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Ayda Badri, Faouzi Najjar, Cheikh Bop, Nejm-Eddine Jaidane, Majdi Hochlaf. State-to-state inelastic rate coefficients of phosphine in collision with He at low to moderate temperature. *Monthly Notices of the Royal Astronomical Society*, 2020, 499 (2), pp.1578-1586. 10.1093/mnras/staa2611. hal-03078779

**HAL Id: hal-03078779**




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Submitted on 16 Dec 2020

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# State-to-state inelastic rate coefficients of phosphine in collision with He at low to moderate temperature

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Accepted 2020 August 20. Received 2020 August 19; in original form 2020 May 20

## ABSTRACT

Several phosphorus-bearing molecules, such as the phosphine of interest here, have been detected in astrophysical media. With the aim of satisfying the precision required by the astrophysical community, we report the rate coefficients of PH<sub>3</sub> in collision with helium from low to moderate temperature. To this end, we constructed the first three-dimensional potential energy surface (3D-PES) of the PH<sub>3</sub>–He van der Waals complex, which governs the nuclear motions. The 3D-PES was worked out by means of the standard coupled cluster with single, double and non-iterative triple excitation approach, in conjunction with the aug-cc-pVQZ basis set and complemented by mid bond functions. This 3D-PES presents a well of 34.92 cm<sup>-1</sup> at  $\{R, \theta, \Phi\} = \{5.76a_0, 90^\circ, 60^\circ\}$ . Afterwards, we incorporated this 3D-PES into time-independent close-coupling quantum dynamical computations to derive the inelastic cross-sections of rotational excitation of (ortho-) para-PH<sub>3</sub> after collision with He up to (1000) 500 cm<sup>-1</sup>. Subsequently, we evaluated the rate coefficients for temperatures up to (100 K) 50 K populating the (41) 42 low-lying rotational levels of (ortho-) para-PH<sub>3</sub>. These data were derived by averaging the cross-sections thermally over the Maxwell–Boltzmann velocity distribution. No general propensity rules are found. We also performed a comparison with the rates for NH<sub>3</sub>–He. Differences are observed that invalidate the use of NH<sub>3</sub> rates for deducing accurate abundances of phosphine in cold astrophysical media. Our results should be of great help in determining accurate PH<sub>3</sub> abundances and, more generally, constraining the interstellar PH<sub>3</sub> chemistry better.

**Key words:** ISM : abundances – ISM: molecules.

## 1 INTRODUCTION

The second-row elements of the periodic table are present in the interstellar medium (ISM) with relatively low cosmic standards. Among them, phosphorous (known also as a biogenic element) is one of the less abundant. In fact, only one out of the 23 known nuclides of phosphorous is stable (<sup>31</sup>P), with a binding energy of ~8.4 MeV (Maciá 2005). However, its formation throughout thermonuclear fusion requires temperatures above 10<sup>9</sup> K. Indeed, the barrier of electrostatic repulsion among the colliding nuclei related to a nuclear charge of  $Z = 15$  (i.e. <sup>31</sup>P formation) imposes a great amount of energy. These items let us expect that thermonuclear reactions leading to the formation of phosphorous can take place only in the cores of massive stars of size 15–100 M<sub>⊙</sub> (Arnett & Arnett 1996; Maciá 2005). For instance, the early origin of the <sup>31</sup>P isotope occurred towards the inner zone of stars sufficiently massive to undergo successive carbon- and neon-burning at approximately  $T = 3 \times 10^9$  K (Woosley 2002). Once produced in the cores of massive stars, this biogenic element is likely carried towards the ISM by supernova explosions (by the birth of planetary nebulae) in the case of very high-mass stars (of relatively high-mass stars) and stellar

