NCCP collisions with \textit{para-}H$_2$: Accurate potential energy surface and quantum dynamics at interstellar temperatures

Ritika $^{\text{a}}$ and T. J. Dhilip Kumar $^{\text{a}\ast}$

Quantum Dynamics Lab, Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar 140001, India

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ABSTRACT

The effect of \textit{para}-hydrogen ($j_p = 0$) collisions on the rotational de-excitation transitions of molecule NCCP is investigated in this study. The scattering information is obtained by spherically averaging a four-dimensional potential energy surface (4DPES) over various H$_2$ molecule orientations. The calculations used the CCSD(T)-F12a method and aug-cc-pVTZ basis set to generate a 4DPES for the NCCP–H$_2$ van der Waals system. Within the NCCP–\textit{para-}H$_2$ 4DPES, a minimum energy point of 191.82 cm$^{-1}$ is attained at a distance of 3.6 Å from the centre of mass of H$_2$ and NCCP. To compute cross-sectional data for NCCP interacting with \textit{para-}H$_2$ ($j_p = 0$), close coupling calculations are employed, encompassing total energies up to 600 cm$^{-1}$. The resulting rate coefficients [$k_{j\rightarrow j'}(T)$] are calculated across a temperature range spanning from 5 K to 200 K. In accordance with propensity, even $\Delta j' = -2$ transitions are highly preferred. Comparatively, the derived $k_{j\rightarrow j'}(T)$ for NCCP–H$_2$ are determined to be 1.5–4.5 times of NCCP–He. This observation implies that relying on a scaling factor of 1.38 to extrapolate rate coefficients for H$_2$ collisions from those of NCCP–He is not a reliable approach.

Key words: astrochemistry – molecular processes – scattering – ISM: abundances – ISM: molecules.

1 INTRODUCTION

The linear molecule NCCP, a phosphorus analogue of NCCN (Kushwaha & Dhilip Kumar 2023), has a stable ground electronic state in a closed-shell singlet configuration (Ritika & Dhilip Kumar 2022). Researchers have characterized its rotational spectrum experimentally across a wide frequency range, spanning from 25 to 820 GHz (Bizzocchi et al. 2001). It has been proposed that this molecule might be detectable in celestial stars like IRC+10216 (Bizzocchi et al. 2001) due to its notably high (3.44 D) value of dipole moment (Cooper et al. 1980). In this astronomical context, other phosphorus-containing species like PN, CP, OP$^+$, PH$_3$, HCP, and CCP have been previously identified (Turner & Bally 1987; Guelin et al. 1990; Turner et al. 1990; Agúndez, Cernicharo & Güellín 2007; Halfen, Clouthier & Ziurys 2008; Milla et al. 2008; Yamaguchi et al. 2011; Haasler et al. 2022; Chahal & Dhilip Kumar 2023).

In the study involving measurements within the 3 mm range, researchers (Agúndez, Cernicharo & Guellín 2014) observed seven rotational lines of NCCP spanning from $J = 15 \rightarrow 14$ to $21 \rightarrow 20$. These observations were made across a temperature range of 30–60 K. A weak line at 9736.7 $\pm$ 1 MHz has been found that matches the frequency of the $J = 18 \rightarrow 17$ transition of NCCP. However, other transitions of NCCP within the 3 mm spectrum either lacked sufficient sensitivity to be detected or were affected by blending with stronger lines. Therefore, the detection of NCCP in the interstellar medium (ISM) is tentative and needs to be confirmed. Assuming this molecule exists in the outer regions, much like the associated CCP species, one can adopt a rotational temperature of 10–50 K for NCCP (Halfen, Clouthier & Ziurys 2008). This temperature is a common parameter for species found in the outer layers. The column density values of NCCP and CCP indicated a slightly lower abundance of NCCP than CCP in the IRC+10216 star. Given the sufficient abundance of reactants in the ISM, it could be formed through the reaction between HNC and CP (Pham-TRAN et al. 2001). Among the C$_2$NP isomers, NCCP is the most stable one (Kwon & McKee 2001) and its internal state distribution can be comprehended by facilitating collisions with the most prevalent gases in the ISM.

