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## Rotational Excitation of the CP(X# ) Open Shell Molecule Due to Collision with He(S)

Cheikh Tidiane Bop, Ndeye Arame Boye Faye, Kamel Hammami, and Nejm-Eddine Jaïdane

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# Rotational Excitation of the $\text{CP}(X^2\Sigma^+)$ Open Shell Molecule due to Collision with $\text{He}(^1S)$

Cheikh T. Bop\*,<sup>1, a)</sup> N. A. B. Faye,<sup>1, b)</sup> K. Hammami,<sup>2, c)</sup> and N. Jaïdane<sup>2, d)</sup>

<sup>1)</sup>Laboratory of Atoms Lasers, Department of Physics, Faculty of Sciences and Techniques, University Cheikh Anta Diop of Dakar

<sup>2)</sup>Laboratory of Atomic Molecular Spectroscopy and Applications, Department of Physics, Faculty of Sciences, University Tunis El Manar, Campus Universities, 1060, Tunis, Tunisia

(Dated: 27 September 2017)

**ABSTRACT:** Phosphorus bearing molecules have been discovered in the circumstellar and interstellar media. Modeling accurately their abundance requires computations of rate coefficients induced by collision with He and  $\text{H}_2$  (i.e the most abundant gaseous components). These calculations may be carried out by first determining high accurate potential energy surface (PES) and cross sections. In this paper, we present the first PES of the  $\text{CP}(X^2\Sigma^+)$ - $\text{He}(^1S)$  van der Waals collisional complex. The ab initio interaction potential was performed using the explicitly correlated restricted coupled cluster approach with simple, double and perturbative triple excitation (RCCSD(T)-F12) in connection with the augmented-correlation consistent-polarized valence triple zeta Gaussian basis set (aug-cc-pVTZ). The potential presents two minima of  $-18.62 \text{ cm}^{-1}$  and  $-18.72 \text{ cm}^{-1}$ . From the PES obtained, we have computed state-to-state excitation cross sections of CP due to collision with He for energies up to  $500 \text{ cm}^{-1}$ . Rotational transitions involving the fine-structure levels of the CP molecule were treated with a recoupling technique based on the scattering matrix calculated with the exact quantum mechanical close coupling method. Discussions on the propensity rules between the fine-structure levels were made and we found that the  $\Delta j = \Delta N$  transitions are favoured with respect to the  $\Delta j \neq \Delta N$  ones. The data presented in this paper may have a great impact in the accurate determination of the CP abundance in space.

## I. INTRODUCTION

One of the rare sources which allows reliably investigations of astrochemical processes is the IRC+10216 carbon-rich circumstellar envelope (CW Leonis star). Indeed, photodissociation processes resulting from external UV radiations, atom-molecule reactions occurring in the outer envelope and thermoequilibrium reactions in the hot atmosphere of the central CW Leonis star contribute to the formation of molecular compost such as P-bearing molecules. Indeed, phosphorus nitride PN,<sup>1</sup> carbon phosphide CP,<sup>1,2</sup> phosphoethyne HCP<sup>1,3</sup> and Phosphapropylylidyne CCP<sup>1,4</sup> were detected towards the IRC+10216 circumstellar envelope. With respect to molecular hydrogen, the abundances of P-bearing molecules in the carbon-rich circumstellar envelope are  $\sim 3 \times 10^{-10}$  for PN,<sup>1</sup>  $\sim 5 \times 10^{-9}$  for CP,<sup>1</sup>  $\sim 3 \times 10^{-8}$  for HCP,<sup>1</sup>  $\sim 10^{-9}$  for CCP<sup>4</sup> and  $\sim 3 \times 10^{-8}$  for phosphine<sup>3</sup> ( $\text{PH}_3$ ).

Along with phosphine, HCP, CP and CCP are the most abundant P-containing molecules in the astronomical source mentioned above. Carbon phosphorus is expected to be originated from HCP photodissociation.<sup>3</sup> The comparison of their relatively close abundances ( $\text{HCP}/\text{CP} \sim 5$ ) supports this idea. Moreover, Halfen et al. suggested that CCP forms mainly from chemical reactions

involving CP.<sup>4</sup> Both hypotheses support that CP plays a crucial role in the chemistry of P-bearing molecules observed in the IRC+10216 circumstellar envelope. In cold dark clouds, the phosphorus nitride abundance ( $\text{PN}/\text{P} \sim 5 \times 10^{-4}$ ) suggests that phosphorus is essentially condensed on dust grains.<sup>5</sup> The formation of molecules containing bond strength comparable to (or larger than) that of CP may occur during grain vaporization processes. Thus, the abundance of carbon phosphorus in hot molecular clouds may be higher than the predicted value. From these items, it is obvious that accurately deriving the CP abundance is of great interest for astrophysicists.