winds. The stable phosphorus thus produced and liberated in the ISM would be ready to react with available atoms, leading to the formation of interstellar P-bearing compounds. Among them, phosphine, PH<sub>3</sub>, of interest in the present work, is expected to be the main reservoir of phosphorous in space. Indeed, PH<sub>3</sub> has been observed in various astronomical environments over these last four decades (Moreno, Marten & Lellouch 2009; Weissstein & Serabyn 1996; Larson 1977; Bregman & Rank 1975). For instance, phosphine was definitely detected in several extraterrestrial environments. In the ISM, it was observed in the circumstellar envelope of the carbon star IRC+10216 (Agúndez et al. 2008; Tenenbaum & Ziurys 2008a). It is supposed to be formed on interstellar grains via successive hydrogenation of atomic phosphorus (Jiménez-Serra et al. 2018) and then desorbs to the gas phase. Phosphine was also identified in the atmospheres of Jupiter and Saturn (Ridgway, Wallace & Smith 1976; Larson et al. 1980). Thanks to the *Herschel* Spectral and Photometric Imaging Receiver (SPIRE), high-resolution far-IR observations of Saturn's atmosphere allowed us to determine the vertical distribution of PH<sub>3</sub>. Moreover, this molecule is most likely present in the atmospheres of brown dwarfs or giant extrasolar planets (Sharp & Burrows 2007). Furthermore, it is connected to the origin of the phosphorus signal in comet 67P/Churyumov–Gerasimenko (Altwegg 2016).

In addition to PH<sub>3</sub>, five other P-containing molecules, namely PN, PO, CP, HCP, CCP and NCCP, have been successfully detected in

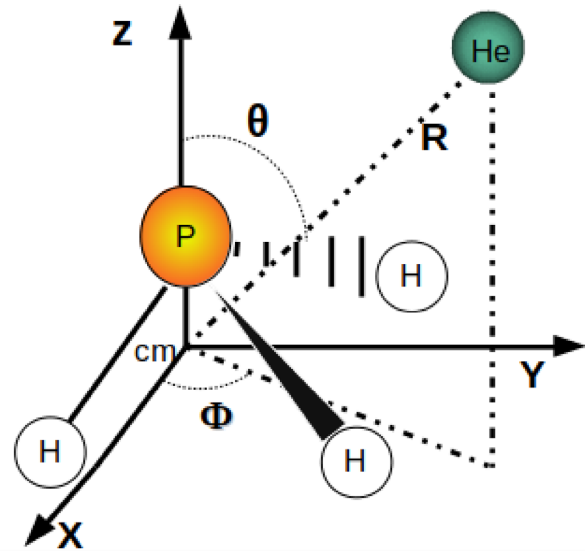
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interstellar and circumstellar regions (Turner & Bally 1987; Ziurys 1987; Guélin et al. 1990; Turner et al. 1990; Agúndez, Cernicharo & Guélin 2007; Halfen, Clouthier & Ziurys 2008; Milam et al. 2008). In terms of abundances,  $\text{PH}_3$  and  $\text{HCP}$ , which are the dominant P-bearers in IRC+10216, hold only 2 (Agúndez et al. 2014) and 5 per cent (Agúndez et al. 2007) of atomic phosphorus, respectively. For other P-bearing compounds, the abundance ratio with respect to P drops to less than 0.001 (e.g.  $\text{PN}/\text{P}$  is about  $5 \times 10^{-4}$ ; Turner et al. 1990). Otherwise, gas-phase molecules in the envelopes of evolved stars lock a greater amount of phosphorus than in IRC+10216. Typically, in the carbon-rich envelope CRL 2668,  $\text{HCP}$  along with  $\text{PH}_3$  holds about half the phosphorus (Milam et al. 2008; Tenenbaum & Ziurys 2008b), while a quarter of almost all the available phosphorus is in the form of  $\text{PN}$  and  $\text{PO}$  towards the oxygen-rich supergiant star VYCMa (Tenenbaum, Woolf & Ziurys 2007; Milam et al. 2008) or towards the star IK Tau (De Beck et al. 2013). These items are in concordance with the hypothesis of Turner et al. (1990), which was based on the weak presence of P-bearers in interstellar clouds, suggesting that phosphorus is depleted in dust grains. Nevertheless, chemical models for identification of the formation pathways of P-bearing molecules in astrophysical media suffer from the lack of accurate abundances for these species to assess the initial elemental abundance of phosphorus, which is connected with the depletion level of P (Chantzios et al. 2020).