Despite the crucial role of phosphorus in biological systems, our understanding of phosphorus gas-phase chemistry is limited (Pasek & Laurota 2005), but the researchers are nowadays focused on interstellar phosphorus chemistry. However, they make conflicting predictions regarding the abundance of the primary phosphorus-containing molecules (Charnley & Millar 1994; Maciá, Hernández & Oró 1997). These models can only be advanced by determining the molecular abundance based on the observations. To model molecular emission from interstellar clouds, it is mandatory to calculate the rate coefficients resulting from collisions with hydrogen, which is the most prevalent species in ISM (Ritika, Kumar & Dhilip Kumar 2022). Hydrogen exists in two nuclear spin states, i.e. \textit{para}-hydrogen ($j_p = 0$) and \textit{ortho}-hydrogen ($j_o = 1$) with a ratio of 1:3 at room temperature (Lee et al. 2006; Kushwaha et al. 2023). However, at extremely low temperatures, hydrogen predominantly exists as \textit{para}-H$_2$ ($j_p = 0$). This paper focuses on determining rotational de-excitation rate coefficients of NCCP in the presence of \textit{para-}H$_2$ at temperatures between 5 and 200 K. Throughout the collision process, it is assumed that \textit{para-}H$_2$ remains in its lowest rotational state ($j_p = 0$). The assumption is valid because within this temperature range,

* E-mail: dhilip@itrpr.ac.in
the probability of exciting of H₂ molecule to the rotational level \(j_b' = 2\) is negligible (Roueff & Lique 2013; Ritika & Dhilip Kumar 2023).

In this work, we have computed a new truncated ab initio four-dimensional potential energy surface (PES) for the NCCP–para-H₂, considering three different orientations of H₂. To achieve this, we employ the explicitly correlated coupled-cluster singles and doubles with perturbative triples with F12 approximation, i.e. the CCSD(T)-F12a method.

The calculations are performed using an augmented correlation consistent polarized valence triple zeta (avTZ) basis set, which has been observed to be the most accurate approximation to CCSD(T)/CBS (complete basis set) method. The close-coupling approach (CC) is further used to investigate the transitions in the collision of NCCP with para-H₂. The results are then compared to the previous findings for the NCCP–He complex. To evaluate the reliability of approximating \(k_{j \rightarrow j'}(T)\) for para-H₂ based on rate coefficients obtained from helium collisions, we use a square-root formula that takes into account the ratio of their reduced masses. The paper’s subsequent sections elaborate on the content presented. Section 2 provides details about the computational aspects of the averaged 2D PES calculations. In Section 3 and 4, we delve into the quantum dynamical calculations and results of the inelastic rotational cross-sections and rate coefficients. The paper is finally concluded in Section 5.

2 AB INITIO CALCULATIONS OF NCCP–H₂

In this study, we focus on rotational collisions between NCCP and para-H₂ at interstellar temperatures. Both molecules, NCCP and H₂ are treated as rigid rotors during the PES calculations. According to a recent investigation by Faure et al. (2016), using state-averaged geometries yield scattering data for the CO–H₂ system that is similar to data obtained through full-dimensional calculations. Therefore, we fix the H₂ bond length at the ground vibrational level’s average distance, \(\langle r_{\text{HH}} \rangle = 0.766\) Å.