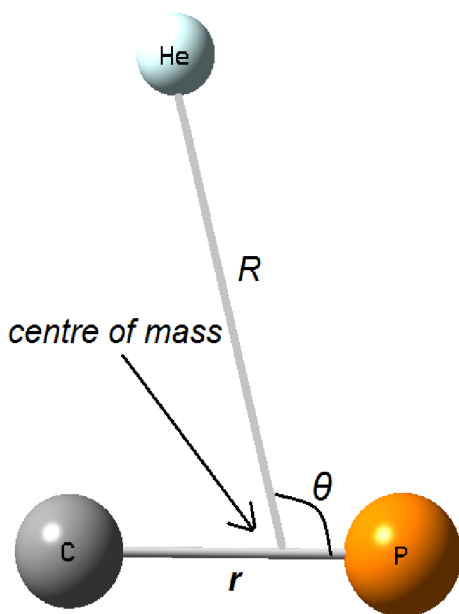
To the best of our knowledge, the only relevant astrophysical investigations (computation of downward rate coefficients) on P-containing compounds are that of Toboła et al.<sup>6</sup> and Hammami et al.<sup>7</sup> on the PN and HCP molecules respectively. The main difference between CP and the P-bearing molecules mentioned above is their electronic structures. PN and HCP are closed shell molecules while CP is an open shell molecule. However, with the development of new experimental techniques, rotational inelastic collision of open shell molecules has been the subject of numerous reports during the last few decades. Rotational energy transfer of diatomic molecules in  $^2\Pi$  and  $^2\Sigma^+$  induced by collision with noble gases (Ng) has received much interest. Therefore, the  $\text{CH}(^2\Pi)$ -Ng,<sup>8</sup>  $\text{OH}(^2\Pi)$ -Ng,<sup>9,10</sup>  $\text{NO}(^2\Pi)$ -Ng<sup>11,12</sup> and  $\text{CN}(^2\Sigma^+)$ -Ng<sup>13,14</sup> systems have been the topics of numerous theoretical as well as experimental investigations. Subsequently, one can remark that little attention was devoted to the CP open shell molecule.

<sup>a)</sup>Electronic mail: [cheikhtidiane.bop@ucad.edu.sn](mailto:cheikhtidiane.bop@ucad.edu.sn)

<sup>b)</sup>Electronic mail: [aramboye.faye@ucad.edu.sn](mailto:aramboye.faye@ucad.edu.sn)

<sup>c)</sup>Electronic mail: [hammami283@gmail.com](mailto:hammami283@gmail.com).

<sup>d)</sup>Electronic mail: [nejmeddine.jaidane@fst.utm.tn](mailto:nejmeddine.jaidane@fst.utm.tn).



**Figure 1:** Definition of the Jacobi coordinates for the CP–He collisional system.

Accurately determining the CP rate coefficients are crucially needed in order to accurately model the carbon phosphorus abundance in the IRC+10216 circumstellar envelope. Without these data along with radiative transitions, astrophysicists are reduced to assuming Local Thermodynamic Equilibrium (LTE) which is rarely verified in space. To satisfy the astrophysical precision required, we have used quantum mechanical treatment to compute the CP rotational cross sections. These calculations are based on a vibrationally averaged two-dimensional potential energy surface (hereafter denoted as vib-av-2D-PES) of the CP-He collisional system. Indeed, Kalugina et al.<sup>10</sup> suggested the use of vib-av-2D-PES rather than rigid rotor approximation to accurately derive downward rate coefficients.

This paper is structured as follows: Section II stands for the computational details (potential energy surface and cross sections), in Section III we present the results and Section IV gives the concluding remarks.

## II. COMPUTATIONAL DETAILS

### A. Interaction potential and analytical fit

The CP–He van der Waals system can be described with the Jacobi coordinates  $\theta$ ,  $r$  and  $R$ :  $\theta$  is the scattering angle between the two distance vectors ( $\mathbf{r}$  and  $\mathbf{R}$ ),  $r$  stands for the CP internuclear distance and  $R$  represents the distance between He and the centre of mass of CP (see Figure 1). These coordinates lead to the three-dimensional PES of the CP-He complex which takes into account the CP vibrational motion in dynamic processes.

Such potentials are preferred to those calculated using the rigid rotor approximation (mainly by keeping the internuclear distance of the molecule held fixed at its experimental equilibrium value)<sup>10</sup>.

We assume that the CP–He complex lies in the  $xz$  plane and the CP bond represents the  $z$  axis. In the calculations of the ab initio 3D-PES, the CP internuclear  $r$ -distance was assigned to 5 values (2.71, 2.76, 2.95, 3.13 and 3.18  $a_0$ ) leading to take into account the vibrational motions between the three lowest levels ( $v = 0 - 2$ ). The scattering angle  $\theta$  was uniformly varied from 0 to 180° with a step size of 10°. The  $R$ -distance was spanned between 4 and 100  $a_0$  using an irregular step. Typically we used the following 53 values (4.00, 4.25, 4.50, 4.75, 5.00, 5.25, 5.50, 5.75, 6.00, 6.25, 6.50, 6.75, 7.00, 7.25, 7.50, 7.75, 8.00, 8.25, 8.50, 8.75, 9.00, 9.25, 9.50, 9.75, 10.0, 10.25, 10.50, 10.75, 11.00, 11.25, 11.50, 11.75, 12.00, 12.25, 12.50, 12.75, 13.00, 13.50, 14.00, 14.50, 15.00, 16.00, 17.00, 18, 0, 19.00, 20.00, 22.00, 24.00, 26.00, 28.00, 30.00, 50.00, and 100.00  $a_0$ ). Therefore, the ab initio potential was generated with 5035 points treated in the  $C_s$  symmetry group.