For the identification of molecules in astrophysical media, one needs accurate determinations of line positions and abundances. For  $\text{PH}_3$ , while its rotation–vibration spectrum is well-established theoretically and experimentally (Sousa-Silva et al. 2015), its abundance is not. Indeed, its abundance is estimated using the collision rates of isovalent ammonia. Therefore, accurately determining the abundances of phosphine may be a clue to understanding its formation and phosphorus chemistry in space.

In order to satisfy astrophysical precision when modelling the abundance of interstellar species observed in media where local thermodynamic equilibrium (LTE) conditions are not reached, one relies on the large velocity gradient approach (LVG). Such a procedure requires preliminary calculations of rate coefficients induced by collision with the most abundant species ( $\text{H}_2$ , H and He), as well as Einstein coefficients. These latter are often known, while collisional rates are not. In the case of a lack of such data for a newly observed molecule, astrophysicists usually deduce its collisional rates from those of isoelectronic species. Indeed, this approximation has been adopted for some molecules (Barlow et al. 2013; Cernicharo et al. 2018) and its limits were pointed out thereafter (Bop et al. 2016). In the case of phosphine, the approximation made by Agúndez et al. (2014), who used the rate coefficients of  $\text{NH}_3$  (Danby et al. 1988; Machin & Roueff 2005), could be *a priori* more reliable. Nevertheless, this hypothesis deserves to be checked by computing the actual  $\text{PH}_3$  rate coefficients.

In this article, we investigate the rotational (de-)excitation of  $\text{PH}_3$  colliding with He. Even if He is not the dominant collision partner in the ISM, the rate coefficients it yields may be used to evaluate those that would be obtained using para- $\text{H}_2$  ( $j = 0$ ) as a projectile. Indeed, this approximation takes its suitability from the fact that para- $\text{H}_2$  ( $j = 0$ ) is spherically symmetric and contains two valence electrons as helium. In addition, using helium as a projectile may be useful in the experimental framework for the interpretation of measured broadening parameters (Pickett, Poynter & Cohen 1981; Levy, Lacombe & Tarrago 1994; Salem et al. 2005). Therefore, we generated the first 3D potential energy surface (3D-PES) of the  $\text{PH}_3$ –He van der Waals complex using the coupled cluster approach. This 3D-PES is mapped in Jacobi coordinates as defined in Fig. 1. Then



**Figure 1.** Description of the body-fixed coordinate system used in the calculations; cm stands for the centre of the  $\text{PH}_3$  molecule.