For NCCP, we use the experimental equilibrium distance (Pham-Tran et al. 2001) with its bond distances \(r_{\text{NC}} = 1.159\) Å, \(r_{\text{CC}} = 1.378\) Å, \(r_{\text{CP}} = 1.554\) Å. The geometric parameters of the NCCP–H₂ system are described using certain angles \((\theta_a, \theta_b, \phi_b, \delta)\) and a distance parameter \(R\), which represents the separation between the centre of mass of both NCCP and H₂ as shown in Fig. 1. The \(\theta_a\) and \(\theta_b\) denote the rotations of NCCP and H₂, respectively, relative to the \(z\)-axis and the symbol \(\delta\) indicates the dihedral angle that describes the relative orientation between NCCP and H₂. The adiabatic 4DPES, which relies on the parameters \(\theta_a, \theta_b, \phi, \delta,\) and \(R\) is computed using CCSD(T)-F12a method described by Adler, Knizia & Werner (2007) and Knizia, Adler & Werner (2009) employing an aVTZ basis set (Dunning 1989; Kendall, Dunning & Harrison 1992).

In the F12 calculations, F12 integrals are computed using density fitting approximations. We have used the ‘ri_basis = aVTZ/MP2FIT’ in PES calculations. We present a comparison in Table 1, where we have examined different CCSD(T)-F12 approximations and basis sets. The errors with respect to CCSD(T)/CBS are evaluated and presented in a table. It is observed that CCSD(T)-F12a/aVTZ proved to be sufficiently accurate in describing van der Waals intermolecular interactions (Tew & Klopper 2006; Roueff & Lique 2013). All calculations are conducted using molpro (Werner et al. 2015) package. The values of \(R\) ranges from 3.0 to 26 Å and there are 19 discrete values of \(\theta_a\) in the grid, ranging from 0° to 180° in increments of 10°. For each combination of \(R\) and \(\theta_a\), we consider three distinct orientations of H₂ molecules, which are given as: \((\theta_b = 0°, \delta = 0°), (\theta_b = 90°, \delta = 0°), (\theta_b = 90°, \delta = 90°)\). Consequently, 2964 geometries are computed for the NCCP–H₂ system in the \(C_\text{b}\) symmetry group, represented by \((R, \theta_a, \theta_b, \phi)\). In all surface computations, we apply the standard Boys & Bernardi approach to rectify the basis set superposition error: (Boys & Bernardi 1970)

\[
V(R, \theta_a, \theta_b, \phi) = E_{\text{NCCP-H}_2}(R, \theta_a, \theta_b, \phi) - E_{\text{NCCP}}(r_{\text{NCCP}}) - E_{\text{H}_2}(r_{\text{H}_2}, \infty) \tag{1}
\]

The collinear configuration of NCCP–H–H occurs when \(\theta_a\) is equal to 0° and \(\theta_b\) is also equal to 0° and H–H–H. NCCP corresponds to the configuration when \(\theta_a = 180°\) and \(\theta_b = 0°\). Fig. 2 displays the one-dimensional potential energy curves of NCCP–H₂ concerning the variable \(R\). It illustrates these curves for three different orientations of H₂ at \(\theta_a = 0°, 90°\), and 180°. As evident from this figure, the potential exhibits strong anisotropy due to the orientation of the H₂. The most favourable interaction arises from a collinear (H and N head-to-head) configuration of H–H–H... NCCP \((\theta_a = 180°\) and \(\theta_b = 0°\)), which is influenced by the H₂ quadrupole and NCCP dipole orientations. In the linear arrangement with angles \(\theta_a = 0°\) and \(\theta_b = 0°\), the interaction is weaker due to a repulsive long-range electrostatic force between the unfavourable NCCP dipole and H₂ quadrupole orientations.

When \(\theta_a = 90°\), the interaction potential shows minor dependency on the rotation of the H₂.