The wave function that asymptotically correlates to the CP( $X^2\Sigma^+$ )–He( $1S$ ) complex is of  $2^1A'$  symmetry. The CP( $A^2\Pi$ ) state is shifted to 7319  $\text{cm}^{-1}$  upwards relative to the  $X^2\Sigma$  one. For the CP( $A^2\Pi$ )–He( $1S$ ) system, the degeneracy in the  $A^2\Pi$  state is lifted (for angular geometries) leading to two adiabatic electronic states  $A'$  and  $A''$ . For the CN molecule, Werner et al.<sup>15</sup> and Lique et al.<sup>13</sup> demonstrated that the two  $2^1A'$  (which stem from the  $X^2\Sigma$  and  $A^2\Pi$  states) mix highly with the CN bond stretching. Although for the CP molecule the  $X^2\Sigma$  and  $A^2\Pi$  states are quite distant, we have calculated with caution the interaction potential corresponding to the lowest  $2^1A'$  state of the CP-He complex. For this purpose, we have carried out after restricted Hartree–Fock, RCCSD(T)-F12<sup>16</sup> calculations using the aug-cc-pVTZ Gaussian basis set.<sup>17,18</sup> As the RCCSD(T)-F12a and RCCSD(T)-F12b approaches lead to very similar potential values, we have considered the RCCSD(T)-F12a data in this paper. The explicitly correlated calculations were performed by following the methodology established in our previous papers.<sup>19,20</sup> The monoconfigurational character of the CP( $X^2\Sigma^+$ )–He( $1S$ ) van der Waals complex was preliminary checked with the CASSCF approach, the weight of the predominant configuration ( $1a'^22a'^23a'^24a'^25a'^21a''^26a'^27a'^28a'^29a'^22a''^210a'^1$ ) of the ground electronic state is greater than 0.92 for all He orientations. All electronic calculations were carried out with the MOLPRO programme suite (version 2010).<sup>21</sup> The RCCSD(T) approach is not size consistency because of the inclusion of triple excitations. To correct this error in order to force the potential to asymptotically decay to zero, we have subtracted the value obtained at 100  $a_0$ . In addition, using the counterpoise procedure of Boys and Bernardi,<sup>22</sup> we have corrected the basis set

superposition error BSSE (see Equation 1).

$$V(r, R, \theta) = E_{CP-He}(r, R, \theta) - E_{CP}(r, R, \theta) - E_{He}(r, R, \theta) \quad (1)$$

In order to perform dynamical calculations, we have used the fitting procedure established by Werner et al.<sup>15</sup> for the CN–He system to obtain the  $V(r, R, \theta)$  expansion (see Equation 2),

$$V(r, R, \theta) = \sum_{n=1}^{N_{max}} \sum_{l=1}^{L_{max}} A_{ln}(R) d_{m,0}^{l+m-1}(\cos\theta) \times (r - r_e)^{n-1} \quad (2)$$

where  $d_{m,0}^{l+m-1}$  stands for the Wigner reduced rotation matrix,  $N_{max}$  and  $L_{max}$  are the numbers of the CP internuclear distances and the scattering angles respectively. In this form (equation 2), the 3D-PES may lead efficiently to the vib-av-2D-PES used in dynamic calculations. Indeed, the  $V(r, R, \theta)$  is calculated with solely 5 r-values while the vibrational wave functions ( $\varphi_v(r)$ ) are computed with a very compact r-grid. Thus using directly equation 3 implies to interpolate the 3D-PES or to truncate the wave functions, which is not recommended. For this purpose, we have averaged the ab initio 3D-PES with the fundamental vibrational wave function of the CP molecule using the following algorithm:

$$V(R, \theta) = \langle \varphi_{v=0}(r) | V(r, R, \theta) | \varphi_{v'=0}(r) \rangle \quad (3)$$

$$V(R, \theta) = \sum_{n=1}^{N_{max}} \sum_{l=1}^{L_{max}} A_{ln}(R) d_{m,0}^{l+m-1}(\cos\theta) \times M_{0,0}(n) \quad (4)$$

$$M_{v,v'}(n) = \langle \varphi_v(r) | (r - r_e)^{n-1} | \varphi_{v'}(r) \rangle$$

The  $\varphi_v$  wave functions were generated with the Fourier Grid Hamiltonian (FGH) method<sup>24,25</sup> from the CP ( $X^2\Sigma^+$ ) potential which is computed at the RCCSD(T)–F12a/aug-cc-pVTZ level of theory. To check the efficiency of our calculations, we represent in Table 1 the spectroscopic constants ( $\omega_e$  vibrational constant,  $B_e$  rotational constant and  $r_e$  the CP equilibrium distance) computed in this work with different level of theories as well as the experimental values.<sup>23</sup> The brackets stand for the relative errors with respect to the measurements. For all the considered level of theories (and more particularly for the CCSD(T)–F12a/aug-cc-pVTZ approach), good agreement is found confirming the accuracy of the potential energy curve used to compute the vibrational wave function. Table 2 shows the most relevant matrix elements  $M_{v,v'}(n)$  computed in this work.