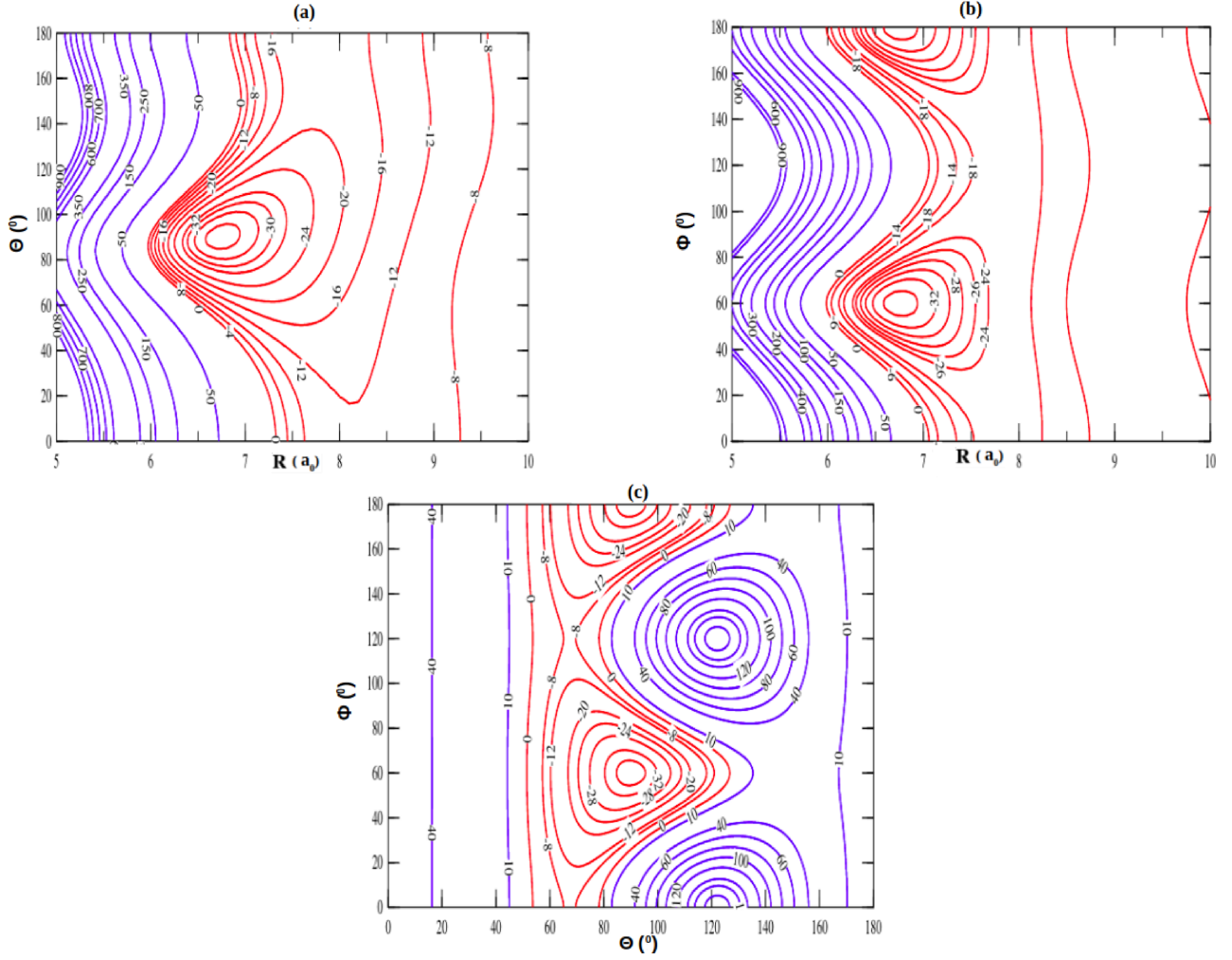
an analytic expansion of the 3D-PES was obtained by fitting the computed energies. Later on, this 3D-PES is incorporated into time-independent quantum nuclear motion treatments to obtain the collision cross-sections and the collision rates after thermal averaging. Both ortho- and para- $\text{PH}_3$  were considered. As said above, the present set of data can be used to estimate the abundances of phosphine better and to model phosphorus chemistry in astrophysical media.

## 2 GENERATION OF THE 3D POTENTIAL ENERGY SURFACE OF $\text{PH}_3$ –HE

### 2.1 Potential energy surface

The system of interest ( $\text{PH}_3$ –He) results from the interaction between a symmetric top molecule and a structureless atom in their ground electronic states,  $\text{PH}_3(\tilde{X}^1A_1)$  and  $\text{He}(^1S)$  respectively. The phosphine monomer was held fixed in its spatial configuration, as recommended by Faure et al. (2005), i.e. using the geometries of the vibrationless state. Typically, the distance between phosphorus (P) and each hydrogen (H) atom was set to  $r_{\text{PH}} = 1.421 \text{ \AA}$  and the angle  $\text{HPH} = 93.3^\circ$  (Herzberg 1966).

Taking into account the relatively large electron number of the titled system, it is desirable to reduce the number of degrees of freedom in the construction of the interaction potential, while keeping its efficiency in yielding accurate dynamic results. For the inelastic scattering of  $\text{NH}_3$  due to He impact, neglecting umbrella inversion motion in the potential construction – as a model treatment – has led to errors in the amplitudes of the resonance peaks of less than 10 per cent relative to those obtained via a more elaborate treatment, where this motion was considered fully in the interacting PES (Gubbels et al. 2012). These errors in the amplitudes are rather small. At first glance, one can omit this motion. Consequently, the complex can be described in the  $\text{PH}_3$  body-fixed (Jacobi) coordinate system using three parameters: (i) the distance ( $R$ ) between mass of phosphine, (ii) the angle ( $\theta$ ), which stands for the rotation of He relative to the  $z$ -axis, and (iii) the rotation of  $\text{PH}_3$  ( $\Phi$ ) with respect to the projection of the collision axis on the  $xy$ -plane (see Fig. 1). Therefore, the 3D-PES was constructed using 42 values of  $R$  ranging from 4 to  $40a_0$ , 19 He orientations