Since our objective involves solving the CC equations to analyse scattering phenomena, expanding the PES function, \(V\), at a given \(R\) value using angular functions is necessary. In the context of scattering between two linear rigid rotors, the potential can be represented as follows (Launay 1977; Flower et al. 1979).

\[
V(R, \theta_a, \theta_b, \phi) = \sum_{l_1l_2\mu} v_{l_1l_2\mu}(R) \times P_{l_1l_2\mu}(\theta_a, \theta_b, \phi) \tag{2}
\]
Figure 2. Plots depict the potential energy of NCCP–H$_2$ w.r.t. $R$ are presented for various orientations, namely $(\delta, \theta_a) = (0^\circ, 0^\circ)$, $(0^\circ, 90^\circ)$, and $(90^\circ, 90^\circ)$. Plot (a) illustrates the case when $\theta_a = 0^\circ$, plot (b) for $\theta_a$ at $90^\circ$, and plot (c) when $\theta_a$ is $180^\circ$.

Figure 3. Spherically averaged 2D contour plot for NCCP–H$_2$ as function of $\theta_a$ and $R$.

Figure 4. Multipolar expansion coefficients versus $R$ for NCCP–H$_2$ at $\lambda = 0$–3.

$$V_{av}(R, \theta_a) = \langle Y_{00}|V|Y_{00}\rangle = \sum_l v_l(R)P_l(\cos \theta_a),$$

where

$$P_{l_{12}\mu}(\theta_a, \theta_b, \delta) = 4\pi \left[ \frac{(2l_{12}+1)}{2}\right]^{-1/2} \begin{bmatrix} Y_{l_{1}\mu}(\theta_a, 0)Y_{l_{2}-\mu}(\theta_b, \delta) \\ + Y_{l_{1}-\mu}(\theta_a, 0)Y_{l_{2}\mu}(\theta_b, \delta) \end{bmatrix}$$

with $\mu \leq \min(l_1, l_2)$. Here, indexes $l_1$ and $l_2$ are connected, respectively, with the rotational motion of NCCP and H$_2$. Specifically, index $l_2$ is even, reflecting the homonuclear geometry of the molecule H$_2$. In specific scenario of collisions involving para-H$_2$ molecules (where $l_0 = 0$), with $l_2 = 0$, and reduced mass $\mu = 0$, the corresponding wavefunction simplifies to $V_{00}(\theta_b, \delta) = 4 \times \pi^{-1/2}$. The expectation value of the potential is then deduced by averaging the total PES over the angular motion $(\theta_b, \delta)$ of the H$_2$ entity:

$$V_{av}(R, \theta_a) = \langle Y_{00}|V|Y_{00}\rangle = \sum_l v_l(R)P_l(\cos \theta_a),$$

where $P_l$ denotes the Legendre polynomials.

Equation (4) has the appropriate form to expand the interaction potential between the fixed rotor and spherical projectile. As mentioned
Figure 5. Plot of inelastic cross-sections of NCCP–$H_2$ with $E_i$ where (a) $\Delta j = -1$ and (b) $\Delta j = -2$.

Figure 6. Propensities for the excitation of NCCP for $E_i = 100, 200$, and $400$ cm$^{-1}$ from $j = 0$ to $j'$.

Figure 7. Rate coefficients of rotational de-excitation of NCCP–para-$H_2$ for selected transitions at 5–200 K.

earlier, in the context of low-energy rotational excitation, the impact of the $J_0 \geq 2$ channels of $H_2$ are ignored. Additionally, the energy difference between $J_0 = 0$ and $J_0' = 2$ levels (510 K) is significantly larger than the thermal kinetic energy ($T \leq 150$ K), suggesting that the influence of closed channels ($J_0 = 0$) on cross-sections is expected to be minor. Therefore, we have chosen to work with the minimal rotational basis of $J_0 = 0$ for para hydrogen. The PES for NCCP–$H_2$ ($J_0 = 0$) is simplified into a 2D-PES, $V_{av}$, computed by averaging the total PES over angles $\theta_a$ and $\delta$.

