



MRCI study on transition dipole moments and transition probabilities of 18 low-lying states of CP⁺ cation

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ABSTRACT

This study calculates the potential energy curves of 18 A-S and 50 Ω states, which arise from the $C(^3P_g) + P(^3P_g)$ dissociation channel of the CP⁺ cation. The calculations are made using the CASSCF method, followed by the icMRCI approach with the Davidson correction. Core–valence correlation and scalar relativistic corrections, as well as extrapolation to the complete basis set limit are included. The transition dipole moments are computed for 25 pairs of A-S states. The spin–orbit coupling effect on the spectroscopic and vibrational properties is evaluated. The Franck–Condon factors and Einstein coefficients of emissions are calculated. Radiative lifetimes are obtained for several vibrational levels of some states. The transitions are evaluated and spectroscopic measurement schemes for observing these A-S states are proposed. The potential energy curves, spectroscopic constants, vibrational levels, transition dipole moments, and transition probabilities reported in this paper can be considered to be very accurate and reliable. Because no experimental observations are currently available, the results obtained here can be used as guidelines for the detection of these states in appropriate spectroscopy experiments, in particular for observations in stellar atmospheres and in interstellar space.

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1. Introduction

Several elements, such as phosphorus, carbon, fluorine, chlorine, and oxygen, have been found to be abundant in various circumstellar environments. Consequently, it is expected that the CP radical and CP⁺ cation can be formed in stellar atmospheres or in interstellar space. That is, the CP radical and CP⁺ cation are of astrophysical interest. As reported in the literature, the CP radical was detected in the circumstellar envelopes of stars and in the interstellar medium [1,2]. However, there have been no astronomical observations of CP⁺ cation to date. In the past few decades, many experimental observations and theoretical spectroscopic calculations have been conducted for several states of the CP radical. Shi et al. [3] in 2013 reviewed the spectroscopic constants and vibrational properties of this radical as of that time. To our surprise, for the CP⁺ cation, no spectroscopic experiments, and only one group of spectroscopic calculations [4] have been made, in which a few spectroscopic constants were evaluated for several low-lying states, and the transition probabilities were not reported. This motivated us to perform the calculations presented herein.

In this work, the potential energy curves (PECs) are calculated for the 18 low-lying states of the CP⁺ cation. In order to improve the accuracy of PECs, core–valence correlation and scalar relativistic corrections, as well as the extrapolation of potential energies to the complete basis

set (CBS) limit are included. To investigate transition probabilities, transition dipole moments (TDMs) between different states are calculated. The spectroscopic constants and vibrational levels are determined. The Franck–Condon (FC) factors and Einstein coefficients of the emissions are evaluated. Radiative lifetimes for some vibrational levels of a number of states are computed. The spectroscopic constants and transition probabilities obtained in this study can be considered to be very reliable and can be used as guidelines for detecting these states in an appropriate spectroscopy experiment.

2. Theory and Method

The ionization energies of C and P atoms are 90,828.35 and 84,580.83 cm^{−1} [5], respectively. The ionization of a P atom is easier than that of a C atom. Therefore, the first dissociation channel of CP⁺ cation is $C(^3P_g) + P(^3P_g)$. The energies of the first and second excited states of atomic C, $C(^1D_g)$ and $C(^1S_g)$, are 10,192.66 and 21,648.03 cm^{−1}. The energy of the first excited state $C^+(^4P_g)$ of the C⁺ cation is approximately 43,003 cm^{−1}. The energies of the first excited states of P⁺ cation and P atom, $P^+(^1D_g)$ and $P(^2D_u)$, are approximately 8821.31 and 11,361 cm^{−1} [5], respectively. As a result, the second and third dissociation asymptotes of CP⁺ cation are $C^+(^2P_u) + P(^4S_u)$ and $C(^3P_g) + P^+(^1D_g)$, whose energies relative to the lowest dissociation limit, $C(^3P_g) + P(^3P_g)$, are 6319.52 and 8821.31 cm^{−1}, respectively. According to the Wigner–Witmer rules [6], the ground states of C atom and P⁺ cation generate a total of 18 electronic states, which are X³Π, 2³Π, 1³Σ[−],

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$1^3\Sigma^+, 2^3\Sigma^+, 1^3\Delta, 1^5\Sigma^+, 2^5\Sigma^+, 1^5\Sigma^-, 1^5\Pi, 2^5\Pi, 1^5\Delta, 1^1\Sigma^+, 2^1\Sigma^+, 1^1\Sigma^-, 1^1\Pi, 2^1\Pi,$ and $1^1\Delta$.