**Figure 2.** Two-dimensional contour plots of the three-dimensional potential energy surface of the  $\text{PH}_3$ –He van der Waals complex. Panels (a), (b) and (c) depict respectively the 3D-PES as a function of  $\theta$  and  $R$  at  $\Phi = 60^\circ$ ,  $\Phi$  and  $R$  at  $\theta = 90^\circ$ , and  $\theta$  and  $\Phi$  at  $R = 6.75 a_0$ . For each panel, the blue (red) contours represent the positive (negative) parts of the potential (in units of  $\text{cm}^{-1}$ ). The reference energy is taken as that of the separated monomers.

( $0^\circ \leq \theta \leq 180^\circ$ ) and seven  $\Phi$  angles in the range  $[0-60^\circ]$ . All these parameters have led to a set of 5586 non-redundant nuclear configurations for which we performed *ab initio* electronic structure computations using the MOLPRO molecular package (Werner et al. 2010). Also, we used symmetry considerations to deduce the energies of the nuclear geometries not covered by our grid of points.

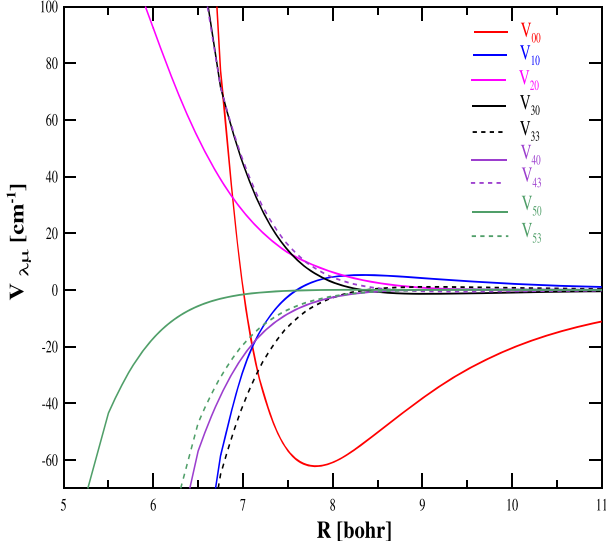
The 3D-PES was calculated using the coupled cluster with single, double and non-iterative triple excitations (CCSD(T)) method (Watts, Gauss & Bartlett 1993) in conjunction with the augmented-consistent correlation-polarized valence triple zeta (aug-cc-pVQZ) Gaussian basis sets of Dunning and co-workers (Dunning 1989), supplemented by the bond functions (bf) of Cybulski & Toczyłowski (1999). These latter (3s3p2d2f1g) were placed at mid-distance between the two monomers. This level of theory will be denoted thereafter as CCSD(T)/aug-cc-pVQZ+bf. In addition, we used the counterpoise procedure of Boys & Bernardi (1970) to correct for the basis set superposition errors (BSSE) using the following expression:

$$V(R, \theta, \Phi) = E_{\text{PH}_3-\text{He}}(R, \theta, \Phi) - E_{\text{PH}_3}(R, \theta, \Phi) - E_{\text{He}}(R, \theta, \Phi). \quad (1)$$

The accuracy of the interaction potentials generated using the methodology elaborated above has been assessed in our previous works (Najar et al. 2017; El Hanini et al. 2019).