$$V_{av}(\theta_a, R) = \frac{1}{3} (V_a + V_b + V_c),$$

where

$$V_a = V(R, \theta_a, \theta_b; 0^0, \delta; 0^0), \quad V_b = V(R, \theta_a, \theta_b; 90^0, \delta; 0^0),$$

$$V_c = V(R, \theta_a, \theta_b; 90^0, \delta; 90^0).$$

The spherically averaged 2D-PES has a global minimum of 125.40 cm$^{-1}$ at $\theta_a = 110^0$ and $R = 3.6$ Å. It is interesting to contrast the differences and similarities between the PES for NCCP–He and our computed reduced PES for NCCP–$H_2$ (Ritika & Dhilip Kumar 2022). The overall behaviour of both PESs is similar, with global minima at $110^0$, but reduced NCCP–$H_2$ has a deeper well measuring 46.40 cm$^{-1}$ at $R = 3.5$ Å. Fig. 3 presents the spherically averaged 2D contour plot for NCCP–$H_2$. For fitting the averaged surface, we have included 29 different radial $(v_l)$ coefficients. The multipole expansion coefficients are presented in Fig. 4 as a function of radial coordinates. Due to the asymmetric nature of NCCP, both even and odd $v_l$ values persist. These calculations offer insightful information regarding the rotational de-excitation rates in NCCP–$H_2$ collisions.

3 ROTATIONAL DE-EXCITATION OF NCCP WITH PARA-$H_2$

3.1 Computational details

The CC method formulated by Arthurs, Dalgarno & Bates (1960) is employed for the determination of the integral inelastic cross-section between different quantum states for NCCP–para-$H_2$ system using the MOLSCAT quantum package (Hutson & Green 1994). The calculations are done using the AIRY propagator, an approach advanced by Alexander & Manolopoulos (1987) in 1987. The NCCP possesses spectroscopic attributes denoted as $B_0$ (0.0902 cm$^{-1}$) and
D$_8$ (6.708 × 10$^{-9}$ cm$^{-1}$), and it has a linear configuration in its electronic state (X$^1\Sigma^+$). The collisional problem is limited to a rigid rotor by disregarding the H$_2$ rotational motion and the NCCP vibrational motion. The range of total energy considered for the dynamic computations spans from 0.5 to 600 cm$^{-1}$, encompassing all resonances. The parameters of the propagator are adjusted to strike a balance between accuracy and computational efficiency. Notably, $R_{\text{min}}$ is set at 3.0 Å while $R_{\text{max}}$ is set at 26 Å. The calculations are conducted using different step sizes depending on the total energy range: $\Delta E_i = 0.1$ cm$^{-1}$ for $E_i \leq 60$ cm$^{-1}$, $\Delta E_i = 0.2$ cm$^{-1}$ for 60–120 cm$^{-1}$, $\Delta E_i = 0.5$ cm$^{-1}$ for 120.5–160 cm$^{-1}$, $\Delta E_i = 1$ cm$^{-1}$ for 161–210 cm$^{-1}$, $\Delta E_i = 5$ cm$^{-1}$ for 215–250 cm$^{-1}$ and $\Delta E_i = 50$ cm$^{-1}$ for 250–600 cm$^{-1}$. This range ensures the inclusion of all resonances with lower energy levels. The STEPS parameter, dictating the grid magnitude for propagation of short range, is set sufficiently high to enable a thorough analysis of low-energy resonances. Typically, STEPS = 10 is set for $E_i$ levels greater than 100 cm$^{-1}$, and STEPS = 20 is used for $E_i$ levels less than 100 cm$^{-1}$. The $j_{\text{max}}$, rotational basis, is determined at a level that allows all coupling coefficients to be taken into account in dynamical calculations. This consideration guarantees the inclusion of both open and closed channels in the analysis, yielding accurate scattering data. For instance, the parameter $j_{\text{max}}$ is initialized at 20 for energy levels ranging up to 60 cm$^{-1}$, with a gradual increment to 60 for energy levels extending up to 600 cm$^{-1}$. The determination of $j_{\text{max}}$ values is achieved through optimization, where the thresholds for inelastic and elastic transitions are defined as OTOL = 0.005 Å$^2$ and DTOL = 0.05 Å$^2$, respectively.