PECs are calculated with the complete active space self-consistent field (CASSCF) method, which is followed by the valence internally contracted multireference interaction (icMRCI) approach with the Davidson correction (icMRCI + Q) [7,8]. Here, the CASSCF is employed as the reference wavefunction for the icMRCI calculations. The calculations are done with the aug-cc-pV5Z (AV5Z) and aug-cc-pV6Z (AV6Z) basis sets [9,10]. All the PECs are calculated within the MOLPRO 2010.1 program package [11] in the C_{2v} point group.

The molecular orbitals (MOs) used for the icMRCI calculations are derived from the CASSCF results. The state-averaged technique is used in the CASSCF calculations. The 18 states are mixed with the equal weight. The eight outermost MOs ($4a_1, 2b_1,$ and $2b_2$) are put into the active space, corresponding to the $5-8\sigma, 2\pi,$ and 3π MOs in the CP^+ cation. A CP^+ cation has a total of 20 electrons. The eight valence electrons are distributed into the eight valence MOs, meaning that this active space is referred to as CAS (8, 8). The remaining 12 inner electrons are put into the six closed-shell MOs ($4a_1, 1b_1,$ and $1b_2$), corresponding to the $1-4\sigma$ and 1π MOs in the CP^+ cation. The icMRCI calculations with the AV6Z basis set have a total of 368 external MOs ($126a_1, 90b_1, 90b_2,$ and $62a_2$). For the CASSCF calculations with the AV6Z basis set, the $A_1, B_1, B_2,$ and A_2 symmetries corresponding to the singlet states have 492, 432, 432, and 408 configuration-state functions (CSFs); those corresponding to the triplet states have 584, 592, 592, and 584 CSFs; and those corresponding to the quintet states have 184, 176, 176, and 184 CSFs, respectively. In addition, the dimensions of CSFs are approximately from 2.42×10^6 to 3.65×10^6 for the $A_1, B_1, B_2,$ and A_2 symmetries.

The TDMs are calculated by the icMRCI approach with the AV6Z basis set. Using the TDMs and PECs, we calculate the FC factors and Einstein coefficients of emissions for a number of electric dipole transitions within the LEVEL program [12]. Supposing that the upper and lower vibrational states are v' and v'' , respectively, the total transition probability of a certain upper level is obtained by summing the Einstein coefficients of emissions from this level state to all the lower vibrational states. Then, the radiative lifetime of a certain upper vibrational state is determined as the reciprocal of total transition probability [13–15]:

$$A_{v'} = \sum_{v''} A_{v'v''} \quad (1)$$

$$\tau_{v'} = \frac{1}{A_{v'}} \quad (2)$$

Here, $A_{v'v''}$ is the rotationless Einstein coefficient of spontaneous emission from an upper vibrational state v' to a lower vibrational state v'' ;

$A_{v'}$ is the total transition probability of an upper vibrational state v' ; and $\tau_{v'}$ is the radiative lifetime of vibrational state v' .

For the icMRCI calculations, the total energy of an electronic state is composed of the reference and correlation energies, and the convergence speed of the reference energy is faster than that of the correlation energy. For this reason, we extrapolate the reference energy and correlation energy to the complete basis set (CBS) limit, respectively, so as to obtain more accurate and reliable PECs. The AV5Z and AV6Z basis sets are employed for the CBS extrapolation. The extrapolation formula is as follows [16]:

$$\Delta E_X^{ref} = E_\infty^{ref} + A^{ref} X^{-\alpha} \quad (3)$$

$$\Delta E_X^{corr} = E_\infty^{corr} + A^{corr} X^{-\beta} \quad (4)$$

Here, ΔE_X^{ref} and ΔE_X^{corr} are the reference and correlation energies, respectively, calculated directly by the aug-cc-pVXZ basis set (here X = 5 and 6). ΔE_∞^{ref} and ΔE_∞^{corr} are the reference and correlation energies,

respectively, obtained by the extrapolation to the CBS limit. The extrapolation parameters α and β are taken as 3.4 and 2.4 for the reference and correlation energies [16], respectively. Here, the PECs obtained by the CBS extrapolation is denoted as 56; for example, when the CBS extrapolation is made with the PECs obtained by the icMRCI + Q calculations, the resultant is denoted as icMRCI + Q / 56.

