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## Collisional Excitation of Interstellar PN by H<sub>2</sub>: New Interaction Potential and Scattering Calculations

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# Collisional excitation of interstellar PN by H<sub>2</sub>: New interaction potential and scattering calculations

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## ABSTRACT

Rotational excitation of interstellar PN molecules induced by collisions with H<sub>2</sub> is investigated. We present the first *ab initio* four-dimensional potential energy surface (PES) for the PN–H<sub>2</sub> van der Waals system. The PES was obtained using an explicitly correlated coupled cluster approach with single, double, and perturbative triple excitations [CCSD(T)-F12b]. The method of interpolating moving least squares was used to construct an analytical PES from these data. The equilibrium structure of the complex was found to be linear, with H<sub>2</sub> aligned at the N end of the PN molecule, at an intermolecular separation of 4.2 Å. The corresponding well-depth is 224.3 cm<sup>-1</sup>. The dissociation energies were found to be 40.19 cm<sup>-1</sup> and 75.05 cm<sup>-1</sup> for complexes of PN with *ortho*-H<sub>2</sub> and *para*-H<sub>2</sub>, respectively. Integral cross sections for rotational excitation in PN–H<sub>2</sub> collisions were calculated using the new PES and were found to be strongly dependent on the rotational level of the H<sub>2</sub> molecule. These new collisional data will be crucial to improve the estimation of PN abundance in the interstellar medium from observational spectra.

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## I. INTRODUCTION

Phosphorus (P) is known to be an essential element for life as we know it. Indeed, it has a central role in biochemical processes since it is a key element in forming deoxyribonucleic acid (DNA) and cell membranes.<sup>1</sup> P-bearing compounds have also been proposed as key catalysts and chemical buffers for the formation of nucleotides.<sup>2</sup> However, the way it arrived on Earth is still not fully understood, especially since the abundance of phosphorus in space is low<sup>3</sup> (P/H ~ 3 × 10<sup>-7</sup>). Hence, there has been an intense interest in searching for P-bearing compounds in astrophysical environments and especially in star-forming regions. So far, only a few simple

P-bearing species (PN, PO, CP, HCP, CCP, and PH<sub>3</sub>) have been identified, mostly toward the circumstellar envelopes of evolved stars.<sup>4</sup>

Among the interstellar P-bearing molecules, PN is perhaps the most interesting one. The first interstellar detection of this molecule was reported more than 30 years ago by Turner and Bally<sup>5</sup> and Ziurys<sup>6</sup> in Ori(KL), W51M, and SgrB2 sources, by observations of the  $j_1 = 2 \rightarrow 1$ ,  $j_1 = 3 \rightarrow 2$ ,  $j_1 = 5 \rightarrow 4$ , and  $j_1 = 6 \rightarrow 5$  rotational transitions ( $j_1$  designates the PN rotational level). This was the first example of a phosphorus-containing species seen in interstellar molecular clouds. Since then, the PN molecule has been observed in both star-forming regions<sup>7–9</sup> and circumstellar

gas.<sup>10,11</sup> Until the recent detection of PO,<sup>12</sup> PN remained the only P-bearing molecule detected in interstellar molecular clouds. With a few exceptions in the last five years (e.g., Rivilla *et al.*<sup>13</sup> and references therein), the number of PN observations has been relatively low compared to other small nitrogen containing species such as CN or NO.

The chemistry of interstellar P-bearing molecules (including PN) has been the object of several studies.<sup>14,15</sup> However, the gas phase chemistry of phosphorus is still not well understood, partly because some of these molecules are very toxic and difficult to study in a laboratory. In particular, there is still an active debate on whether PN or PO is more abundant in various astrophysical objects.<sup>13,15</sup> Studying the amount of PN in astrophysical objects can provide information for other P-bearing species and help in better constraining the phosphorus chemistry in the universe. An accurate determination of PN abundance in the interstellar medium (ISM) from spectral line data requires collisional rate coefficients with the most abundant interstellar species—usually the H<sub>2</sub> molecule—since collisional processes contribute, in competition with the radiative ones, to the molecular excitation. Without these rates, only approximate estimates of the molecular abundance are possible assuming local thermodynamic equilibrium (LTE), which is generally not a good approximation.<sup>16</sup>

Excitation studies of the PN molecule started more than a decade ago. The first study on collisions of PN with He (as a surrogate for H<sub>2</sub>) was performed by Toboła *et al.*<sup>17</sup> using quantum scattering calculations. These authors provided collisional rate coefficients between the first 31 rotational energy levels of PN for temperatures up to 300 K. These data were used in astrochemical models in order to derive the PN abundance from the observational spectra.<sup>10,11,13,18</sup> However, it is now well established<sup>16</sup> that rate coefficients for collisions with H<sub>2</sub> are generally different from those for collisions with He and that strong abundance determination errors can result from the use of uncertain collisional data.<sup>19,20</sup>

More recently, Najar *et al.*<sup>21</sup> studied the rotational excitation of PN by collisions with H<sub>2</sub> and provided rate coefficients for the rotational (de-)excitation of PN by *para*-H<sub>2</sub>. They found significant differences from the PN-He data of Toboła *et al.*,<sup>17</sup> confirming that actual H<sub>2</sub> rate coefficients are needed. However, those authors computed and used a potential energy surface (PES) averaged over the H<sub>2</sub> rotation, resulting in a simplified dynamical calculation only valid for the collisional excitation by H<sub>2</sub>(*j*<sub>2</sub> = 0) (*j*<sub>2</sub> designates the H<sub>2</sub> rotational level) at low temperatures. Therefore, the validity of the approximation used by Najar *et al.*<sup>21</sup> also needs to be checked. Moreover, as PN is also observed in astrophysical environments where the *ortho*-to-*para*-H<sub>2</sub> ratio is expected to be large, it seems also important to provide new rate coefficients for the rotational excitation of PN by H<sub>2</sub>(*j*<sub>2</sub> > 0). Such collisional data will provide the astronomical community with the necessary tools to interpret PN emission and to make the most of the observations.