3.2 De-excitation cross-sections

Figs 5(a) and 5(b) indicate the de-excitation cross-section variation with respect to the total energy when it interacts with the perturber, H$_2$. The analysis discloses that rotational shifts are feasible for transitions of even-to-even, odd-to-odd, odd-to-even, and even-to-odd nature. The molecular asymmetry of NCCP results in transitions that produce both even and odd $\Delta j$ values and its energy levels allow both odd and even $j$ values. Both illustrations reveal the presence of shape and Feshbach resonances (FR) within energy limits up to $E_i = 300$ cm$^{-1}$ (Christoffel & Bowman 1983). The FR are pronounced at $E_i \leq 130$ cm$^{-1}$ but wane as $E_i$ rises, disappearing past 300 cm$^{-1}$.

Quasi-bound states are detected as a consequence of the H$_2$ projectile being confined within a potential well. This confinement gives rise to FR, which persists until the H$_2$ possesses sufficient energy to get out of the trap. In contrast, shape resonances emerge as a result of tunnelling effects that enable the H$_2$ projectile to pass through the centrifugal barrier. Moreover, as the $j$ value increases, the cross-section trend generally ascends, consistent with typical rotational de-excitation behaviour.

Fig. 5(a) and 5(b) depict the rotational de-excitation cross-sections for both $\Delta j = -1$ and $\Delta j = -2$ transitions among the eight rotational levels. As $j$ rises (from $j = 1$ to 4 for $\Delta j = -1$ and 3 to 5 for $\Delta j = -2$), the cross-sections in both cases show an increase. The information on variation of final state ($j'$) concerning cross-sections are provided in Fig. 6. The cross-sections decrease as the collision energy is increased from 100 cm$^{-1}$ to 400 cm$^{-1}$. These results demonstrate a notable inclination towards favouring even values of $\Delta j$ compared to odd ones. The same propensity is observed in other phosphorus-containing systems such as PN–H$_2$ by Najar et al. (2017) and HPO–He by El Hamni et al. (2021), where $\Delta j = -2$ favours.

![Figure 8. Rate coefficients of NCCP-para-H$_2$ and NCCP-He for $\Delta j = -1$ transitions.](https://academic.oup.com/mnras/article/527/4/9826/7472093)

4 rate coefficients of nccp-para-H$_2$ and comparison with nccp-he

Here, the $k_{j \rightarrow j'}(T)$ for NCCP-para-H$_2$ interaction is calculated by thermally averaging the cross-sections obtained from CC calculations at various temperatures. The temperature range used for the measurements is 5–200 K. The rate coefficients between state ($j$) and ($j'$) are calculated using the following Boltzmann average formula:

$$k_{j \rightarrow j'}(T) = \frac{8 \hbar k T}{\pi \mu} \left( k_B T \right)^2 \int_0^{\infty} \sigma_{j \rightarrow j'}(E_k) E_k \exp \left( -\frac{E_k}{k_B T} \right) dE_k. \quad (6)$$

The kinetic energy is given as $E_k = E_i - E_j$, with $E_j$ showing the rotational energy and $k_B$ denoting the Boltzmann constant. The reduced mass and temperature are symbolized by $\mu$ and $T$, respectively.

Fig. 7 illustrates the rate coefficients of interest as a function of temperature. The observed trends confirm the same propensity that favours even $\Delta j = -2$ transitions over $\Delta j = -1$ transitions. The obtained values of $k_{j \rightarrow j'}(T)$ for NCCP-para-H$_2$ are compared with previously determined rate coefficients of NCCP–He. It is generally assumed that $k_{\text{He}}$ can be deduced from $k_{\text{He}}$ by using a scaling factor (SF) that takes into account the difference in their reduced masses. The SF for NCCP can be determined using the following equation:

$$SF = \frac{k_{\text{He}}}{k_{\text{He}}} = \frac{\mu_{\text{NCCP-He}}}{\mu_{\text{NCCP-H}_2}} = \sqrt{\frac{3.7831}{1.9587}} = 1.38 \quad (7)$$

