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Article

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

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(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 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 CP($X^2\Sigma^+$)−He(^{1}S) 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 cm^{-1} and -18.72 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 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,[1] carbon phosphide CP,[1,2] phosphaethyne HCP[1,3] and Phosphapropynylidyne CCP[1,4] 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,[1] $\sim 5 \times 10^{-9}$ for CP,[1] $\sim 3 \times 10^{-8}$ for HCP,[1] $\sim 10^{-9}$ for CCP[4] and $\sim 3 \times 10^{-8}$ for phosphine[3] (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.[3] The comparison of their relatively close abundances (HCP/CP$\sim$ 5) supports this idea. Moreover, Halfen et al. suggested that CCP forms mainly from chemical reactions involving CP.[4] 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 (PN/P $\sim 5 \times 10^{-4}$) suggests that phosphorus is essentially condensed on dust grains.[5] 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.[6] and Hammami et al.[7] 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 sell 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 CH($^2\Pi$)-Ng,[8] OH($^2\Pi$)-Ng,[9,10] NO($^2\Pi$)-Ng[11,12] and CN($^2\Sigma^+$)-Ng[13,14] 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.

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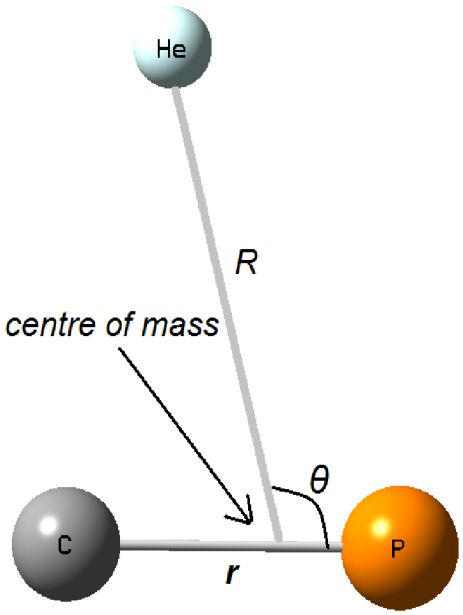

Figure 1: Definition of the Jacobi coordinates for the CP–He collisional system.

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.[10] 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 θ, r and R: θ 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)[10].

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 ($\upsilon = 0-2$). The scattering angle θ 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 $^2A'$ symmetry. The CP($A^2\Pi$) state is shifted to 7319 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.[15] and Lique et al.[13] demonstrated that the two $^2A'$ (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 $^2A'$ state of the CP-He complex. For this purpose, we have carried out after restricted Hartree–Fock, RCCSD(T)-F12[16] calculations using the aug–cc–pVTZ Gaussian basis set.[17,18] 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.[19,20] 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 ($1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 1a''^2 6a'^2 7a'^2 8a'^2 9a'^2 2a''^2 10a'^1$) 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).[21] The RCCSD(T) approach is not size consistence 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,[22] 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.[15] 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:

$$V(R,\theta) =< \varphi_{v=0}(r) \mid V(r,R,\theta) \mid \varphi_{v'=0}(r) > \quad (3)$$

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

$$M_{v,v'}(n) =< \varphi_v(r) \mid (r-r_e)^{n-1} \mid \varphi_{v'}(r) >$$

. The φ_v wave functions were generated with the Fourier Grid Hamiltonian (FGH) method[24,25] 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 (ω_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.[23] 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 computations. The potential has been implemented in the MOLSCAT[26] code using the VSTAR procedure.

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

Level of theory	ω_e (cm^{-1})	B_e (cm^{-1})	r_e (Å)
CCSD(T)-F12a/aug-cc-pVTZ	1242.471	0.793	1.567
	(0.21%)	(0.76%)	(0.32%)
CCSD(T)-F12b/aug-cc-pVTZ	1242.681	0.793	1.567
	(0.23%)	(0.76%)	(0.32%)
MRCI/aug-cc-pV5Z	1227.017	0.790	1.569
	(1.04%)	(1.14%)	(0.45%)
MRCI+Q/aug-cc-pV5Z	1230.993	0.792	1.568
	(0.72%)	(0.88%)	(0.38%)
EXP[23]	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

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

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 ($\gamma_e = 7.5 \times 10^{-6}$).[23] 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.[27,28] 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[29] and implemented in the