The aim of this study is to obtain inelastic cross sections for collisions between PN and H<sub>2</sub> using quantum scattering calculations. The computation of such data usually takes place within the Born–Oppenheimer approximation for the separation of electronic and nuclear motions. Scattering cross sections are, thus, obtained by solving for the motion of the nuclei on an electronic PES, which is independent of the masses and spins of the nuclei.

In this paper, we present the calculation of a new four-dimensional (4D) PES for the ground electronic state of the PN–H<sub>2</sub> collisional system. Then, the dissociation energy of the complex with *ortho*-H<sub>2</sub> and *para*-H<sub>2</sub> is provided. Such data can be useful for future spectroscopical studies. Finally, using this new PES, rotational excitation of PN with both *para*-H<sub>2</sub> and *ortho*-H<sub>2</sub> is studied. This paper is organized as follows: Sec. II describes the calculation of the PES. Section III presents the bound state calculations. Section IV contains a concise description of the collisional excitation calculations and of the scattering results. Concluding remarks are presented in Sec. V.

## II. PN–H<sub>2</sub> POTENTIAL ENERGY SURFACE

The coordinates used to define the 4D PN–H<sub>2</sub> PES:  $R$ ,  $\theta_1$ ,  $\theta_2$ , and  $\varphi$ , are depicted in Fig. 1.  $\vec{R}$  is the vector between the centers of mass of the two fragments, and  $\vec{r}_1$  and  $\vec{r}_2$  are vectors aligned with the bond axes of the fragments ( $\vec{r}_1$  for PN and  $\vec{r}_2$  for H<sub>2</sub>). The coordinate  $R$  is the length of the vector  $\vec{R}$ , while coordinates  $\theta_1$  and  $\theta_2$  represent the angles between  $\vec{R}$  and the vectors  $\vec{r}_1$  and  $\vec{r}_2$ , respectively. The fourth coordinate is the dihedral (out of plane) torsional angle, labeled  $\varphi$ , which is the angle between the vectors  $\vec{R} \times \vec{r}_1$  and  $\vec{R} \times \vec{r}_2$ .

### A. Electronic structure calculations

In this study, both monomers are approximated as rigid held at their ground state vibrationally averaged structures. It is a good approximation in this application to consider only the intermonomer coordinates because their frequencies are all much less than those of the intra-monomer coordinates. The bond distance for H<sub>2</sub> was fixed at 0.766 651 1 Å, the vibrationally averaged bond distance for *para*-H<sub>2</sub>, while the <sup>31</sup>P<sup>14</sup>N molecule was held rigid at 1.493 50 Å, consistent with the experimental rotational constant of 23 495.204 19(41) MHz.<sup>22</sup> Masses of 1.007 825 032 23 amu, 14.003 074 004 43 amu, and 30.973 761 998 42 amu were used for <sup>1</sup>H, <sup>14</sup>N, and <sup>31</sup>P, respectively.

All *ab initio* calculations were performed using the MOLPRO electronic structure code package.<sup>23</sup> The final high-level PES was constructed using *ab initio* data computed with explicitly correlated coupled cluster theory.<sup>24</sup> The complete basis set limit was

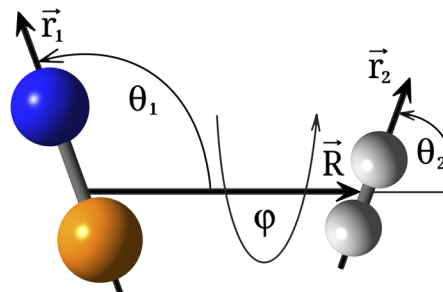


FIG. 1. Coordinates used to describe the PN–H<sub>2</sub> interaction.  $R$ : center-of-mass separation (length of  $\vec{R}$ );  $\theta_1$  and  $\theta_2$ : angles between  $\vec{R}$  and the vectors  $\vec{r}_1$  and  $\vec{r}_2$ ;  $\varphi$ : torsional angle.

estimated by extrapolating calculations in the coupled cluster approach with single, double, and perturbative triple excitations [CCSD(T)-F12b/VTZ-F12] and CCSD(T)-F12b/VQZ-F12 levels, using the  $I^{-3}$  formula.<sup>25</sup> Exploiting the system's symmetry, energies were only needed in the reduced angular range:  $0 < \theta_1 < 180^\circ$ ,  $0 < \theta_2 < 90^\circ$ , and  $0 < \varphi < 180^\circ$ . As discussed below, a lower-level guide surface (to avoid computing high-level data at inaccessible geometries) was also constructed; this was done using *ab initio* data at the CCSD(T)-F12b/VDZ-F12 level of theory.

