E+04	0.0975	6	6	7.40E+03	0.7122
5	5	1.37E+03	0.4489	3	4	9.47E+03	0.0294	6	7	8.85E+02	0.1407
5	6	2.66E+01	0.1631	3	5	3.43E+04	0.2006	7	5	4.76E+01	0.0051
6	3	1.23E+01	0.0005	3	6	1.48E+04	0.1856	7	6	3.03E+03	0.1427
6	4	3.68E+02	0.0023	3	7	2.42E+03	0.0826	7	7	7.17E+03	0.6591

^a EC refers to Einstein coefficient.^b FC denotes as Franck-Condon factor.

we calculate the Einstein coefficients and Franck-Condon factors of these transition systems, some large ones are presented in Tables 8–10.

The two lowest quartet excited states are the $1^4\Sigma^+$ and $1^4\Delta$ states. They cannot decay by a dipole allowed transition. The $1^4\Pi$ state is the first excited state that has dipole allowed transitions. It can decay to the lower $1^4\Sigma^+$ and $1^4\Delta$ states, however, the small energy difference between the $1^4\Pi$ and $1^4\Delta$ states means that the

radiative lifetimes of the $1^4\Pi$ state are mainly determined by the $1^4\Pi - 1^4\Sigma^+$ transition. For example, the radiative lifetimes of the $1^4\Pi$ state determined only by the $1^4\Pi - 1^4\Sigma^+$ system are 232.04, 94.07, 55.72, and 39.06 μs for $\nu = 0, 1, 2$, and 3, respectively. The radiative lifetimes of the $1^4\Pi$ state evaluated only by the $1^4\Pi - 1^4\Delta$ system are 184.42, 3.75, 0.66, and 0.27 ms for $\nu = 0, 1, 2$, and 3, respectively. Combining the $1^4\Pi - 1^4\Sigma^+$ and $1^4\Pi - 1^4\Delta$ systems, the radiative lifetimes of the $1^4\Pi$ state are 231.75, 91.77, 51.41, and

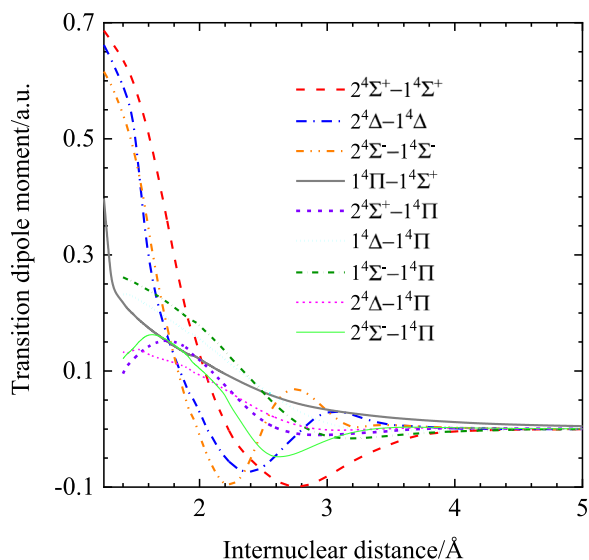


Fig. 3. The calculated TDMs versus the internuclear distance for nine band transition systems between the $1^4\Sigma^+$, $2^4\Sigma^+$, $1^4\Pi$, $1^4\Sigma^-$, $2^4\Sigma^-$, $1^4\Delta$ and $2^4\Delta$ states.

34.08 μs for $\nu=0,1,2$, and 3, respectively. It should be noted that our calculated Einstein coefficients are in good agreement with those computed by Gu et al. [20].

The $1^4\Sigma^-$ state can only decay to the $1^4\Pi$ state due to the selection rules of electric dipole transitions. Because of the large difference in R_e values for the $1^4\Pi$ and $1^4\Sigma^-$ states, there are several strong transitions for higher ν' and lower ν'' . For instance, the Einstein coefficients of the $1^4\Sigma^- - 1^4\Pi$ system for $\nu''=0$ are 5.27×10^3 , 1.69×10^4 , 2.75×10^4 , 2.67×10^4 , and $1.68 \times 10^4 \text{ s}^{-1}$, for $\nu'=1, 2, 3, 4$, and 5, respectively.