MOLSCAT code[26] to compute the spin independent scattering matrix ($S^{J_t}_{Nl,N'l'}$) which led to the the spin independent transition matrix ($T^{J_t}_{Nl,N'l'}$).

$$T^{J_t}_{Nl,N'l'} = \delta_{NN',ll'} - S^{J_t}_{Nl,N'l'} \quad (6)$$

Thus, we are able to compute the matrix elements $T^{J}_{Nl,N'l'}$ governing the transitions involving the fine structure levels of the CP($X^2\Sigma^+$) molecule.

$$T^{K}_{Nl,N'l'} = (2K+1)(-1)^{N+l'} \sum_{J_t} (-1)^{J_t}(2J_t+1) \times \begin{Bmatrix} N & N' & K \\ l' & l & J_t \end{Bmatrix} T^{J_t}_{Nl,N'l'} \quad (7)$$

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

Therefore, the inelastic cross sections $\sigma_{N_j \longrightarrow N'_{j'}}$ can be calculated form the opacity tensor $P^K(N, N')$ with the recoupling method proposed by Corey et al.[30]

$$P^K(N, N') = \frac{1}{2K+1} \sum_{ll'} |T^{K}_{Nl,N'l'}|^2 \quad (8)$$

$$\sigma_{N_j \longrightarrow N'_{j'}} = \frac{\pi}{k_N^2}(2j'+1) \sum_K \begin{Bmatrix} N' & N & K \\ j' & j & S \end{Bmatrix}^2 P^K(N, N') \quad (9)$$

where k_j is the wave vector and $\{:::\}$ is a 6-j symbol of Wigner. Such a methodology was used by Hammami et al.[27] 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 $\sigma_{N \longrightarrow N'}$ 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 2×10^{-3} $\AA^2$ for all transitions.

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

In the spin independent scattering matrix calculation, the energy range was spanned as follows: for E $\leq$ 50 cm^{-1} the grid spacing was set to 0.1 cm^{-1}, for 50 $\leq$ E $\leq$ 100 cm^{-1} to 0.2 cm^{-1}, for 100 $\leq$ E $\leq$ 150 cm^{-1} to 0.5 cm^{-1}, for 150 $\leq$ E $\leq$ 250 cm^{-1} to 1 cm^{-1} and for 250 $\leq$ E $\leq$ 500 cm^{-1} to 5 cm^{-1}. The rotational levels of CP may be obtained from the expansion proposed by Alexander[28] 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.[31] 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 cm^{-1} and 10 for the higher energy values. The integration limits were set to R_{min} = 2.5 a_0 and R_{max} = 90 a_0. Then, we have setted J_{max} = 12 for E $\leq$ 50 cm^{-1}, J_{max} = 13 for 50 $\leq$ E $\leq$ 100 cm^{-1}, J_{max} = 14 for 100 $\leq$ E $\leq$ 150 cm^{-1}, J_{max} = 15 for 150 $\leq$ E $\leq$ 250 cm^{-1} and J_{max} = 18 for 250 $\leq$ E $\leq$ 500 cm^{-1}. In addition, for elastic (inelastic) transitions the diagonal (off-diagonal) tolerance was set to DTOL = 0.01 $\AA^2$ (OTOL = 0.001 $\AA^2$). 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 cm^{-1}, J_t = 58 at 100, J_{tot} = 65 at 150 cm^{-1} and 93 at 500 cm^{-1}.

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

$\mu = 3.57$ au	$J_{max} = 12, 13, 14, 15, 18, 20, 22$
$B_e = 0.7988$ cm^{-1},[23]	STEPS = 20, 10
DTOL = 0.01 $\AA^2$	$R_{max} = 90$ a_0
OTOL = 0.001 $\AA^2$	$R_{min} = 2.5$ a_0

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 θ). The red (blue) contours stand for the negatives (positive) energy values (in units of cm^{-1}). This PES presents two minima of 18.62 cm^{-1} and 18.72 cm^{-1} that occur at (R, θ) = (8.07 a_0, 0°) and (8.05 a_0, 132.5°) 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, θ) = (7.65 a_0, 80°). Although the CP-He and CN-He[13] 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.[13] reported a unique potential well of 21.28 cm^{-1} for the CN-He complex at θ = 118° and R = 6.8 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 (θ = 180°, 90° and 0°). The potential is characterized by: a well depth of 18.62 cm^{-1} located at R = 8.07 a_0 for θ = 0°, a minimum of 17.02 cm^{-1} at 7.62 a_0 for θ = 90° and a potential well of 17.03 cm^{-1} at 8.84 a_0 for θ = 180°. These quite close well depths obtained at relatively similar R-distances (R = 7.6–8.8 a_0), confirm the low anisotropy of the PES as one can see from Figure 2.