## B. Analytical representation

As we have done in the past for other van der Waals (vdW) linear dimers,<sup>26–35</sup> the 4D PES analytical representation was constructed using an automated interpolating moving least-squares methodology, which has been recently released as a software package under the name AUTOSURF.<sup>36</sup> As usual,<sup>37</sup> a local fit was expanded about each data point, and the final potential was obtained as the normalized weighted sum of the local fits. The procedure has been described in detail elsewhere.<sup>31,36,38</sup>

The shortest intermonomer center-of-mass distance considered is  $R = 2.4$  Å, with the additional restriction of a maximum repulsive energy of 6 kcal/mol ( $\sim 2100$  cm<sup>-1</sup>) relative to the separated monomer asymptote. The fitted range of the PES extends to  $R = 22.0$  Å. For each of the local fits, a fitting basis of 301 functions is used. As has been previously described,<sup>37</sup> our default fitting basis is a product of radial functions and angular functions (associated Legendre polynomials with a cosine-based torsional function). Note that due to the use of many local expansions, each with their own coefficients, the overall flexibility of the basis is much greater than what would be implied by these parameters if used as a single expansion. To guide the placement of the high-level data—and avoid computing and discarding computationally expensive *ab initio* energies in highly repulsive regions—a lower-level guide PES

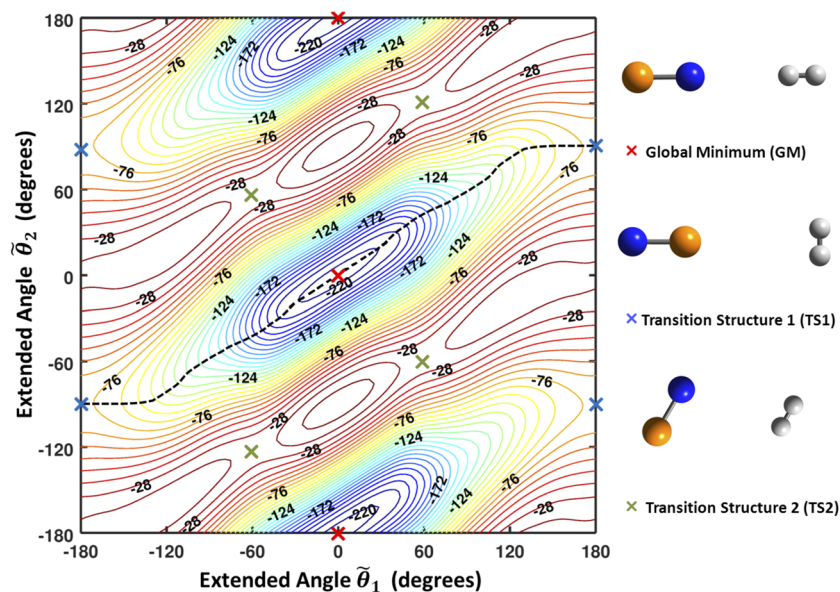
was constructed using 2176 symmetry-unique points, distributed using a Sobol sequence<sup>39</sup> biased to sample the short range region more densely. For the high-level PES, the global root-mean-squared fitting error was 0.16 cm<sup>-1</sup> (0.05 cm<sup>-1</sup> for energy-regions below the asymptote) and the total number of automatically generated symmetry-unique points needed to reach that target was 3759. The analytical representation of the PES is included as the [supplementary material](#).

## C. Characterization of the PES

Figure 2 shows a 2D representation of the PES (denoted  $R$ -optimized) for planar configurations, as a function of the extended angles  $\tilde{\theta}_1$  and  $\tilde{\theta}_2$ . The position of stationary points and the corresponding molecular configurations are also highlighted in the figure. The extended angle coordinates have been described elsewhere.<sup>27</sup> For planar geometries ( $\varphi = 0^\circ$  for quadrants II and IV and  $\varphi = 180^\circ$  for quadrants I and III), the plot describes the complete ranges of  $\tilde{\theta}_1$  and  $\tilde{\theta}_2$ , relaxing the intermonomer distance coordinate  $R$  for each pair of angles. This type of plot provides unique insight into the isomers in the system, since for many systems—those (such as this one) without non-planar minima—the plot will include all isomers and the relevant isomerization paths between them, making it easy to visualize planar motions during which  $\varphi$  changes from 0 to 180°. There is only one physical well in the PES, which appears twice in the extended angle plot, reflecting the symmetry of the H<sub>2</sub> molecule.

The PES is characterized by a single isomer [labeled global minimum (GM)] corresponding to a linear structure—with H<sub>2</sub> aligned at the N end of the PN molecule—with a well-depth ( $D_e$ ) of 224.3 cm<sup>-1</sup>. The energies and geometric parameters of the global minimum and transition structures (TSs) are reported in Table I.

In constructing their 2D PES, Najar *et al.*<sup>21</sup> employed a standard coupled cluster with a triple-zeta basis set, CCSD(T)/AVTZ,



**FIG. 2.**  $R$ -optimized contour plot of the PES as a function of the extended angles  $\tilde{\theta}_1$  and  $\tilde{\theta}_2$ . For each pair of angles, the energy (given in cm<sup>-1</sup>) is minimized with respect to the center-of-mass distance  $R$ . The position of each stationary point—and the corresponding molecular configuration—is also highlighted. The dashed line represents the disrotatory energy path connecting equivalent minima. See the text for details.