The $2^4\Delta$ state has dipole allowed transitions to the $1^4\Delta$ and $1^4\Pi$ states. The emission to the $1^4\Pi$ state is about one order of magnitude larger than to the $1^4\Delta$ state. Therefore, the contribution of the $2^4\Delta - 1^4\Pi$ system to the radiative lifetimes of the $2^4\Delta$

state is larger than that of the $2^4\Delta - 1^4\Delta$ system. For higher-lying vibrational levels, such influence decreases because the radiative lifetimes of the $2^4\Delta - 1^4\Pi$ and $2^4\Delta - 1^4\Delta$ systems are of the same order.

For the $2^4\Sigma^+$ state, it can undergo dipole allowed transitions to the $1^4\Sigma^+$ and $1^4\Pi$ states. The calculated transition probabilities show that there seems to be comparable in band intensity for the $2^4\Sigma^+ - 1^4\Sigma^+$ and $2^4\Sigma^+ - 1^4\Pi$ systems. Hence, both two systems contribute to the radiative lifetimes of the $2^4\Sigma^+$ state, which are estimated to be very small, about hundreds of nanoseconds.

As shown in Fig. 1, the $2^4\Sigma^-$ state has a single barrier, which is formed by avoiding crossing between the $2^4\Sigma^-$ and $3^4\Sigma^-$ states in the neighborhood of 2.4 Å. Because the energy at the top of barrier is higher than that at the dissociation limit, the dissociation energy is obtained between the energy at the equilibrium internuclear distance and that at the top of barrier. This state is quite shallow, which can only support 3 vibrational levels. It has dipole allowed transitions to the $1^4\Sigma^-$ and $1^4\Pi$ states, but the radiative lifetimes of the $2^4\Sigma^-$ state are essentially determined by decay to the $1^4\Pi$ state.

3.4. Electric dipole transitions between sextet states

In the work of Gu et al. [20], the $1^6\Sigma^+$ state was predicted to locate at approximately $32,600 \text{ cm}^{-1}$ by the MRD-CI calculations. The author predicted a single-well PEC for this state. Our icMRCI+Q/56+CV+DK calculations confirm the single-well potential of this state lying about $37,800 \text{ cm}^{-1}$. Our T_e value is about 5000 cm^{-1} higher than that of Gu et al. [20]. We attribute such difference to the higher level of theory used in our work. The $2^6\Sigma^+$ state was first studied by Shi et al. [15]. Our calculated spectroscopic constants are in good agreement with those of Shi et al. [15]. It should be noted that the energy separation between $2^6\Sigma^+$ and $1^4\Sigma^-$ states is about $17,000 \text{ cm}^{-1}$. In such a large separation, there should be other electronic states, which are not produced well in this work due to the mixing of their wave functions. Maybe a larger active space is needed to produce them well.

Table 8

Einstein coefficients (s^{-1}) and Franck-Condon factors of the $1^4\Pi - 1^4\Sigma^+$, $1^4\Pi - 1^4\Delta$ and $1^4\Sigma^- - 1^4\Pi$ systems for CP radical.