The so averaged interaction potential (i.e. the vib-av-2D-PES) was fitted on the basis of Legendre polynomial functions including terms up to  $\lambda_{max} = 18$ . This lead to the basic input required in the rotational cross section

**Table 1:** Calculated equilibrium constants for CP( $X^2\Sigma^+$ ) in comparison with the experimental values.

Level of theory	$\omega_e$ (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )	$r_e$ (Å)
CCSD(T)–F12a/aug-cc-pVTZ	1242.471 (0.21%)	0.793 (0.76%)	1.567 (0.32%)
CCSD(T)–F12b/aug-cc-pVTZ	1242.681 (0.23%)	0.793 (0.76%)	1.567 (0.32%)
MRCI/aug-cc-pV5Z	1227.017 (1.04%)	0.790 (1.14%)	1.569 (0.45%)
MRCI+Q/aug-cc-pV5Z	1230.993 (0.72%)	0.792 (0.88%)	1.568 (0.38%)
EXP <sup>23</sup>	1239.807	0.799	1.562

**Table 2:** Most relevant matrix elements calculated in this work. The  $M_{0,0}(n)$  elements were used to construct the vib-av-2D-PES.

n	$M_{0,0}(n)$	$M_{0,1}(n)$	$M_{0,2}(n)$	$M_{1,1}(n)$	$M_{1,2}(n)$	$M_{2,2}(n)$
1	1.0000	0.0000	0.0000	1.0000	0.0000	1.0000
2	0.0208	0.0750	0.0039	0.0374	-0.1063	0.0544
3	0.0061	0.0039	-0.0077	0.0184	-0.0086	0.0314
4	0.0039	0.0014	-0.0069	0.0018	-0.0042	0.0043
5	0.0011	0.0001	-0.0003	0.0006	-0.0006	0.0017

computations. The potential has been implemented in the MOLSCAT<sup>26</sup> code using the VSTAR procedure.

$$V(R, \theta) = \sum_{\lambda=0}^{\lambda_{max}} V_{\lambda}(R) P_{\lambda}(\cos\theta) \quad (5)$$

## B. Dynamic calculations

The molecular levels of CP( $X^2\Sigma^+$ ) may be characterized in the Hund’s case (b) limit as the spin-splitting constant is very small ( $\gamma_e = 7.5 \times 10^{-6}$ ).<sup>23</sup> Therefore, the fine structure of the molecule are labeled  $N_j$  (with  $j = N + S$ ), where  $j$  represents the total angular momentum of the molecule,  $N$  stands for the angular momentum of rotation and  $S$  ( $= 1/2$  for  $^2\Sigma^+$  molecules) is the electronic spin. For  $j = N + 1/2$  ( $j = N - 1/2$ ), the states are denoted  $e$  ( $f$ ). In this paper, we have carried out the calculations without taking into account the hyperfine structure of the CP molecule.

The CP–He potential energy surface is independent of the electronic spin which thus plays a spectator role while  $N$  is highly coupled to  $l$  (the orbital angular momentum) due to the anisotropy of the PES.<sup>27,28</sup> Therefore,  $S$  can be safely decoupled to  $N$  and  $l$ , this lead to define new quantum numbers  $J = J_t + S$  and  $J_t = N + l$ . Then, the dynamical task is reduced to the collision of a molecule in a  $^1\Sigma^+$  electronic state with  $J_t$  its total angular momentum. We have used the close coupling approach developed by Arthur & Dalgarno<sup>29</sup> and implemented in the

MOLSCAT code<sup>26</sup> to compute the spin independent scattering matrix ( $S_{Nl,N'l'}^{J_t}$ ) which led to the spin independent transition matrix ( $T_{Nl,N'l'}^{J_t}$ ).

$$T_{Nl,N'l'}^{J_t} = \delta_{Nl,N'l'} - S_{Nl,N'l'}^{J_t} \quad (6)$$

Thus, we are able to compute the matrix elements  $T_{Nl,N'l'}^J$  governing the transitions involving the fine structure levels of the CP( $X^2\Sigma^+$ ) molecule.

$$T_{Nl,N'l'}^K = (2K+1)(-1)^{N+l'} \sum_{J_t} (-1)^{J_t} (2J_t+1) \times \left\{ \begin{matrix} N & N' & K \\ l' & l & J_t \end{matrix} \right\} T_{Nl,N'l'}^{J_t} \quad (7)$$

$$|N - N'| \leq K \leq (N + N')$$

Therefore, the inelastic cross sections  $\sigma_{N_j \rightarrow N'_j}$  can be calculated from the opacity tensor  $P^K(N, N')$  with the recoupling method proposed by Corey et al.<sup>30</sup>

$$P^K(N, N') = \frac{1}{2K+1} \sum_{l'} |T_{Nl,N'l'}^K|^2 \quad (8)$$

$$\sigma_{N_j \rightarrow N'_j} = \frac{\pi}{k_N^2} (2j'+1) \sum_K \left\{ \begin{matrix} N' & N & K \\ j' & j & S \end{matrix} \right\}^2 P^K(N, N') \quad (9)$$

where  $k_j$  is the wave vector and  $\{:::\}$  is a 6-j symbol of Wigner. Such a methodology was used by Hammami et al.<sup>27</sup> to compute tensor cross sections for the MgH( $X^2\Sigma^+$ )-He( $^1S$ ) van der Waals collisional system. In order to test the accuracy of the recoupling technique, we computed the  $\sigma_{N \rightarrow N'}$  cross sections (see equation 10) and compare with the data obtained using the exact close coupling approach implemented in the MOLSCAT code. Good agreement is found between both calculations since differences are less than  $2 \times 10^{-3} \text{ \AA}^2$  for all transitions.