**TABLE I.** Geometric parameters and potential energy for the global minimum (GM) and transition structures (TSs) of the PN-H<sub>2</sub> complex. Units are angstroms, degrees, and cm<sup>-1</sup>.

	GM	TS1	TS2
$R$	4.218	4.265	4.078
$\theta_1$	0.0	180.0	58.3
$\theta_2$	0.0	90.0	58.2
$\varphi$	...	...	0.0
$V$	-224.3	-75.0	-23.0

but also added mid-bond functions and corrected for the basis set superposition error. They reported a well-depth of 219.8 cm<sup>-1</sup> at that level (slightly shallower than our PES) but also listed a number of other benchmarks including a well-depth value of 224.0 cm<sup>-1</sup> for CCSD(T)/CBS (very close to our result of 224.3 cm<sup>-1</sup> obtained with an explicitly correlated method). The electronic structure energy values reported by Najar *et al.* are quite similar to ours for a variety of configurations, such that it seems that the main difference between the two studies is that of their reduced dimensionality and associated averaging over orientations.

Various motions of the monomers can move the system from the global minimum to an equivalent structure on the PES. The minimum energy path between the minima, highlighted in Fig. 2 (dashed line), represents a disrotatory (or geared) motion that moves the system along a planar low-energy path, passing through transition structure 1 (TS1). A disrotatory path between minima is common in complexes formed by two linear monomers with planar minima.<sup>27,28,31</sup> It is easily identified as it follows an angle of roughly 45° from lower left to upper right in the extended angle plot (cf. Fig. 2). Following the path, exiting the plot on the right side, the path would reenter the plot from the left (at the same value of  $\theta_2$ ), thus connecting with the next well up in the plot. Also in Fig. 2, a second planar path is seen, moving almost vertically between minima in the plot, passing through a much higher-energy transition structure (TS2). This movement effectively rotates the H<sub>2</sub> molecule 180°, while the PN molecule relaxes slightly and then gets

back again to  $\theta_1 = 0^\circ$  without flipping. In this system, given only one physical well, unlike numerous other van der Waals systems we have studied, no tunneling splittings are anticipated in the rovibrational levels.

Figure 3 shows 1D cuts of the potential as a function of  $R$ , upon approach, holding fixed the relative orientations of the monomers. The variation in those cuts gives some indication of the anisotropy of the interactions. It is worth highlighting that all of the *ab initio* energies plotted in Fig. 3 were not used in the PES-construction process and, thus, serve to confirm the overall quality of our fitted potential. In order to better appreciate the topography of the PES near the global minimum, and the anisotropy of the interaction with respect to the PN and H<sub>2</sub> rotations, additional 2D plots of the potential were made and are shown in Fig. 4. The plots in Fig. 4 explore the region around the minimum by presenting both the  $(R, \theta_1)$  and  $(R, \theta_2)$  planes that cross it.

A subroutine of the PES is provided as the [supplementary material](#).

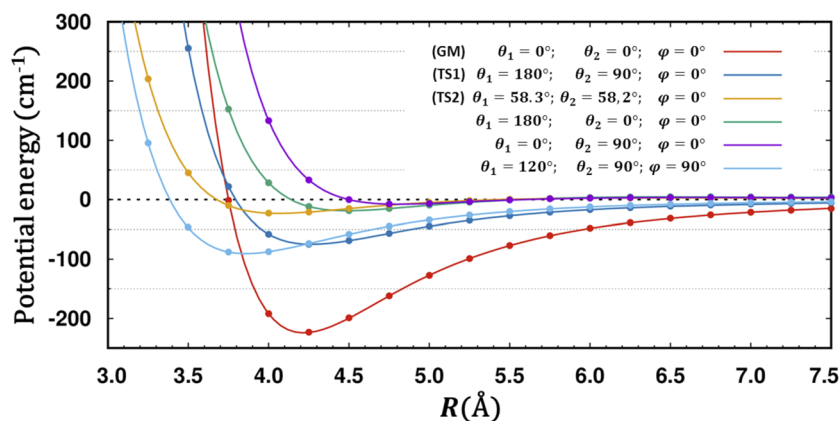
### III. PN-H<sub>2</sub> DISSOCIATION ENERGY

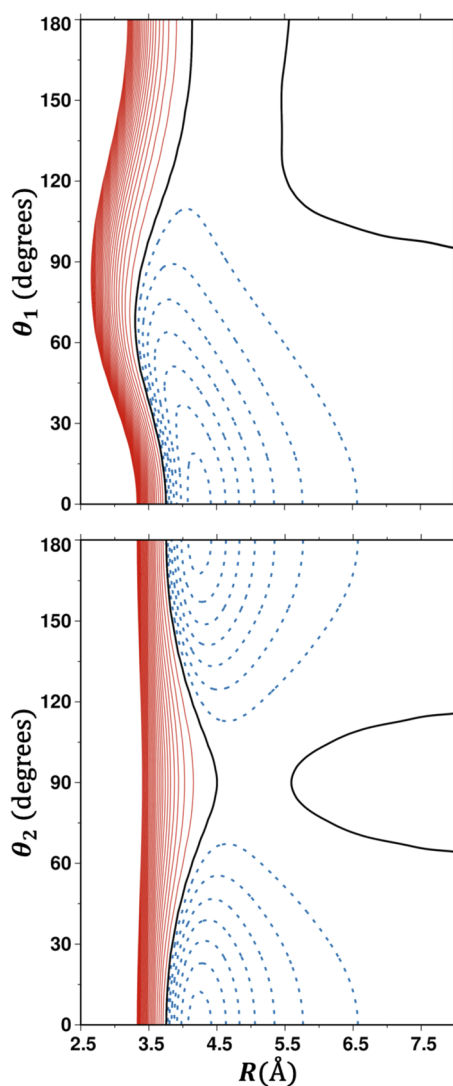
The PN-H<sub>2</sub> dissociation energy was computed with a close-coupling method using the BOUND program.<sup>40</sup> The coupled equations were solved using the log-derivative method of Manolopoulos.<sup>41</sup> The propagator step size was set to 0.05 Å in order to converge the bound states.