$1^4\Pi - 1^4\Sigma^+$				$1^4\Pi - 1^4\Delta$				$1^4\Sigma^- - 1^4\Pi$			
ν'	ν''	EC ^a	FC ^b	ν'	ν''	EC	FC	ν'	ν''	EC	FC
0	0	1.06E+03	0.0548	1	0	2.23E+02	0.1295	0	0	5.51E+02	0.0473
0	1	1.72E+03	0.1766	1	1	4.33E+01	0.2037	0	1	4.23E+02	0.1300
0	2	1.12E+03	0.2628	2	0	1.32E+03	0.1877	0	2	6.17E+01	0.1868
0	3	3.58E+02	0.2404	2	1	1.79E+02	0.0817	1	0	5.27E+03	0.1661
1	0	5.35E+03	0.1461	3	0	3.43E+03	0.1867	1	1	2.87E+03	0.2046
1	1	4.24E+03	0.2026	3	1	3.16E+01	0.0038	1	2	3.61E+02	0.0801
1	2	5.87E+02	0.0538	3	2	2.57E+02	0.0969	2	0	1.69E+04	0.2634
2	0	1.26E+04	0.2013	3	3	2.33E+01	0.0441	2	1	2.33E+03	0.0654
2	1	2.56E+03	0.0656	4	0	5.95E+03	0.1569	2	2	2.88E+02	0.0178
2	2	6.27E+02	0.0276	4	1	3.48E+02	0.0179	2	3	5.81E+02	0.0987
2	3	1.69E+03	0.1371	4	2	8.02E+02	0.0892	3	0	2.75E+04	0.2503
3	0	1.89E+04	0.1905	5	0	7.57E+03	0.1113	3	1	5.74E+02	0.0084
3	2	4.46E+03	0.1087	5	1	2.60E+03	0.0658	3	2	5.33E+03	0.1357
3	3	7.37E+02	0.0304	5	2	5.65E+02	0.0262	3	3	7.81E+02	0.0400
4	0	2.26E+04	0.1521	5	3	6.05E+02	0.0612	3	4	1.05E+02	0.0876
4	1	3.17E+03	0.3120	5	4	1.04E+02	0.0272	4	0	2.67E+04	0.1583
4	2	5.41E+03	0.0796	6	0	7.96E+03	0.0719	4	1	1.59E+04	0.1373
4	3	5.97E+02	0.0138	6	1	6.87E+03	0.0985	4	2	3.68E+03	0.0494
4	4	2.47E+03	0.0932	6	3	1.69E+03	0.0743	4	3	1.42E+03	0.03238
5	0	2.17E+04	0.1026	7	0	7.25E+03	0.0431	4	4	2.13E+03	0.0944
5	1	1.25E+04	0.0827	7	1	1.14E+04	0.1018	5	0	1.68E+04	0.0703
5	2	1.54E+03	0.0146	7	2	1.44E+03	0.0202	5	1	3.67E+04	0.2109
5	3	5.22E+03	0.0748	7	3	1.53E+03	0.0348	5	2	1.85E+03	0.0157

^a EC refers to Einstein coefficient.

^b FC denotes as Franck-Condon factor.

Table 9Einstein coefficients (s^{-1}) and Franck-Condon factors of the $2^4\Delta-1^4\Delta$, $2^4\Delta-1^4\Pi$ and $2^4\Sigma^+-1^4\Sigma^+$ systems for CP radical.

$2^4\Delta-1^4\Delta$				$2^4\Delta-1^4\Pi$				$2^4\Sigma^+-1^4\Sigma^+$			
ν'	ν''	EC ^a	FC ^b	ν'	ν''	EC	FC	ν'	ν''	EC	FC
0	2	1.90E+03	0.0288	0	0	6.73E+04	0.4331	0	0	8.27E+03	0.0024
0	3	2.81E+03	0.0778	0	1	3.86E+04	0.3651	0	1	3.42E+04	0.0151
0	4	2.66E+03	0.1444	0	2	9.54E+03	0.1400	0	2	7.11E+04	0.0478
0	5	1.59E+03	0.1924	0	3	1.69E+03	0.03811	0	3	9.95E+04	0.1013
1	0	1.01E+03	0.0036	1	0	6.77E+04	0.2984	0	4	1.03E+05	0.1578
1	1	4.27E+03	0.0244	1	2	2.68E+04	0.2460	0	5	7.96E+04	0.1868
1	2	7.60E+03	0.0720	1	3	1.95E+04	0.2770	0	6	4.56E+04	0.1743
1	3	7.23E+03	0.1185	1	4	5.22E+03	0.1190	0	7	1.84E+04	0.1319
1	4	3.68E+03	0.1083	2	0	4.78E+04	0.1507	1	0	5.04E+04	0.0111
1	5	8.00E+02	0.0417	2	1	3.50E+04	0.1571	1	1	1.45E+05	0.0474
2	0	4.44E+03	0.0111	2	2	1.47E+04	0.0886	1	2	1.91E+05	0.0945
2	1	1.40E+04	0.0543	2	3	4.49E+03	0.0418	1	3	1.48E+05	0.1112
2	2	1.67E+04	0.1040	2	4	1.70E+04	0.2358	1	4	6.76E+04	0.0755
2	3	8.30E+03	0.0872	2	5	9.21E+03	0.2039	1	5	1.27E+04	0.0192
2	4	9.37E+02	0.0176	2	6	2.20E+03	0.0810	2	0	1.64E+05	0.0278
3	0	1.32E+04	0.0239	3	0	2.77E+04	0.0653	2	1	3.27E+05	0.0187
3	1	3.07E+04	0.0838	3	1	6.28E+04	0.2046	2	2	2.55E+05	0.0963
3	2	2.24E+04	0.0958	3	2	1.95E+03	0.0098	2	3	7.93E+04	0.0474
3	3	3.47E+03	0.0254	3	3	2.56E+04	0.1582	2	4	1.83E+03	0.0022
3	4	7.43E+02	0.0068	3	5	8.42E+03	0.1175	2	5	1.35E+04	0.0166
3	5	3.29E+03	0.0612	3	6	9.99E+03	0.2200	2	6	2.96E+04	0.0586
3	6	1.38E+03	0.0494	3	7	3.90E+03	0.1404	2	7	2.06E+04	0.0631
4	0	2.76E+04	0.0371	4	0	1.29E+04	0.0240	3	0	3.89E+05	0.0525
4	1	4.58E+04	0.0909	4	1	5.44E+04	0.1332	3	1	5.46E+05	0.1073
4	2	1.73E+04	0.0527	4	2	3.10E+04	0.1039	3	2	2.27E+05	0.0678
4	4	6.29E+03	0.0438	4	3	5.54E+03	0.0232	3	3	6.82E+03	0.0043
4	5	3.93E+03	0.0459	4	4	1.71E+04	0.1077	3	4	3.49E+04	0.0545