$$\sigma_{N \rightarrow N'} = \frac{\pi}{k_N^2} \frac{1}{(2N+1)} \sum_K P^K(N, N') \quad (10)$$

In the spin independent scattering matrix calculation, the energy range was spanned as follows: for  $E \leq 50 \text{ cm}^{-1}$  the grid spacing was set to  $0.1 \text{ cm}^{-1}$ , for  $50 \leq E \leq 100 \text{ cm}^{-1}$  to  $0.2 \text{ cm}^{-1}$ , for  $100 \leq E \leq 150 \text{ cm}^{-1}$  to  $0.5 \text{ cm}^{-1}$ , for  $150 \leq E \leq 250 \text{ cm}^{-1}$  to  $1 \text{ cm}^{-1}$  and for  $250 \leq E \leq 500 \text{ cm}^{-1}$  to  $5 \text{ cm}^{-1}$ . The rotational levels of CP may be obtained from the expansion proposed by Alexander<sup>28</sup> with the rotational constant  $B_e$  reported in table 3. To solve the coupled equations, the diabatic modified log derivative approach of Manolopoulos was used.<sup>31</sup> This requires to perform some convergence tests to fix the parameters of the propagator. The STEPS-parameter which is inversely proportional to the grid of integration was set to 20 for  $E \leq 100 \text{ cm}^{-1}$  and 10 for the higher energy values. The integration limits were set

**Table 3:** Optimized parameters, of the diabatic log derivative approach, used in this work.

$\mu = 3.57 \text{ au}$	$J_{max} = 12, 13, 14, 15, 18, 20, 22$
$B_e = 0.7988 \text{ cm}^{-1,23}$	STEPS = 20, 10
DTOL = $0.01 \text{ \AA}^2$	$R_{max} = 90 \text{ a}_0$
OTOL = $0.001 \text{ \AA}^2$	$R_{min} = 2.5 \text{ a}_0$

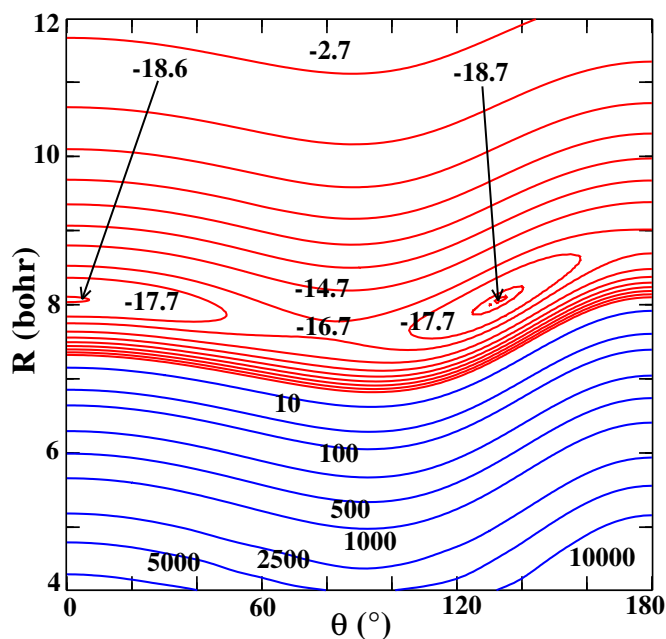
to  $R_{min} = 2.5 \text{ a}_0$  and  $R_{max} = 90 \text{ a}_0$ . Then, we have setted  $J_{max} = 12$  for  $E \leq 50 \text{ cm}^{-1}$ ,  $J_{max} = 13$  for  $50 \leq E \leq 100 \text{ cm}^{-1}$ ,  $J_{max} = 14$  for  $100 \leq E \leq 150 \text{ cm}^{-1}$ ,  $J_{max} = 15$  for  $150 \leq E \leq 250 \text{ cm}^{-1}$  and  $J_{max} = 18$  for  $250 \leq E \leq 500 \text{ cm}^{-1}$ . In addition, for elastic (inelastic) transitions the diagonal (off-diagonal) tolerance was set to DTOL =  $0.01 \text{ \AA}^2$  (OTOL =  $0.001 \text{ \AA}^2$ ). This allowed to set  $J_t$  large enough to ensure the convergence of both elastic and inelastic cross sections. For instance, we have obtained  $J_{tot} = 48$  at  $50 \text{ cm}^{-1}$ ,  $J_t = 58$  at 100,  $J_{tot} = 65$  at  $150 \text{ cm}^{-1}$  and 93 at  $500 \text{ cm}^{-1}$ .