The two molecules were considered rigid-rotors, adopting the data compiled by Herzberg and Huber:<sup>42</sup> we used molecular constants  $B_{e1} = 0.7864854$  cm<sup>-1</sup>,  $\alpha_{e1} = 0.0055364$  cm<sup>-1</sup>, and  $D_{e1} = 1.091 \times 10^{-6}$  cm<sup>-1</sup> for the PN molecule and  $B_{e2} = 60.853$  cm<sup>-1</sup>,  $\alpha_{e2} = 3.062$  cm<sup>-1</sup>, and  $D_{e2} = 4.71 \times 10^{-2}$  cm<sup>-1</sup> for the H<sub>2</sub> molecule. The basis describing the rotation of PN and H<sub>2</sub> molecules included the first 23 and 6 rotational states, respectively.

The expansion of the potential  $V(R, \theta_1, \theta_2, \varphi)$  was performed over angular functions for each  $R$  distance as described by Green,<sup>43</sup>

$$V(R, \theta_1, \theta_2, \varphi) = \sum_{l_1, l_2, l} v_{l_1, l_2, l}(R) A_{l_1, l_2, l}(\theta_1, \theta_2, \varphi), \quad (1)$$

**FIG. 3.** The energy along various radial cuts defined by different relative orientations of the monomers is plotted. Lines represent the fitted PES, and points represent *ab initio* calculations (not used in the fit).



**FIG. 4.** 2D cuts of the PES exploring the region around the global minimum for planar geometries ( $\varphi = 0^\circ$ ), holding the angles  $\theta_2$  (upper panel) and  $\theta_1$  (lower panel) fixed. Energies are in  $\text{cm}^{-1}$ . Red contours represent positive energies (intervals of  $60 \text{ cm}^{-1}$ ), the black contour is the zero energy, and blue dashed contours represent negative energies (intervals of  $30 \text{ cm}^{-1}$ ).

where  $A_{l_1, l_2, l}(\theta_1, \theta_2, \varphi)$  is constructed from coupled spherical functions  $Y_{l_i, m_i}(\theta_i, \varphi)$  and the rotational angular momenta of PN and  $\text{H}_2$ . In our case, the potential was expanded including  $0 \leq l_1 \leq 18$  for the PN molecule and  $0 \leq l_2 \leq 6$  for the  $\text{H}_2$  molecule.

Our calculated ground state dissociation energies ( $D_0$ ) are equal to  $40.19 \text{ cm}^{-1}$  and  $75.05 \text{ cm}^{-1}$  for complexes with *ortho*- $\text{H}_2$  and *para*- $\text{H}_2$ , respectively. The  $D_e$  and  $D_0$  values obtained in the present work suggest that the zero-point energy associated with the intermolecular vibrations and internal rotations accounts for  $\sim 2/3$  of the well-depth.

To the best of our knowledge, no measurements of the binding energy  $D_0$  of PN- $\text{H}_2$  have been reported. Such measurements would be useful for validation of the PES, complementing the spectroscopic level structure. Indeed, scattering calculations depend on the shape and the well-depth of the PES, and the dissociation energy is influenced by both. The PES provided here will be useful for any future study of the rovibrational bound states.

#### IV. SCATTERING CALCULATIONS

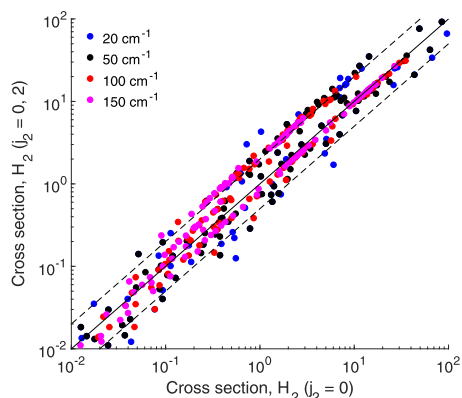
We computed integral cross sections for the rotational excitation of PN induced by both *para*- $\text{H}_2$  ( $j_2 = 0$ ) and *ortho*- $\text{H}_2$  ( $j_2 = 1$ ) using the quantum close-coupling approach implemented in the MOLSCAT non-reactive scattering code.<sup>44</sup> The hyperfine structure of the PN molecules, due to the non-zero nuclear spin of the nitrogen atom, is neglected in these calculations since the hyperfine structure is not resolved in the astronomical spectra. It can, however, be considered from the present data using recoupling techniques as described by Lanza and Lique.<sup>45</sup> The expansion of the potential  $V(R, \theta_1, \theta_2, \varphi)$  over angular functions was performed as described in Sec. III for the calculation of the PN- $\text{H}_2$  dissociation energy. As for dissociation energy calculations, the close-coupled equations of inelastic scattering were solved using the log-derivative propagator of Manolopoulos,<sup>41</sup> starting from  $R_{\min} = 2.12 \text{ \AA}$  to  $R_{\max} = 21.7 \text{ \AA}$ .