We display in Fig. 2 the two-dimensional cuts of the 3D-PES of the  $\text{PH}_3$ –He weakly bound system as a function of two Jacobi coordinates, whereas the third one was kept fixed at its equilibrium value in the  $\text{PH}_3$ –He minimum. Indeed, we give the 3D-PES as a function of  $\theta$  and  $R$  at  $\Phi = 60^\circ$ ,  $\Phi$  and  $R$  at  $\theta = 90^\circ$  and  $\theta$  and  $\Phi$  for  $R = 6.75$  bohr. The positive parts of the 3D-PES are in blue and the negative ones are in red, where the reference energy is taken as that of the separated  $\text{PH}_3$  and He species. In terms of anisotropy, the interaction between helium and phosphine exhibits a relatively strong anisotropy.

Fig. 2 shows that the 3D-PES has a unique potential well of  $34.92 \text{ cm}^{-1}$ , which occurs at  $\theta = 90^\circ$ ,  $\Phi = 60^\circ$  and  $R = 6.75$  bohr. This minimum is found at the same coordinates in Fig. 2(a) and (b), where the 2D cuts are periodical with a period of  $120^\circ$  relative to the  $\Phi$ -axis, as expected for this  $C_{3v}$  symmetry molecule. Minimal energy configurations thus correspond to an He atom located between two H atoms and in the plane parallel to that formed by the three H atoms, whereas maxima of the potential occur where the He is in the plane containing the P, H bond and  $C_3$  axis.



**Figure 3.** Dependence of selected radial coefficients (in units of  $\text{cm}^{-1}$ ) with respect to  $R$ .

## 2.2 Analytic fit

In order to derive the radial coefficients  $V_{\lambda\mu}(R)$  required for the dynamical calculations, we expanded the 3D-PES of  $\text{PH}_3\text{-He}$  over the normalized spherical harmonic functions  $Y_{\lambda\mu}(\theta, \Phi)$  as follows:

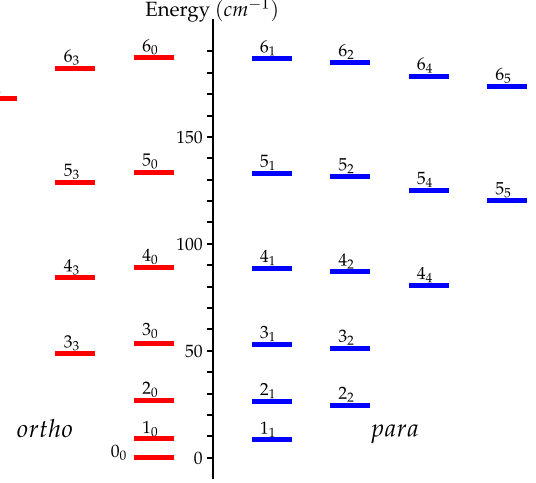
$$V(R, \theta, \Phi) = \sum_{\lambda\mu} V_{\lambda\mu}(R) Y_{\lambda\mu}(\theta, \Phi). \quad (2)$$

Due to the  $C_{3v}$  symmetry of the phosphine molecule, only radial terms for which  $\mu = 3n$  ( $n$  being integer) are involved in the expansion (equation 2); the others are vanishing. Therefore, using the cubic spline routine, 70 radial coefficients ( $0 \leq \lambda \leq 18$  and  $0 \leq \mu \leq 18$ ) were needed to reproduce the *ab initio* potential reasonably within relative errors less than 5 per cent.

Fig. 3 depicts the variation of some radial coefficients ( $V_{00}$ ,  $V_{10}$ ,  $V_{20}$ ,  $V_{30}$ ,  $V_{33}$ ,  $V_{40}$  and  $V_{43}$ ) along the  $R$  Jacobi coordinate. The  $V_{00}$ ,  $V_{20}$ ,  $V_{30}$  and  $V_{43}$  terms have upward concavities, while the others are oriented downward. A close examination of this figure reveals that, for  $\mu = 0$ , the term related to  $\lambda = 3$  outweighs the others with respect to the isotropic radial coefficient, namely  $V_{00}$ . This is also the case for  $\mu = 3$  and  $\lambda = 4$ . Therefore, no clear predominance pattern can be associated with the index pair  $\lambda\mu$ . This lack of well-defined propensity scheme will have consequences on the behaviour of cross-sections. The radial coefficients derived from the  $\text{NH}_3\text{-He}$  interacting potential show similar patterns, except for the terms involving  $\mu = 3$  (Gubbels et al. 2012). Typically, the terms  $V_{33}$  and  $V_{43}$  are oriented downward and upward (upward and downward) for  $\text{PH}_3\text{-He}$  ( $\text{NH}_3\text{-He}$ ), respectively (i.e. they even present differences in sign at short range, as can be seen by comparison with fig. 3 of Gubbels et al. 2012).