### III. RESULTS AND DISCUSSIONS

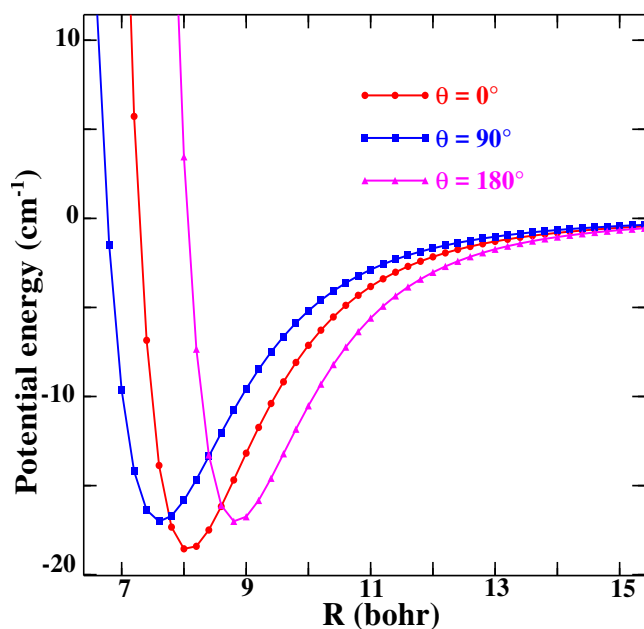
#### A. Potential energy surface

We present in Figure 2 the contour plots of the CP-He potential energy surface as a function of the Jacobi coordinates (R and  $\theta$ ). The red (blue) contours stand for the negatives (positive) energy values (in units of  $\text{cm}^{-1}$ ). This PES presents two minima of  $18.62 \text{ cm}^{-1}$  and  $18.72 \text{ cm}^{-1}$  that occur at  $(R, \theta) = (8.07 \text{ a}_0, 0^\circ)$  and  $(8.05 \text{ a}_0, 132.5^\circ)$  respectively. Between these potential wells, is located a transition state of  $16.86$  below the CP( $X^2\Sigma^+$ )-He( $^1S$ ) asymptote at the coordinates  $(R, \theta) = (7.65 \text{ a}_0, 80^\circ)$ . Although the CP-He and CN-He<sup>13</sup> complexes are isovalent, some differences are notified between their respective interaction potentials. That concerns particularly the intermediary distances (around the potential wells). The CP-He van der Waal system presents two minima as mentioned above while Lique et al.<sup>13</sup> reported a unique potential well of  $21.28 \text{ cm}^{-1}$  for the CN-He complex at  $\theta = 118^\circ$  and  $R = 6.8 \text{ a}_0$ . It is noteworthy that the C atom is not disposed in the same configuration for both collisional systems.

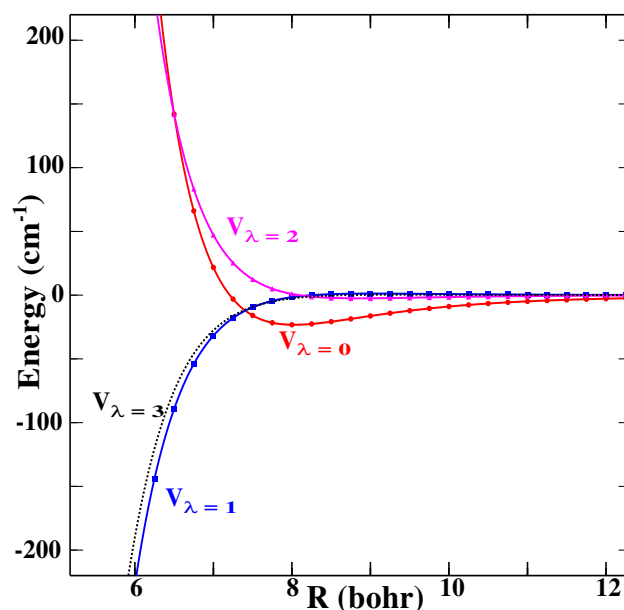
For a better appreciation of the anisotropy of the CP-He interaction, we present in Figure 3 cuts of the CP-He potential as a function of the R-distance for three He orientations ( $\theta = 180^\circ, 90^\circ$  and  $0^\circ$ ). The potential is characterized by: a well depth of  $18.62 \text{ cm}^{-1}$  located at  $R = 8.07 \text{ a}_0$  for  $\theta = 0^\circ$ , a minimum of  $17.02 \text{ cm}^{-1}$  at  $7.62 \text{ a}_0$  for  $\theta = 90^\circ$  and a potential well of  $17.03 \text{ cm}^{-1}$  at  $8.84 \text{ a}_0$  for  $\theta = 180^\circ$ . These quite close well depths obtained at relatively similar R-distances ( $R = 7.6\text{--}8.8 \text{ a}_0$ ), confirm the low anisotropy of the PES as one can see from Figure 2.



**Figure 2:** Contour plots of the CP-He potential energy surface as a function of the  $R$  and  $\theta$  Jacobi coordinates. The red (blue) contours represent the negative (positive) energies (in unit of  $\text{cm}^{-1}$ ). From  $-16.7 \text{ cm}^{-1}$  to  $-2.7 \text{ cm}^{-1}$ , the contours are spaced to  $2 \text{ cm}^{-1}$ . The zero energy corresponds to the  $\text{CP}(X^2\Sigma^+)-\text{He}(1S)$  dissociation limit.