The above approximation suggests that the cross-sections involving para-H$_2$ ($j_p = 0$) and He are the same and this SF of 1.38 is only attributed to the reduced mass factor incorporated in equation (6), which determines the associated rate coefficients. Since a limited number of systems have been examined with both He and H$_2$, it’s necessary to verify the accuracy of this approximation. Fig. 8 provides a comparison of $k_{j \rightarrow j'}(T)$ data, comparing the results for NCCP–He with NCCP–H$_2$. This indicates that accurate collisional rate coefficients using helium collision cannot be achieved for para-H$_2$ interactions. The observed differences in the results are expected due to the difference in the well-depth of both NCCP–He and NCCP–H$_2$. NCCP–H$_2$ has three times deeper well than NCCP–He resulting in a different range of resonances presented in Fig. 5. The ratios of
Table 2. Calculated values of $k_{j \rightarrow f}(T)$ (in $10^{-11}$ cm$^3$ s$^{-1}$ molecule$^{-1}$) for NCCP–$para$-H$_2$ and NCCP–He and their ratio.

<table>
<thead>
<tr>
<th>$j \rightarrow f$</th>
<th>$T = 10$ K</th>
<th>$k_{He}$</th>
<th>$k_{H_2}/k_{He}$</th>
<th>$k_{H_2}$</th>
<th>$k_{He}$</th>
<th>$k_{H_2}/k_{He}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 $\rightarrow$ 3</td>
<td>3.41</td>
<td>0.75</td>
<td>4.54</td>
<td>1.71</td>
<td>0.52</td>
<td>3.28</td>
</tr>
<tr>
<td>4 $\rightarrow$ 2</td>
<td>2.90</td>
<td>1.04</td>
<td>2.78</td>
<td>1.55</td>
<td>0.68</td>
<td>2.27</td>
</tr>
<tr>
<td>3 $\rightarrow$ 1</td>
<td>2.33</td>
<td>0.84</td>
<td>2.65</td>
<td>1.21</td>
<td>0.59</td>
<td>2.05</td>
</tr>
<tr>
<td>2 $\rightarrow$ 0</td>
<td>0.91</td>
<td>0.41</td>
<td>2.21</td>
<td>0.54</td>
<td>0.30</td>
<td>1.80</td>
</tr>
<tr>
<td>4 $\rightarrow$ 3</td>
<td>1.76</td>
<td>0.68</td>
<td>2.58</td>
<td>0.85</td>
<td>0.45</td>
<td>1.88</td>
</tr>
<tr>
<td>3 $\rightarrow$ 2</td>
<td>1.46</td>
<td>0.58</td>
<td>2.51</td>
<td>0.73</td>
<td>0.40</td>
<td>1.82</td>
</tr>
<tr>
<td>2 $\rightarrow$ 1</td>
<td>0.99</td>
<td>0.46</td>
<td>2.15</td>
<td>0.52</td>
<td>0.29</td>
<td>1.79</td>
</tr>
<tr>
<td>1 $\rightarrow$ 0</td>
<td>0.35</td>
<td>0.22</td>
<td>1.59</td>
<td>0.19</td>
<td>0.13</td>
<td>1.46</td>
</tr>
</tbody>
</table>

Figure 9. Comparison of rate coefficients of NCCP with $para$-H$_2$ and He along with the SF (1.38) at T = 10 K and 50 K.