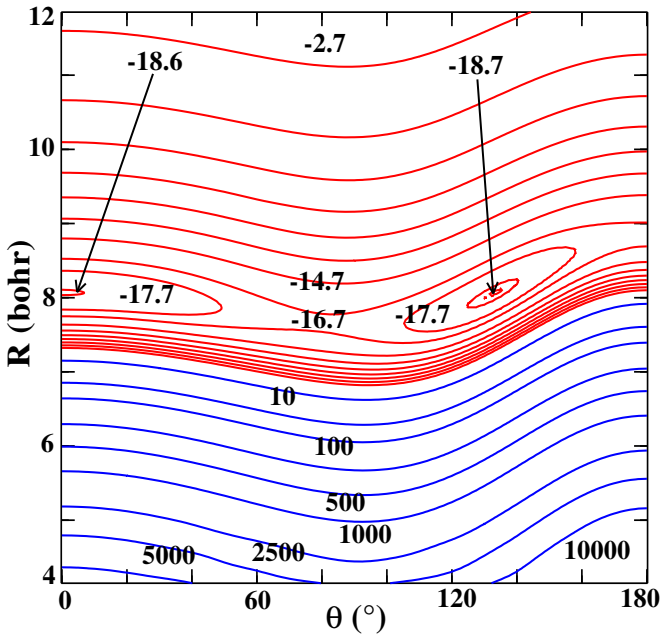

Figure 2: Contour plots of the CP-He potential energy surface as a function of the R and θ Jacobi coordinates. The red (blue) contours represent the negative (positive) energies (in unit of cm^{-1}). From -16.7 cm^{-1} to -2.7 cm^{-1}, the contours are spaced to 2 cm^{-1}. The zero energy corresponds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

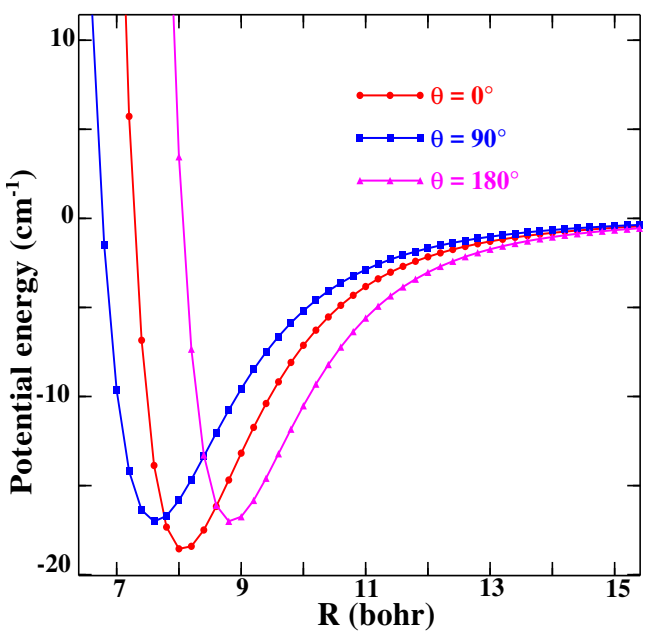

Figure 3: Cuts of the CP-He interaction potential as a function of the R-distance for three He orientations (θ = 180°, 90° and 0°).