**Figure 3:** Cuts of the CP-He interaction potential as a function of the  $R$ -distance for three He orientations ( $\theta = 180^\circ, 90^\circ$  and  $0^\circ$ ).



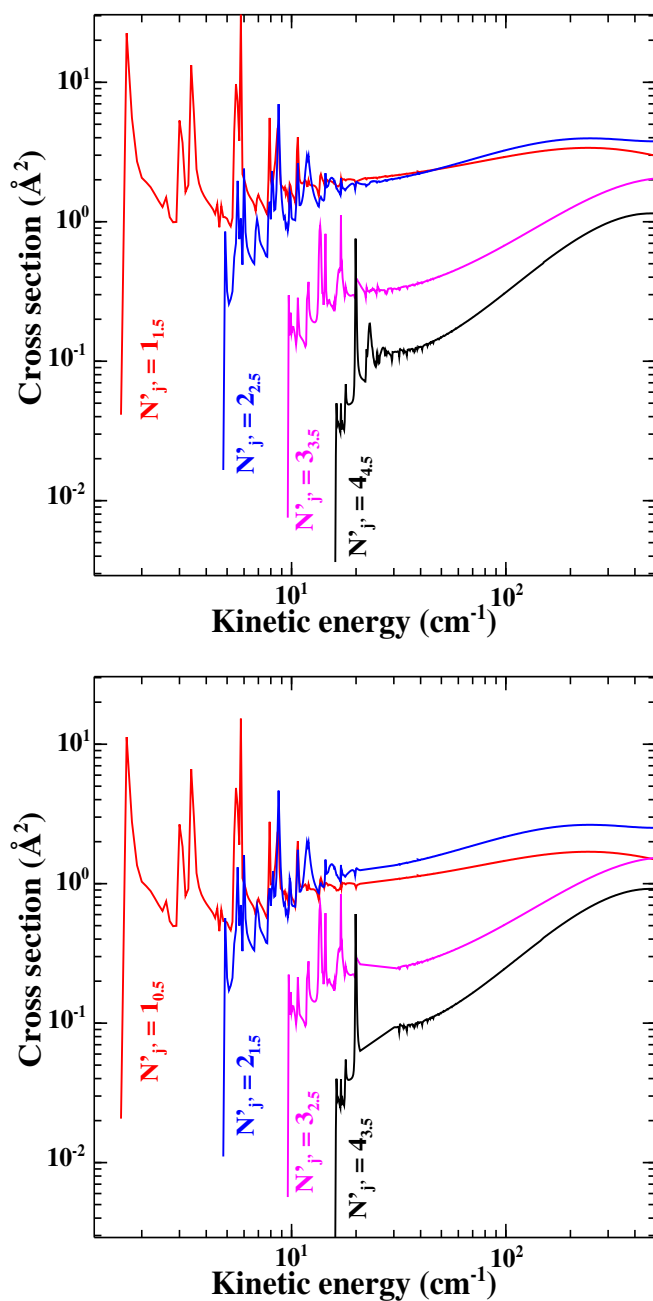
**Figure 4:** Radial coefficients expansion, as a function of  $R$  Jacobi coordinate, corresponding to the four first terms  $V_{\lambda=0-3}$ .

Figure 4 depicts the expansion of the four first terms of the radial coefficients  $V_{\lambda=0-3}$  as a function of  $R$ . For  $\lambda = 0$  and  $2$ , the concavity of the curves is directed upwards while it is oriented downwards for  $\lambda = 1$  and  $3$ . Similar findings were observed in the works of Nkem et al.<sup>32</sup> and Ajili & Hammami.<sup>33</sup> For the anisotropic terms (i.e. the radial coefficients for which  $\lambda > 0$ ), the largest in magnitude is  $V_2$ . The influence of this behavior on the cross sections will be discussed in the next section.

## B. Integral inelastic cross sections

In order to discuss to propensity rules, we have calculated the integral inelastic cross sections of the CP due to collision with He for energies up to  $500 \text{ cm}^{-1}$ . Fig. 5 depicts the dependence on the kinetic energy of inelastic cross sections for  $\Delta j = \Delta N$  (upper panel) and  $\Delta j \neq \Delta N$  (lower panel) transitions out of  $N_j = 0_{0.5}$ . In the upper panel (lower panel), an inversion occurs between the  $0_{0.5} \rightarrow 1_{1.5}$  ( $0_{0.5} \rightarrow 1_{0.5}$ ) and  $0_{0.5} \rightarrow 2_{2.5}$  ( $0_{0.5} \rightarrow 2_{1.5}$ ) transitions. A similar behaviour was observed for the CN molecule.<sup>13</sup>