^a EC refers to Einstein coefficient.^b FC denotes as Franck-Condon factor.**Table 10**Einstein coefficients (s^{-1}) and Franck-Condon factors of the $2^4\Sigma^+-1^4\Pi$, $2^4\Sigma^--1^4\Sigma^-$ and $2^4\Sigma^--1^4\Pi$ systems for CP radical.

$2^4\Sigma^+-1^4\Pi$				$2^4\Sigma^--1^4\Sigma^-$				$2^4\Sigma^--1^4\Pi$			
ν'	ν''	EC ^a	FC ^b	ν'	ν''	EC	FC	ν'	ν''	EC	FC
0	0	3.15E+05	0.4978	0	0	1.14E+02	0.0006	0	0	4.00E+05	0.3826
0	1	1.24E+05	0.3124	0	1	5.21E+02	0.0057	0	1	2.49E+05	0.3605
0	2	2.93E+04	0.1212	0	2	9.80E+02	0.0252	0	2	7.14E+04	0.1662
1	0	2.85E+05	0.3032	0	3	9.04E+02	0.0700	0	3	1.55E+04	0.0574
1	1	1.43E+04	0.0216	0	4	3.15E+02	0.1338	0	4	2.19E+03	0.0141
1	2	8.10E+04	0.2044	0	5	1.74E+00	0.1848	0	5	1.42E+02	0.0027
1	3	5.78E+04	0.2371	0	6	4.16E+02	0.1951	0	6	2.43E+00	0.0004
1	4	1.89E+04	0.1306	0	7	1.13E+03	0.1620	0	7	2.70E+00	0.0001
2	0	1.66E+05	0.1244	0	8	1.37E+03	0.1064	1	0	4.31E+05	0.2873
2	1	1.86E+05	0.2077	0	9	9.50E+02	0.0580	1	1	1.24E+03	0.0012
2	2	3.10E+04	0.0554	0	10	4.08E+02	0.0268	1	3	1.10E+05	0.1603
2	3	4.09E+03	0.0108	0	11	1.29E+02	0.0105	1	4	4.02E+04	0.1651
2	4	2.87E+04	0.1231	0	12	3.87E+01	0.0035	1	5	9.81E+03	0.0722
2	5	2.46E+04	0.1738	0	13	9.40E+00	0.0011	1	6	1.44E+03	0.0247
2	6	1.08E+04	0.1329	0	14	9.23E-01	0.0003	1	7	6.68E+01	0.0072
3	0	8.61E+04	0.0473	1	0	7.94E+02	0.0027	2	0	3.06E+05	0.1490
3	1	3.04E+05	0.2488	1	1	2.93E+03	0.0188	2	1	1.03E+05	0.0725
3	2	1.88E+04	0.0213	1	2	4.28E+03	0.0591	2	2	1.26E+05	0.1278
3	3	6.13E+04	0.1173	1	3	2.99E+03	0.1048	2	3	2.56E+02	0.0004
3	4	1.41E+04	0.0431	1	4	9.07E+02	0.1068	2	4	3.85E+04	0.0991
3	6	1.07E+04	0.0795	1	5	7.83E+01	0.0518	2	5	4.22E+04	0.1923
3	7	1.11E+04	0.1399	1	6	8.22E+00	0.0025	2	6	1.77E+04	0.1607

^a EC refers to Einstein coefficient.^b FC denotes as Franck-Condon factor.