Inelastic cross sections were obtained between the first 11 rotational levels of PN ( $0 \leq j_1 \leq 10$ ). The integration parameters were chosen to ensure convergence of these cross sections for collisional energies ranging from  $1 \text{ cm}^{-1}$  up to  $150 \text{ cm}^{-1}$ . At each energy, the maximum value of the total angular momentum needed to obtain cross sections converged to better than  $1 \times 10^{-3} \text{ \AA}^2$  was automatically set by the MOLSCAT program.

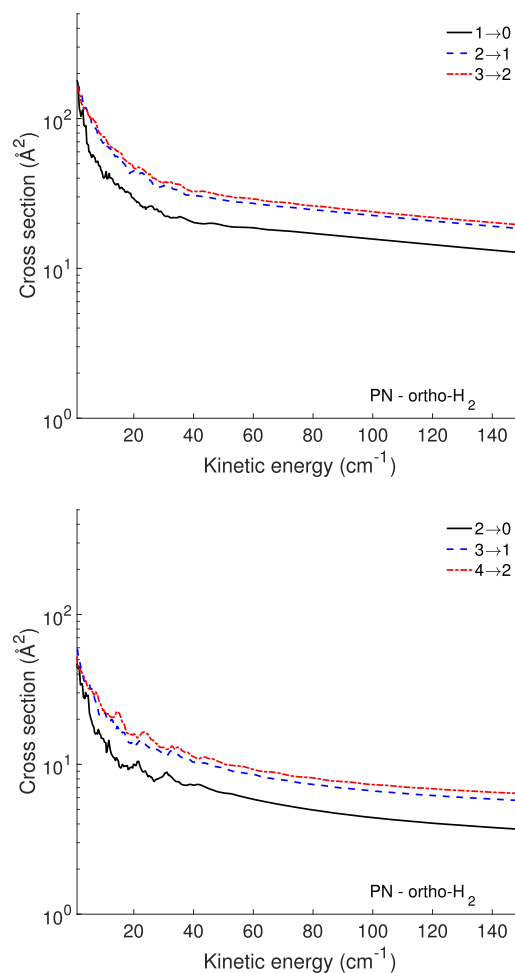
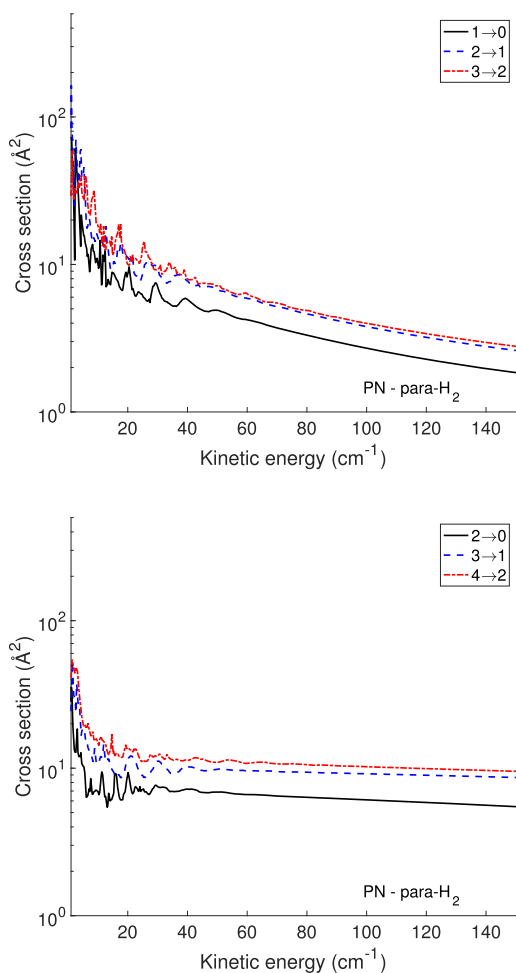
The size of the rotational basis was studied carefully in order to ensure convergence of the cross sections. The first 19 rotational states ( $0 \leq j_1 \leq 18$ ) of PN were included in the basis set. Two sets of calculations were performed: calculations have been done either considering only the ground rotational states of *para*- $\text{H}_2$  and *ortho*- $\text{H}_2$  ( $j_2 = 0$  and  $j_2 = 1$ , respectively) or expanding the basis to the first two rotational levels ( $j_2 = 0, 2$  and  $j_2 = 1, 3$ ).

In Fig. 5, a comparison between those two sets of calculations is presented for four different values of the total collisional energy. As can be seen, considering only the first rotational state of the  $\text{H}_2$  molecule in the rotational basis leads to inaccuracies higher than a factor of 2 for the cross section values at all the considered energies. It should be noted that differences higher than a factor of 4 can be observed at low collisional energy ( $20 \text{ cm}^{-1}$ ), where the cross sections exhibit strong shape and Feshbach resonances. It is then essential to add at least one closed  $\text{H}_2$  level in the basis set, and we also found (not shown here) that including the  $j_2 = 4$  level of  $\text{H}_2$  in the basis set does not affect the magnitude of the cross sections. Similar conclusions were also found for the *ortho*- $\text{H}_2$  basis so that we have retained the first two rotational states of *para*- $\text{H}_2$  and *ortho*- $\text{H}_2$  in the rotational basis set.