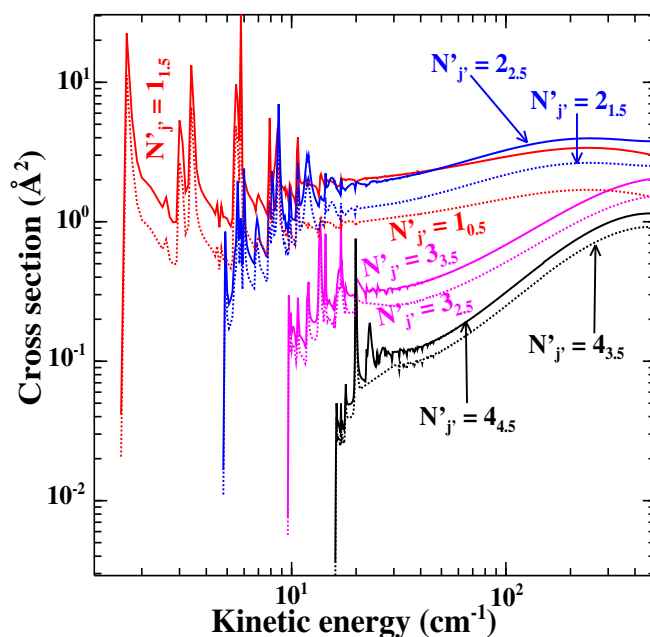
Furthermore, one can see from from this figure, that the energy grid used in this work covers totally the resonances and leads to an asymptotic behaviour of cross sections. The correct description of resonances (Feshbach and shape resonances), observed at low energy, confirms the necessity of the fine step size used in the calculations. The Feshbach resonances may be owed to a temporary trapping of He by the potential well leading to



**Figure 5:** Dependence on the kinetic energy of inelastic cross sections for  $\Delta j = \Delta N$  (upper panel) and  $\Delta j \neq \Delta N$  (lower panel) transitions out of  $N_j = 0_{0,5}$ .

a formation of quasi-bound states of the CP-He van der Waals complex. The Shape resonances are interpreted as quasi-bound states that occur from tunneling via the centrifugal energy barrier.

Both panels of the Figure 5 show that the  $0_{0,5} \rightarrow 2_{j'}$  transitions outweigh the  $0_{0,5} \rightarrow 1_{j'}$  transitions almost in the entire energy range while the  $0_{0,5} \rightarrow 3_{j'}$  transitions predominate the  $0_{0,5} \rightarrow 4_{j'}$  transitions. This behaviour shows that there is no propensity rule with respect to



**Figure 6:** Dependence on the kinetic energy of inelastic cross sections for  $0_{0,5} \rightarrow N'_{j'}$  transitions.

the parity of  $\Delta N$ . Contrarily for the CN-He collisional system, propensity rules in favour of even  $\Delta N$  transitions were notified. Such a finding was interpreted by McCurdy & Miler<sup>34</sup> as a result of the near-homonuclear symmetry of the interaction potential. In addition, this behaviour has already been observed experimentally for the NO open shell molecule in collision with Ar.<sup>35</sup>

In Fig. 6, we display the dependence on the kinetic energy of inelastic cross sections for  $\Delta j = \Delta N$  (solid lines) along with  $\Delta j \neq \Delta N$  (dashed lines) transitions. For each  $N'$  value, the excitations to  $e$  levels outweigh the transitions to  $f$  states. This leads to a propensity rule that favours the  $\Delta j = \Delta N$  transitions as observed for the CN molecule. This finding was theoretically predicted by Alexander et al.<sup>36</sup> for diatomic molecules in a  $^2\Sigma$  electronic state and confirmed by Lique et al.<sup>13</sup> for the CN( $X^2\Sigma^+$ ) molecule. The propensity rules presented here are expected to persist in rate coefficients.

#### IV. CONCLUSION

Rotational integral cross sections of carbon phosphorus due to collision with helium have been computed with the close coupling quantum mechanical method for the energy range of 1.6–500  $\text{cm}^{-1}$ . These dynamic calculations were carried out on an averaged potential energy surface. This latter was generated from the first three-dimensional ab initio interaction potential of the CP( $X^2\Sigma^+$ )-He( $1S$ ) van der Waals complex. The explicitly correlated restricted coupled cluster approach with simple, double and perturbative triple excitation (RCCSD(T)-F12) in



connection with the augmented-correlation consistent-polarized valence triple zeta Gaussian basis set (aug-cc-pVTZ) was used to construct the 3D-PES in the Jacobi coordinate system ( $r$ ,  $R$  and  $\theta$ ).

In this paper, we have studied the propensity rules among the fine structure rotational levels of the CP molecule. As expected, it is observed that the transitions involving equal  $\Delta j$  and  $\Delta N$  values are larger than the excitation for which  $\Delta j \neq \Delta N$ . We expect that the data presented in this study will revive experiments on rotational energy transfer of CP induced by collision with He such as that of Fei et al.<sup>14</sup> on the  $\text{CN}(X^2\Sigma^+) - \text{He}(^1S)$  collisional system and also experiments that take into account the fine structure levels.

The potential computed in this work may be used later to perform a complete set of the cross sections (i.e. up to  $1500 \text{ cm}^{-1}$  below the CP excited vibrational states) including the hyperfine structure of the CP molecule. Such a full description of cross sections may lead to the collisional rate coefficients which are of great interest to accurately model the abundance of CP in space.

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