Core–valence correlation and scalar relativistic corrections are calculated with the cc-pCV5Z [17,18] and cc-pV5Z-DK [19] basis sets, respectively. The eight electrons in the $2s2p$ orbitals of the P atom and the two electrons in the $1s$ orbitals of the C atom are referred to as “core electrons” when the core–valence correlation correction is calculated. The difference of energies obtained by the core–valence correlation and frozen–core calculations is the contribution to the total energy by the core–valence correlation correction. For the purpose of concise of description, this contribution is denoted as CV. The cc-pV5Z-DK basis set with the DKH3 approximation [20,21] and the cc-pV5Z basis set without DKH3 approximation are used to calculate the potential energies, respectively. The difference between the two energies is the contribution to the total energy by the scalar relativistic correction, which is denoted as DK. When both the core–valence correlation and scalar relativistic corrections are added to the PECs determined by the icMRCI + Q / 56 calculations, the resultant is denoted as icMRCI + Q / 56 + CV + DK.

Spin–orbit coupling (SOC) effect is calculated by the state interaction approach [22]. These calculations are at the level of icMRCI theory, with the all–electron cc-pCV5Z basis set within the MOLPRO 2010.1 program package [11] in the C_{2v} point group. In detail, the all–electron cc-pCV5Z basis set with and without spin–orbit operator is used to calculate the potential energies, respectively. The difference between the two energies is the contribution to the total energy by the SOC effect and is denoted as SOC. Adding the SOC splitting energy to the one obtained by the icMRCI + Q / 56 + CV + DK calculations, we obtain the final PEC of each Ω state and denote it as icMRCI + Q / 56 + CV + DK + SOC.

From the PECs, the spectroscopic constants are evaluated for each state. The PECs are fitted to an analytical form by cubic splines. The rovibrational constants are first determined from the analytic potential by solving the rovibrational Schrödinger equation, and then the spectroscopic constants are evaluated by fitting the vibrational levels. For a certain electronic state, we use the first 10 vibrational levels to fit the spectroscopic constants when the number of vibrational levels is more than 10; when the total number of vibrational levels is less than 10, we employ all the vibrational levels to evaluate the spectroscopic constants.

Five states ($1^3\Sigma^+, 1^5\Sigma^+, 1^5\Sigma^-, 1^5\Delta,$ and $2^5\Sigma^+$) have a single barrier. Here we briefly describe the approach to determine the D_e value of this kind of state. When the potential energy at the top of the barrier is higher than that at the dissociation asymptote, the D_e value is obtained from the difference of potential energies at the top of this barrier and at the bottom of its well. When the potential energy at the top of this barrier is lower than that at the dissociation limit, the D_e value is determined from the difference of potential energies at the bottom of potential well and at the dissociation limit.

3. Results and Discussion

Using the icMRCI + Q / 56 + CV + DK approach, we determine the PECs of 18 states. To show the details of each PEC, we depict them in Figs. 1–3 only over a small internuclear separation range. Of these states, the $2^5\Pi$ state is repulsive. The $1^3\Sigma^+, 1^5\Sigma^+, 1^5\Sigma^-,$ and $1^5\Delta$ states have a double well. The $2^5\Sigma^+$ state has a single well and a barrier. This barrier can be clearly distinguished in Fig. 3. Because the double well of $1^5\Sigma^+$ state is too shallow, we cannot clearly see it in the figure.

For the purposes of discussion of the transitions, we give the leading valence configurations of 17 bound states around their respective equilibrium positions in Table S1 of the Supplementary Material. Those are calculated by the icMRCI approach with the AV6Z basis set. In

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