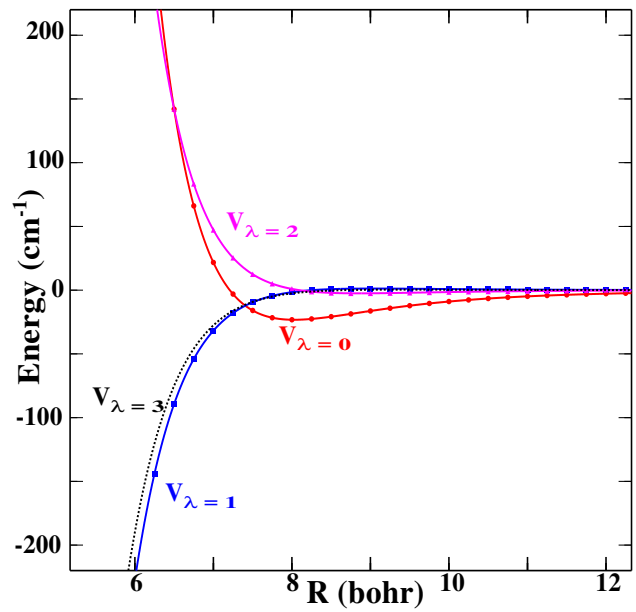

Figure 4: Radial coefficients expansion, as a function of R Jacobi coordinate, corresponding to the four first terms $V_{\lambda=0-3}$.

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.[32] and Ajili & Hammami.[33] 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 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 $0_{0.5} \longrightarrow 1_{1.5}$ ($0_{0.5} \longrightarrow 1_{0.5}$) and $0_{0.5} \longrightarrow 2_{2.5}$ ($0_{0.5} \longrightarrow 2_{1.5}$) transitions. A similar behaviour was observed for the CN molecule.[13]

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

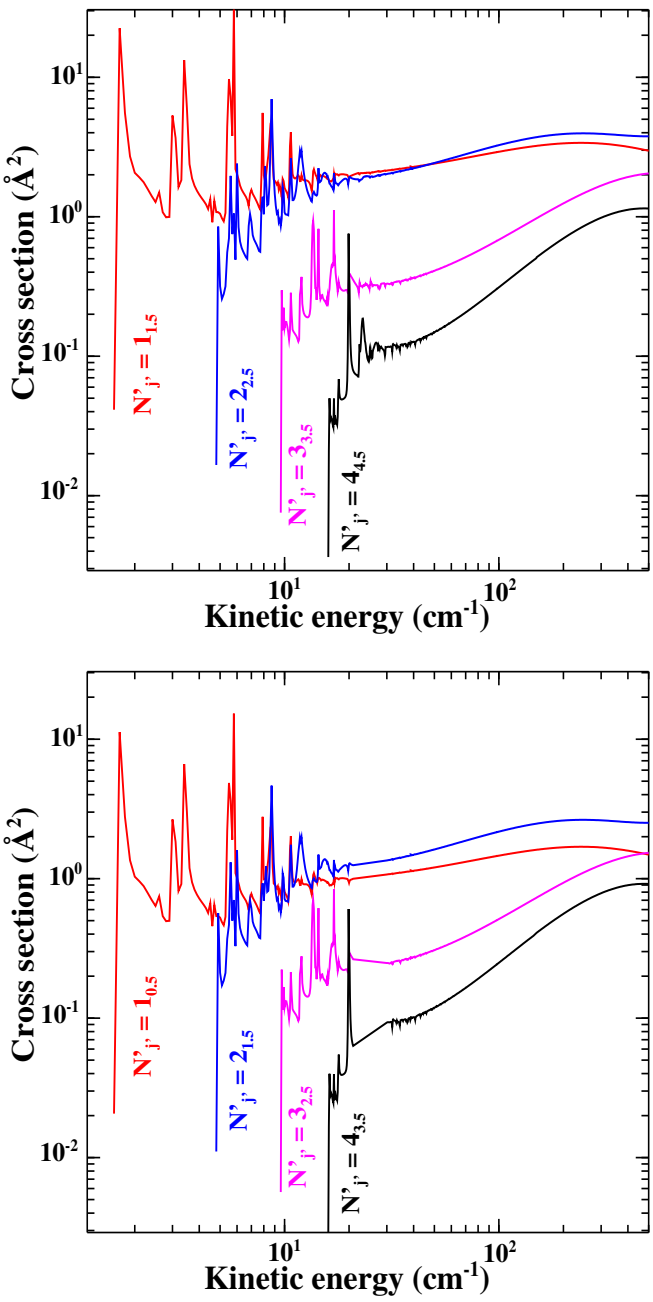

Figure 5: Dependence on the kinetic energy of inelastic cross sections for $\Delta j = \Delta N$ (upper panel) and $\Delta j \neq \Delta N$ (lower panel) transitions out of $N_j = 0_{0.5}$.