The $k_{j \rightarrow f}(T)$, i.e. [NCCP–$para$-H$_2$($J_p = 0$)/NCCP–He], are tabulated in Table 2. Table 2 shows that the ratio is inconsistent and exhibits fluctuations at $T = 10$ K and $T = 50$ K. At low-temperature values, the differences between the two sets of systems are more pronounced, and as the temperature rises further, the correspondence between the two sets of coefficients would likely become quite favourable. The outcomes align with the earlier research by Lique et al. (2007) concerning collisions involving SO and H$_2$. In an attempt to examine these differences, we have also graphed the rate coefficients for various transitions at $T = 10$ K and $T = 50$ K as illustrated in Fig. 9. The estimated abundance of NCCP in molecular clouds could have been revised in light of these recently calculated rate coefficients. The bending frequency ($v_2$, Kwon & McKee 2001) for NCCP is found to be 206 cm$^{-1}$, but the infrared intensities of the vibrational transitions of linear NCCP are all very small, almost negligible due to very less polarity in the NCCP bonds. Strictly speaking, our dynamical calculations for rigid model NCCP are valid for energies lower than the lowest frequency (bending) of NCCP molecule, i.e. $< 206$ cm$^{-1}$. Nonetheless, several benchmarks on molecules colliding with H$_2$ or He demonstrated that a complete consideration of vibrational degrees of freedom is not needed to account for the effect of vibration (Halvick et al. 2011; Denis-Alpizar, Stoecklin & Halvick 2014; Papp et al. 2017). With the exception of a few cases, such as quasi floppy molecule which is linear (e.g. C$_3$; Al Mogren et al. 2014; Denis-Alpizar, Stoecklin & Halvick 2014), where minor differences between rigid and non-rigid models were found, almost identical results were obtained without and with considering the vibrations. For the NCCP molecule, this should be the case.

5 SUMMARY AND CONCLUSIONS

The collisional cross-sections involving NCCP and $para$-H$_2$ are computed using the exact CC approach. These computations span a wide spectrum of $E_c$ ranging from 0.5–600 cm$^{-1}$. Using Boltzmann velocity distribution, the cross-sections are averaged to calculate $k_{j \rightarrow f}(T)$ for $T$ up to 200 K. The accuracy of quantum dynamical data highly depends on the interaction potentials of colliding entities developed for the collision between NCCP and H$_2$. To model this collision, a new NCCP–H$_2$ 4DPES is computed using the CCSD(T)-F12a/aug-cc-pVTZ level of theory. This PES is subsequently averaged to 2DPEs using three distinct angular orientations of H$_2$. Within the averaged NCCP–H$_2$ PES, a global energy minimum of 125.40 cm$^{-1}$ is identified, which is notably deeper than the 46.40 cm$^{-1}$ minimum energy observed in the NCCP–He collision. The point of maximum depth was found at an angle of 110° for both collision systems. Upon expansion of PES, both systems demonstrate analogous trends and shapes. The isotropic term $v_0$ increases by about $\sim 20$ cm$^{-1}$ due to the lower minimum energy of the NCCP–H$_2$ collision. Furthermore, the spectrum of resonances in the NCCP–$para$-H$_2$ collision spans a wide range, extending to around 200 cm$^{-1}$. In contrast, the NCCP–He collision’s range only encompassed approximately 50 cm$^{-1}$. Comparing the newly calculated $k_{j \rightarrow f}(T)$ for NCCP–$para$-H$_2$ collisions with the existing
NCCP–He rate coefficients reveals notable distinctions, particularly at lower temperatures. The rate coefficients for collisions with He appear to provide a plausible model for interactions with para-H₂ at moderately higher temperatures. It’s crucial to highlight that the SF cannot be deemed a dependable approach for replicating para-H₂ collisions. Analysing the data, it becomes evident that the rate coefficients for NCCP–H₂ collisions are 1.5–4.5 times greater than those for NCCP–He collisions. Modelling the NCCP abundance in the ISM will be simpler owing to new insights into collision rates and other dynamic properties between H₂ and NCCP.

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DATA AVAILABILITY

The data underlying this article are available in the article and in its online supplementary material.

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SUPPORTING INFORMATION

Supplementary data are available at MNRAS online.

suppl_data

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