Table 11Einstein coefficients (s^{-1}) and Franck-Condon factors of the $2^6\Sigma^+ - 1^6\Sigma^+$ system for CP radical.

ν'	ν''	EC ^a	FC ^b	ν'	ν''	EC	FC	ν'	ν''	EC	FC
0	4	1.45E+04	0.0786	3	0	5.01E+04	0.0048	5	5	3.66E+04	0.0372
0	5	1.22E+05	0.1760	3	1	2.09E+05	0.0345	6	0	9.58E+05	0.0381
0	6	3.86E+05	0.2673	3	2	2.93E+05	0.0918	6	1	1.57E+06	0.0917
1	2	1.96E+04	0.0241	3	3	1.38E+05	0.0966	6	2	4.18E+05	0.0371
1	3	1.10E+04	0.0769	3	4	1.03E+04	0.0169	6	3	4.37E+04	0.0073
1	5	2.83E+04	0.1244	4	0	1.69E+05	0.0117	6	4	1.96E+05	0.0529
1	6	1.03E+04	0.0205	4	1	5.39E+05	0.0601	6	5	7.79E+03	0.0021
1	7	8.98E+04	0.0419	4	2	5.18E+05	0.1001	6	6	1.66E+04	0.0395
2	0	1.08E+04	0.0015	4	3	1.12E+05	0.0413	7	0	1.75E+06	0.0574
2	1	5.66E+04	0.0147	4	4	3.31E+03	0.0045	7	1	1.88E+06	0.0836
2	2	1.03E+05	0.0586	5	0	4.44E+05	0.0230	7	2	1.20E+05	0.0074
2	3	6.85E+04	0.1147	5	1	1.04E+06	0.0825	7	3	2.93E+05	0.0326
2	4	9.89E+03	0.0951	5	2	5.96E+05	0.0763	7	4	1.67E+05	0.0293
2	6	2.53E+04	0.0411	5	3	1.47E+04	0.0030	7	5	2.25E+04	0.0095
2	7	9.25E+04	0.0981	5	4	8.40E+04	0.0397	7	6	4.39E+04	0.0336

^a EC refers to Einstein coefficient.^b FC denotes as Franck-Condon factor.**Table 12**Radiative lifetimes of the first 15 vibrational levels for the $B^2\Sigma^+$, $A^2\Pi$, $1^2\Sigma^-$, $1^2\Delta$, $2^2\Delta$, $2^2\Sigma^-$, $2^4\Sigma^+$, $1^4\Pi$, $1^4\Sigma^-$, $2^4\Delta$, $2^4\Sigma^-$ and $2^6\Sigma^+$ states of CP radical.