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 $0_{0.5} \longrightarrow 2_{j'}$ transitions outweigh the $0_{0.5} \longrightarrow 1_{j'}$ transitions almost in the entire energy range while the $0_{0.5} \longrightarrow 3_{j'}$ transitions predominate the $0_{0.5} \longrightarrow 4_{j'}$ transitions. This behaviour shows that there is no propensity rule with respect to

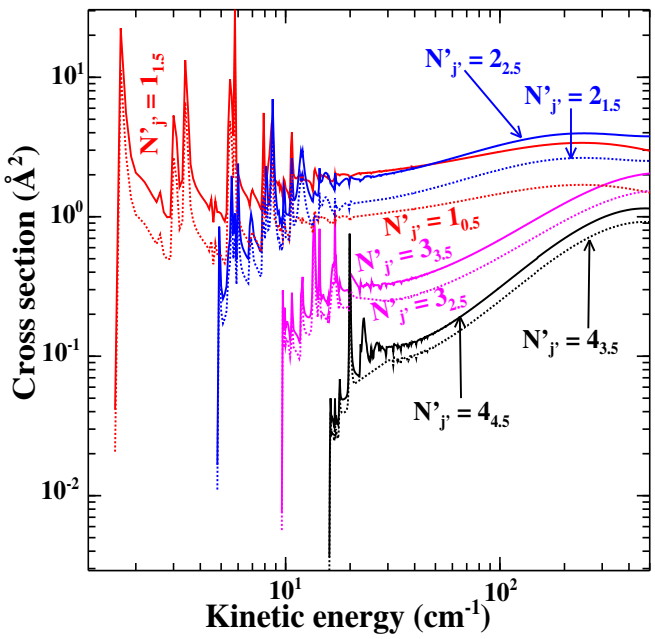

Figure 6: Dependence on the kinetic energy of inelastic cross sections for $0_{0.5} \longrightarrow N'_{j'}$ transitions.

the parity of ΔN. Contrarily for the CN-He collisional system, propensity rules in favour of even ΔN transitions were notified. Such a finding was interpreted by McCurdy & Miler[34] 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.[35]

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 favourites the $\Delta j = \Delta N$ transitions as observed for the CN molecule. This finding was theoretically predicted by Alexander et al.[36] for diatomic molecules in a $^2\Sigma$ electronic state and confirmed by Lique et al.[13] 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 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 θ).

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 Δj and ΔN 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.[14] on the CN($X^2\Sigma^+$)–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 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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REFERENCES

[1] Milam, S. N.; Halfen, D. T.; Tenenbaum, E. D.; Apponi, AJ; Woolf, N. J. and Ziurys, L. M. Constraining Phosphorus Chemistry in Carbon-and Oxygen-Rich Circumstellar Envelopes: Observations of PN, HCP, and CP. *The Astrophysical Journal.* **2008**, 684, 618

[2] Guélin, M.; Cernicharo, J.; Paubert, G. and Turner, B. E. Free CP in IRC+ 10216. *Astronomy and Astrophysics.* **1990**, 230, L9–L11

[3] Agúndez, M.; Cernicharo, J. and Guélin, M. Discovery of Phosphaethyne (HCP) in Space: Phosphorus Chemistry in Circumstellar Envelopes. *The Astrophysical Journal Letters.* **2007**, 662, L91

[4] Halfen, D. T.; Clouthier, D. J. and Ziurys, L. M. Detection of the CCP Radical (X2Πr) in IRC+ 10216: A New Interstellar Phosphorus-Containing Species. *The Astrophysical Journal Letters.* **2008**, 677, L101

[5] Turner, B. E.; Tsuji, T.; Bally, J.; Guelin, M. and Cernicharo, J. Phosphorus in the Dense Interstellar Medium. *The Astrophysical Journal.* **1990**, 365, 569–585

[6] Toboła, R.; Kłos, J.; Lique, F.; Chałasiński, G. and Alexander, M. H. Rotational Excitation and De-excitation of PN Molecules by He Atoms. *Astronomy & Astrophysics.* **2007**, 468, 1123–1127