## 3 DYNAMICAL CALCULATIONS

In this work, we are interested in the study of the rotational energy transfer of  $\text{PH}_3$  after collision with He.  $\text{PH}_3$  is a symmetric top rotor type molecule. Usually,  $j_k^\epsilon$  is used to label the energy levels of such molecules, where the quantum number  $j$  stands for the total angular momentum and  $k$  its projection over the  $C_3$  axis, while  $\epsilon = \pm$  denotes the symmetry index. For a given rotational energy level, the parity of the rotation-inversion wavefunction and



**Figure 4.** Diagram of the  $\text{PH}_3$  rotational energy levels ( $E_{jk}$ ). The energies are labelled as  $j_k$ . See text for the definition of these two quantum numbers. Their energies are given in Tables S1 and S2 in the Supplementary Material.

**Table 1.** Parameters used in the dynamical calculations to solve the coupled equations by means of the log derivative propagator. DTOL and OTOL stand for diagonal tolerance and off-diagonal tolerance, respectively.

|                                |                               |
|--------------------------------|-------------------------------|
| ortho: $j_k^\epsilon = 16_1^0$ | para: $j_k^\epsilon = 14_1^0$ |
| $R_{\min} = 3a_0$              | $R_{\max} = 35a_0$            |
| STEPS = 10–200                 | $\mu = 3.581 \text{ au}$      |
| DTOL = $0.01 \text{ \AA}^2$    | OTOL = $0.005 \text{ \AA}^2$  |