Collision energy variation of the cross sections for the rotational de-excitation of PN( $j_1$ ) induced by both *para*- $\text{H}_2$  and *ortho*- $\text{H}_2$  is illustrated in Fig. 6 for selected transitions with  $\Delta j_1 = 1$  and  $\Delta j_1 = 2$ .



**FIG. 5.** Comparison between cross sections (in units of  $\text{\AA}^2$ ) for the collisional (de)excitation of PN by  $\text{H}_2$  obtained including only the ground rotational level of  $\text{H}_2$  ( $j_2 = 0$ ) or including the first two rotational levels ( $j_2 = 0, 2$ ) in the rotational basis. The two dashed lines delimit the region where the cross sections differ by less than a factor of 2.

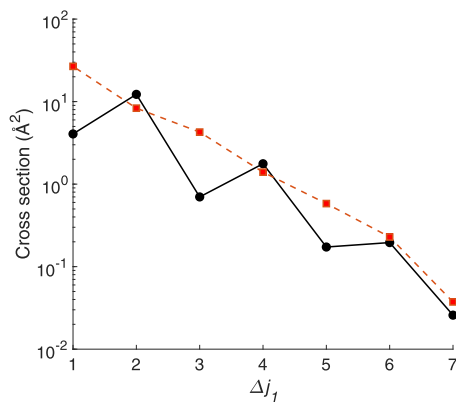


**FIG. 6.** Collision energy variation of the cross sections for the rotational de-excitation of PN induced by collisions with *para*- $\text{H}_2$  (left panels) and *ortho*- $\text{H}_2$  (right panels) for selected transitions with  $\Delta j_1 = 1$  (upper panels) and  $\Delta j_1 = 2$  (lower panels).

For collisions with *para*- $\text{H}_2$ , the cross sections exhibit strong resonances at low collisional energy. Resonances with lower amplitudes are also observed for collisions with *ortho*- $\text{H}_2$ . This relates to the creation of quasi-bound states within the deep vdW well of the PN- $\text{H}_2$  complex before its dissociation, as already discussed by Najar *et al.*<sup>21</sup>

For transitions with  $\Delta j_1 = 1$ , the values of the cross sections for collisions with *ortho*- $\text{H}_2$  are significantly larger than those for collisions with *para*- $\text{H}_2$ , the differences being typically of a factor of 4 at low energy and up to almost an order of magnitude at highest energies. However, this trend is no longer observed for transitions with  $\Delta j_1 = 2$ , cross sections for collisions with *ortho*- $\text{H}_2$  being even lower than those for collisions with *para*- $\text{H}_2$  at high energy. Actually, we found that the *ortho*- $\text{H}_2$  cross sections are much larger than the *para*- $\text{H}_2$  ones only for odd  $\Delta j_1$  transitions (see Fig. 7).

The  $j_2$  dependence of the cross sections is due to the large anisotropy of the PES with respect to  $\text{H}_2$  rotations and can be explained by the magnitude of the radial coefficients  $v_{l_1 l_2 l}(R)$  of Eq. (1). The radial coefficients that mainly contribute to cross



**FIG. 7.** Rotational de-excitation cross sections of  $\text{PN}(j_1 = 7)$  to  $\text{PN}(j_1')$  induced by collisions with *para*- $\text{H}_2$  (circles) and *ortho*- $\text{H}_2$  (squares) for a collision energy of  $100 \text{ cm}^{-1}$ .

sections with  $j_2 \rightarrow j_2'$  transitions are those with  $l_2$  in the  $|j_2 - j_2'| < l_2 < |j_2 + j_2'|$  range. Hence, for collisions with *para*- $\text{H}_2$  ( $j_2 = 0$ ), only the  $l_2 = 0$  term contributes, whereas, for collisions with *ortho*- $\text{H}_2$  ( $j_2 = 1$ ),  $l_2 = 0$  and 2 terms contribute. The radial coefficients with  $l_2 = 2$  are not negligible compared to the one with  $l_2 = 0$  and explain the difference for collisions with  $\text{H}_2(j_2 = 0)$  and  $\text{H}_2(j_2 = 1)$ . The differences between *para*- $\text{H}_2$  and *ortho*- $\text{H}_2$  cross sections are more marked for transitions with odd  $\Delta j_1$  since  $v_{l_1, l_2}(R)$  terms with odd  $l_1$  and  $l_2 = 2$  are stronger than those with even  $l_1$  and  $l_2 = 2$ .