[7] Hammami, K.; Owono, L. C. O.; Jaidane, N. and Lakhdar, Z. B. State To State Rotational Integral Cross Sections and Rate Coefficients of HP Collision with He at Low Temperature. *l8Journal of Molecular Structure: THEOCHEM.* **2008**, 860, 45–51

[8] Marinakis, S.; Dean, I. L.; Kłos, J. and Lique, F. Collisional Excitation of CH (X 2 Π) by He: New ab initio Potential Energy Surfaces and Scattering Calculations. *Physical Chemistry Chemical Physics.* **2015**, 17, 21583–21593

[9] Schreel, K.; Schleipen, J.; and Eppink, A. and Meulen, J. J. ter. State-To-State Cross Sections for Rotational Excitation of OH by Collisions with He and Ar. *The Journal of chemical physics.* **1993**, 99, 8713–8722

[10] Kalugina, Y.; Lique, F. and Marinakis, S. New ab initio potential energy surfaces for the ro-vibrational excitation of OH (X 2 Π) by He. *Physical Chemistry Chemical Physics.* **2014**, 16, 13500–13507

[11] Beutner, V.; Zhang, S. G.; Meyer, H. and Kłos, J. The Near-IR Spectrum of NO ($\tilde{X}^2\Pi$)-He Detected through Excitation into the $\tilde{A}$-State Continuum: A joint Experimental and Theoretical Study. *The Journal of chemical physics.* **2016**, 145, 124318

[12] Sumiyoshi, Y. and Endo, Y. Intermolecular Potential Energy Surface between Ne and NO (2Πr). *The Journal of Physical Chemistry A.* **2009**, 114, 4798–4804

[13] Lique, F.; Spielfiedel, A.; Feautrier, N.; Schneider, I. F.; Kłos, J. and Alexander, M. H. Rotational Excitation of CN (XΣ 2+) by He: Theory and Comparison with Experiments. *The Journal of chemical physics.* **2010**, 132, 024303

[14] Fei, R.; Lambert, H. M.; Carrington, T.; Filseth, S. V.; Sadowski, C. M. and Dugan, C. H. Direct Measurement of Thermal Rate Constants for State-To-State Rotational Energy Transfer in Collisions of CN (X2Σ+, v= 2, N) with He. *The Journal of chemical physics.* **1994**, 100, 1190–1201

[15] Werner, H.-J.; Follmeg, B. and Alexander, M. H. Adiabatic and Diabatic Potential Energy Surfaces for Collisions of CN (X2Σ+, A 2Π) with He. *The Journal of chemical physics.* **1988**, 89, 3139–3151

[16] Knizia, G.; Adler, T. B and Werner, H.-J. Simplified CCSD(T)-F12 Methods: Theory and Benchmarks. *The Journal of Chemical Physic. s***2009**, 130, 054104

[17] Kendall, R. A.; Dunning Jr, T. H. and Harrison, R. J. Electron Affinities of the First-Row Atoms Revisited. Systematic Basis Sets and Wave Functions. *The Journal of Chemical Physics.* **1992**, 96, 6796–6806

[18] Dunning Jr, T. H. Gaussian Basis Sets for use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. *The Journal of chemical physics.* **1989**, 90, 1007–1023

[19] Bop, C. T.; Hammami, K.; Niane, A.; Faye, N. A. B. and Jaïdane, N. Rotational Excitation of 36ArH+ by He at Low Temperature. *Monthly Noticies of the Royal Astronomical Society.* **2017**, 465, 1137–1143.

[20] Bop, C. T.; Hammami, K. and Faye, N. A. B. Collisional Rates Based on the First Potential Energy Surface of the NeH+- He System. *Monthly Notices of the Royal Astronomical Society.* **2017**, 470, 2911–2917

[21] Werner, H. J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Lindh, R.; Mitrushenkov, A.; Rauhut, G ..et al. MOLPRO, Version 2010.1, a Package of Ab Initio Programs. *See http://www. molpro. net.* **2010**

[22] Boys, S. F. and Bernardi, de F. The Calculation of Small Molecular Interactions by the Differences of Separate Total Enegies. Some Procedures With Reduced Errors. *Molecular Physics.* **1970**, 19, 553–566

[23] Ram, R. S. and Bernath, P. F. Fourier Transform Spectroscopy of the A2Πi-X2Σ+ System of CP. *Journal of Molecular Spectroscopy.* **1987**, 122, 282–292