ν'	$A^2\Pi$	$B^2\Sigma^+$	$1^2\Sigma^-$	$1^2\Delta$	$2^2\Delta$	$2^2\Sigma^-$	$2^4\Sigma^+$	$1^4\Pi$	$1^4\Sigma^-$	$2^4\Delta$	$2^4\Sigma^-$	$2^6\Sigma^+$
	$\tau/\mu s$	τ/ns	$\tau/\mu s$	$\tau/\mu s$	$\tau/\mu s$	$\tau/\mu s$	$\tau/\mu s$	$\tau/\mu s$	$\tau/\mu s$	$\tau/\mu s$	$\tau/\mu s$	τ/ns
0	40.86	221.9	33.57	19.97	8.102	2.078	1.062	231.8	966.3	7.823	1.354	562.6
1	25.77	197.6	29.70	19.98	7.853	2.038	0.898	91.77	117.7	6.856	1.421	447.6
2	18.34	178.7	26.63	19.99	7.571	1.998	0.737	51.41	49.36	5.619	1.566	346.2
3	13.98	164.7	24.11	19.98	7.263	1.957	0.545	34.08	29.07	4.531		265.8
4	11.13	153.7	21.96	19.97	6.931	1.918	0.389	23.57	19.95	3.872		205.4
5	9.138	143.8	20.14	19.95	6.579	1.879	0.460	17.78	14.92	3.415		152.9
6	7.703	134.4	18.55	19.92	6.227	1.838	0.423	13.79	12.05	3.016		123.1
7	6.636	126.7	17.15	19.89	5.899	1.798	0.395	11.05	10.32	2.674		87.72
8	5.795	120.7	15.95	19.83	5.598	1.759	0.312	9.094	8.723	2.466		73.21
9	5.114	115.7	14.87	19.53	5.300	1.722	0.330	7.387	7.674	2.346		71.90
10	4.559	110.8	13.72	18.38	4.955	1.685	0.255	6.388	7.089	2.296		62.40
11	4.086	106.3	12.39	16.87	4.571	1.648	0.239	5.422	5.989	2.252		68.62
12	3.721	102.4	11.31	16.63	4.255	1.609	0.214	4.771	5.526	2.227		65.94
13	3.387	99.39	10.51	15.80	4.010	1.568	0.188	4.172	5.139	2.163		75.31
14	3.130	96.75	9.782	15.51	3.778	1.528	0.189	3.722	4.562	2.064		82.31

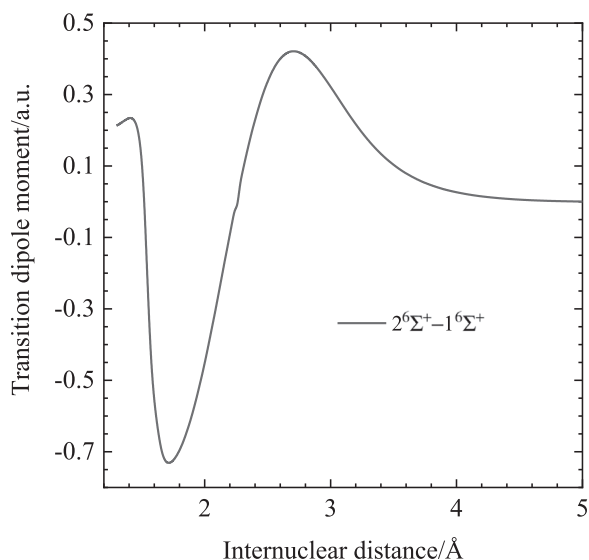
**Fig. 4.** The calculated TDMs versus the internuclear distance for the $2^6\Sigma^+ - 1^6\Sigma^+$ band transition system.

Fig. 4 shows the TDMs of the $2^6\Sigma^+ - 1^6\Sigma^+$ system. Because of the large TDMs and the large energy separation between the $2^6\Sigma^+$ and $1^6\Sigma^+$ states, many strong transitions are obtained of the order

of $10^5 s^{-1}$, just as presented in **Table 11**. We deduce the following radiative lifetimes for the $2^6\Sigma^+$ state ($\nu = 0, 1, 2, 3$): 562.6, 447.6, 346.2, and 265.8 ns, respectively. The radiative lifetimes of the $2^6\Sigma^+$ state are so small that they are expected to be observed by an appropriate spectroscopic technique. To aid in possible detection of this state, we calculate the band origins, which show that strong transitions lie in the ultraviolet (UV) band.

4. Conclusions

In this work, we have performed the icMRCI+Q/56+CV+DK calculations for PECs of the $X^2\Sigma^+$, $B^2\Sigma^+$, $A^2\Pi$, $1^2\Sigma^-$, $1^2\Delta$, $2^2\Delta$, $2^2\Sigma^-$, $1^4\Sigma^+$, $2^4\Sigma^+$, $1^4\Pi$, $1^4\Delta$, $1^4\Sigma^-$, $2^4\Delta$, $2^4\Sigma^-$, $1^6\Sigma^+$ and $2^6\Sigma^+$ states and have determined the TDMs at the icMRCI/AV6Z level of theory. The calculated spectroscopic parameters are in good agreement with previous theoretical and experimental data. The energy levels, Einstein coefficients, Franck-Condon factors are given. Many transition data, especially for quartet and sextet states, are unavailable in the literature. Vibrational radiative lifetimes of the $B^2\Sigma^+$, $A^2\Pi$, $1^2\Sigma^-$, $1^2\Delta$, $2^2\Delta$, $2^2\Sigma^-$, $2^4\Sigma^+$, $1^4\Pi$, $1^4\Sigma^-$, $2^4\Delta$, $2^4\Sigma^-$ and $2^6\Sigma^+$ states are also evaluated. Some specific conclusions are shown below:

- (1) For the $1^2\Sigma^- - A^2\Pi$, $1^2\Delta - A^2\Pi$, $2^2\Delta - A^2\Pi$, $2^2\Sigma^- - A^2\Pi$, $2^4\Delta - 1^4\Pi$ and $2^6\Sigma^+ - 1^6\Sigma^+$ systems, strong emissions are mainly in the UV band. For the $B^2\Sigma^+ - A^2\Pi$, $2^4\Delta - 1^4\Delta$, $2^4\Sigma^+ - 1^4\Pi$, $2^4\Sigma^- - 1^4\Sigma^-$ and $2^4\Sigma^- - 1^4\Pi$ systems, intense emissions lie

in the visible band. For the $A^2\Pi-X^2\Sigma^+$, $2^2\Delta-1^2\Delta$, $2^2\Sigma^- - 1^2\Sigma^-$, $1^4\Pi-1^4\Sigma^+$, $1^4\Pi-1^4\Delta$ and $1^4\Sigma^- - 1^4\Pi$ systems, strong emissions are mainly in the infrared region. The spectral range of the $B^2\Sigma^+-X^2\Sigma^+$ system is in the UV and visible band. The strong emission lines of the $2^4\Sigma^+-1^4\Sigma^+$ system extend from UV to near-infrared region.

- (2) Einstein coefficients of many spontaneous emissions are large for the $A^2\Pi-X^2\Sigma^+$, $B^2\Sigma^+-A^2\Pi$, $B^2\Sigma^+-X^2\Sigma^+$, $1^2\Sigma^- - A^2\Pi$, $1^2\Delta-A^2\Pi$, $2^2\Delta-A^2\Pi$, $2^2\Sigma^- - A^2\Pi$, $1^4\Pi-1^4\Sigma^+$, $1^4\Sigma^- - 1^4\Pi$, $2^4\Delta-1^4\Delta$, $2^4\Delta-1^4\Pi$, $2^4\Sigma^+-1^4\Sigma^+$, $2^4\Sigma^+-1^4\Pi$, $2^4\Sigma^- - 1^4\Pi$, $2^6\Sigma^+-1^6\Sigma^+$ systems. Thus they can be measured in appropriate spectroscopic experiments. Because Einstein coefficients for the $2^2\Delta-1^2\Delta$, $2^2\Sigma^- - 1^2\Sigma^-$, $2^4\Sigma^- - 1^4\Sigma^-$ systems are not very large, these emissions may be observed with great efforts. There seems to be little hope of measuring the $1^4\Pi-1^4\Delta$ system due to the large radiative lifetimes of low-lying vibrational levels.
- (3) Radiative lifetimes of vibrational levels are of the order of 10^{-8} – 10^{-7} s for the $B^2\Sigma^+$ and $2^6\Sigma^+$ states, 10^{-7} – 10^{-6} s for $2^4\Sigma^+$ state, 10^{-6} s for the $2^2\Delta$, $2^2\Sigma^-$, $2^4\Delta$ and $2^4\Sigma^-$ states, 10^{-6} – 10^{-5} s for $A^2\Pi$ and $1^2\Sigma^-$ states, 10^{-6} – 10^{-4} s for the $1^4\Pi$ and $1^4\Sigma^-$ states, and 10^{-5} s for the $1^2\Delta$ state. It is worth noting that the radiative lifetimes of vibrational levels for these states will be further decreased when the rotational transitions within each electronic state and the perturbation effects among these states are included.
- (4) The discrepancy between the calculated Franck-Condon factors and those determined by RKR method is below 3% for the $A^2\Pi-X^2\Sigma^+$ system. We are therefore confident that the transition probabilities are predicted to be accurate and reliable. Data from this work will serve as a reference for experimental observations.

Acknowledgements

We acknowledge the support from the National Natural Science Foundation of China under Grant no. 51336002, 51421063. We are also grateful to the two anonymous reviewers who provided kind and helpful suggestions.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jqsrt.2019.03.023.

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