In Fig. 7, we present de-excitation cross sections out of  $\text{PN}(j_1 = 7)$  induced by collisions with *para*- $\text{H}_2$  and *ortho*- $\text{H}_2$  for a collision energy of  $100 \text{ cm}^{-1}$ . The propensity rules depend on the quantum state of the  $\text{H}_2$  molecule. Collisions with  $\text{H}_2(j_2 = 0)$  show a remarkably strong propensity for even  $\Delta j_1$  transitions. The explanation of such behavior could be found in the features of the PES. As also found by Najar *et al.*,<sup>21</sup> the averaged PES over the rotational wave function of  $\text{H}_2(j_2 = 0)$  (i.e., a spherical average of the PES) exhibits an almost near-homonuclear symmetry, leading to propensity rules in favor of even  $\Delta j_1$ . For collisions with  $\text{H}_2(j_2 = 1)$ , a simple propensity in favor of  $\Delta j_1 = 1$  is observed and the cross sections follow an energy-gap law behavior with  $\Delta j_1 = 1 > \Delta j_1 = 2 > \Delta j_1 = 3 \dots$

In Table II, we compare, at a total energy of  $100 \text{ cm}^{-1}$ , the cross sections previously obtained by Najar *et al.*<sup>21</sup> and those obtained in this work. The cross sections are reported for a total energy of  $100 \text{ cm}^{-1}$ , avoiding bias by shifted resonances at lower energy.

When comparing results by Najar *et al.*<sup>21</sup> to our data [CC,  $\text{H}_2$  ( $j = 0, 2$ )], differences higher than 30% are generally observed with the exception of cross section values for transitions involving  $\Delta j_1 = 2$ .

Two main causes can be considered for the differences observed: (i) different levels of electronic structure theory were employed to generate the PESs and (ii) Najar *et al.*<sup>21</sup> averaged their PES over the angular motion of the  $\text{H}_2$  molecule, neglecting the anisotropy effects with respect to the  $\text{H}_2$  rotation.

As already discussed above, considering a structure-less  $\text{H}_2$  molecule for scattering calculations of this system leads to

**TABLE II.** Comparison between cross sections previously obtained by Najar *et al.*<sup>21</sup> and those obtained in this work for a total energy of  $100 \text{ cm}^{-1}$ .

$j_1 \rightarrow j_1'$	Najar <i>et al.</i> <sup>21</sup>	This work	
	CC	CC, $\text{H}_2(j = 0, 2)$	CC, $\text{H}_2(j = 0)$
$1 \rightarrow 0$	1.86	2.74	1.24
$2 \rightarrow 0$	6.16	6.16	6.32
$2 \rightarrow 1$	2.69	3.96	1.75
$6 \rightarrow 4$	13.09	12.83	13.68
$10 \rightarrow 8$	33.70	31.15	31.55
$10 \rightarrow 7$	2.29	3.42	1.75
$10 \rightarrow 6$	4.56	3.35	5.69

inaccuracies that can be higher than a factor of 2. In Table II, we also report our cross sections obtained when including only the  $\text{H}_2(j_2 = 0)$  level in the rotational basis set. The comparison of these data with those of Najar *et al.*<sup>21</sup> will probe the direct impact of the two PESs since the two scattering calculations are then equivalent. Differences between 20 and up to more than 50% can be seen in the general case. Again, transitions with  $\Delta j_1 = 2$  present a better agreement with differences lower than 10%.

From this comparison, given the similarity found between the employed electronic structure methods (discussed above), one can conclude that the differences between the two sets of data are primarily due to the effects of the  $\text{H}_2$  rotational structure neglected by Najar *et al.*<sup>21</sup> Therefore, we recommend the use of our new collisional data in astrophysical applications.

## V. CONCLUSIONS

We have computed the first 4D PES for the  $\text{PN}-\text{H}_2$  vdW system at the CCSD(T)-F12b level of theory, together with an extrapolation to the complete basis set limit. The global minimum ( $\Delta E = -224.3 \text{ cm}^{-1}$ ) corresponds to a linear geometry with the  $\text{H}_2$  molecule approaching the N-atom of the PN molecule. The new PES, in addition to accounting for the full  $\text{H}_2$  rotation, is slightly deeper than the one of Najar *et al.*<sup>21</sup> The calculated dissociation energy of the *ortho*- $\text{H}_2$  ( $D_0 = 75.05 \text{ cm}^{-1}$ ) and *para*- $\text{H}_2$  ( $D_0 = 40.19 \text{ cm}^{-1}$ ) complexes was also determined. The PES permits calculation of rovibrational bound states suitable for experimental comparisons.

Scattering calculations were performed using this new high-level PES. The results can be summarized as follows:

- The inelastic cross sections depend significantly on the rotational level of the colliding  $\text{H}_2$  molecule. The cross sections for collisions with *para*- $\text{H}_2$  ( $j_2 = 0$ ) are globally smaller than the ones for collisions with  $\text{H}_2(j_2 = 1)$  even though the differences strongly depend on  $\Delta j_1$  of the rotational transitions.
- For *para*- $\text{H}_2$  collisions, a strong propensity for even  $\Delta j_1$  appears, whereas, for *ortho*- $\text{H}_2$ , cross sections follow an energy-gap law behavior with  $\Delta j_1 = 1 > \Delta j_1 = 2 > \Delta j_1 = 3 \dots$
- We found that obtaining accurate collisional cross sections requires the inclusion of  $\text{H}_2$  closed channels.



These results can be used to improve the modeling of PN abundance in the ISM and, hence, improve our knowledge of phosphorus chemistry in space. This might be a key to understanding the origin of life on Earth. Finally, the present calculations will be extended to higher rotational levels and higher collision energies to better cover the astrophysical needs, especially for the interpretation of observations in warm regions of the ISM.

## SUPPLEMENTARY MATERIAL

A Fortran subroutine of the potential energy surface is available as the [supplementary material](#).

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## DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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