[24] Marston, C. C. and Balint-Kurti, G. G. The Fourier Grid Hamiltonian Method for Bound State Eigenvalues and Eigenfunctions. *The Journal of Chemical Physics.* **1989**, 91, 3571–3576

[25] Marston, C C. and Balint-Kurti, G. G. The Fourier Grid Hamiltonian Method for Bound State Eigenvalues and Eigenfunctions. *The Journal of Chemical Physics.* **1989**, 91, 3571–3576

[26] Hutson, J. M. and Green, S. MOLSCAT Computer Code, Version 14. *Collaborative Computational Project.* **1994**

[27] Hammami, K.; Jaidane, N.; Feautrier, N.; Spielfiedel, A. and Lique, F. Tensor Cross Sections and Collisional Depolarization of MgH by He Atoms. *Chemical Physics Letters.* **2010**, 484, 148–153

[28] Alexander, M. H. Rotationally Inelastic Collisions Between a Diatomic Molecule in a 2Σ+ Electronic State and a Structureless Target. *The Journal of Chemical Physics.* **19**, 76, 3637–3645

[29] Arthurs, A. M. and Dalgarno, A. The Theory of Scattering by a Rigid Rotator. *The Royal Society.* **1960**, 256, 540–551.

[30] Corey, G. C.; Alexander, M. H. and Schaefer, J. Quantum Studies of Inelastic Collisions of O2 (X 3Σ- g) with He: Polarization Effects and Collisional Propensity Rules. *The Journal of chemical physics.* **1986**, 85, 2726–2737

[31] Manolopoulos, D. E. An Improved Log Derivative Method for Inelastic Scattering. *The Journal of chemical physics.* **1968**, 58, 6425–6429

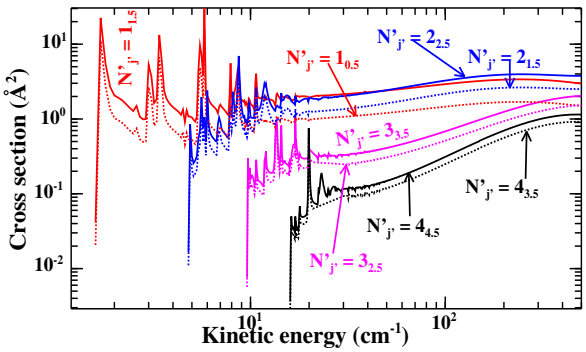
[32] Nkem, C.; Hammami, K.; Halalaw, I. Y.; Owono, L. C. O. and Jaidane, N. Rotational Excitation of Protonated Hydrogen Cyanide (HCNH+) by He Atom at Low Temperature. *Astrophysics and Space Science.* **2013**, 556, A82

[33] Ajili, Y. and Hammami, K. Induced Rotational Excitation of the Fluoromethylidynium 12CF+ and 13CF+ through Collision with Helium. *Astronomy & Astrophysics.* **2013**, 556, A82

[34] McCurdy, C. W and Miller, W. H. Interference Effects in Rotational State Distributions: Propensity and Inverse Propensity. *The Journal of Chemical Physics.* **1977**, 67, 463–468

[35] Andresen, P.; Joswig, H. Pauly, H. and Schinke, R. Resolution of Interference Effects in the Rotational Excitation of NO (N= O) by Ar. *The Journal of Chemical Physics.* **1982**, 77, 2204–2205

[36] Alexander, M. H.; Smedley, J. E. and Corey, Gregory C. On the Physical Origin of Propensity Rules in Collisions Involving Molecules in 2Σ Electronic States. *The Journal of chemical physics.* **1986**, 84, 3049–3058


Cross section (Å^2)
Kinetic energy (cm^{-1})
10^1
10^0
10^{-1}
10^{-2}
10^1
10^2
N'$_{j'}$ = 1$_{1.5}$
N'$_{j'}$ = 1$_{0.5}$
N'$_{j'}$ = 2$_{2.5}$
N'$_{j'}$ = 2$_{1.5}$
N'$_{j'}$ = 3$_{3.5}$
N'$_{j'}$ = 3$_{2.5}$
N'$_{j'}$ = 4$_{4.5}$
N'$_{j'}$ = 4$_{3.5}$

TOC graphic