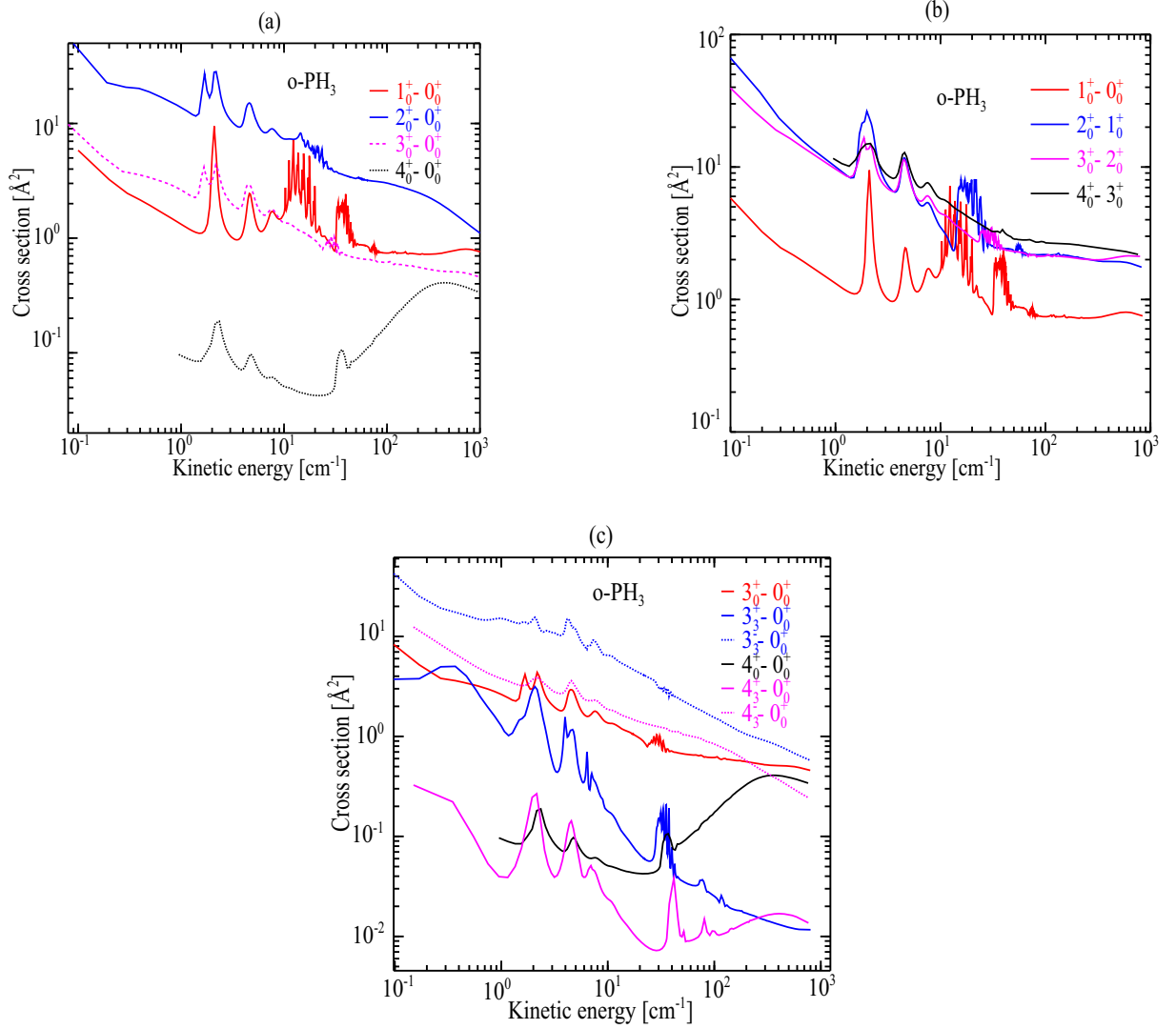
the symmetry of the umbrella inversion are  $(-1)^{j+k+1}\epsilon$  and  $(-1)^{j+1}\epsilon$ , respectively (Rist, Alexander & Valiron 1993). Due to the  $C_{3v}$  symmetry of the  $\text{PH}_3$  molecule, the three hydrogen atoms of phosphine are identical in terms of spatial configuration. Thus, the rotational levels are split into ortho- $\text{PH}_3$  (o- $\text{PH}_3$ ) and para- $\text{PH}_3$  (p- $\text{PH}_3$ ), which stand for  $k = 3n$  and  $k \neq 3n$  ( $n$  being integer), respectively. As  $k$  can take any value except multiples of 3, the p- $\text{PH}_3$  rotational energy levels are denser than the o- $\text{PH}_3$  ones (see Fig. 4). These energy levels can be calculated using the spectroscopic constants  $A = B = 4.4524 \text{ cm}^{-1}$  and  $C = 3.919 \text{ cm}^{-1}$  by means of equation (3), where  $\hbar^2/2I_x = X$  (Stroup, Oetjen & Bell 1953):

$$E_{jk} = \frac{\hbar^2}{2I_b} j(j+1) + \left( \frac{\hbar^2}{2I_c} - \frac{\hbar^2}{2I_b} \right) k^2. \quad (3)$$

As the conversion o- $\text{PH}_3$  to p- $\text{PH}_3$  (and vice versa) is forbidden, the ortho and para scattering channels are treated separately in the cross-section computations.

### 3.1 Cross-sections

The quantum nuclear treatment detailed in this section was performed with the MOLSCAT computer code (Hutson & Green 1994) using the time-independent close coupling method (Arthurs & Dalgarno 1960), along with the log derivative propagator (Manolopoulos 1986). Preliminary tests were done in order to fix the parameters of the propagator (see Table 1), such as the integration boundaries ( $R_{\min}$  and  $R_{\max}$ ), the size of the rotational basis ( $j_{\max}$  and  $k_{\max}$ ) and the integration step, which depends on the variable STEPS. These optimized values have been selected within a convergence threshold of 1.0 per cent  $\text{\AA}^2$ . Thereafter, the total energy ( $E$ ) was smoothly



**Figure 5.** Inelastic cross-sections of  $o\text{-PH}_3$ , induced by collision with He, versus the kinetic energy; panels (a), (b) and (c) are for de-excitations involving selected low-lying rotational levels.

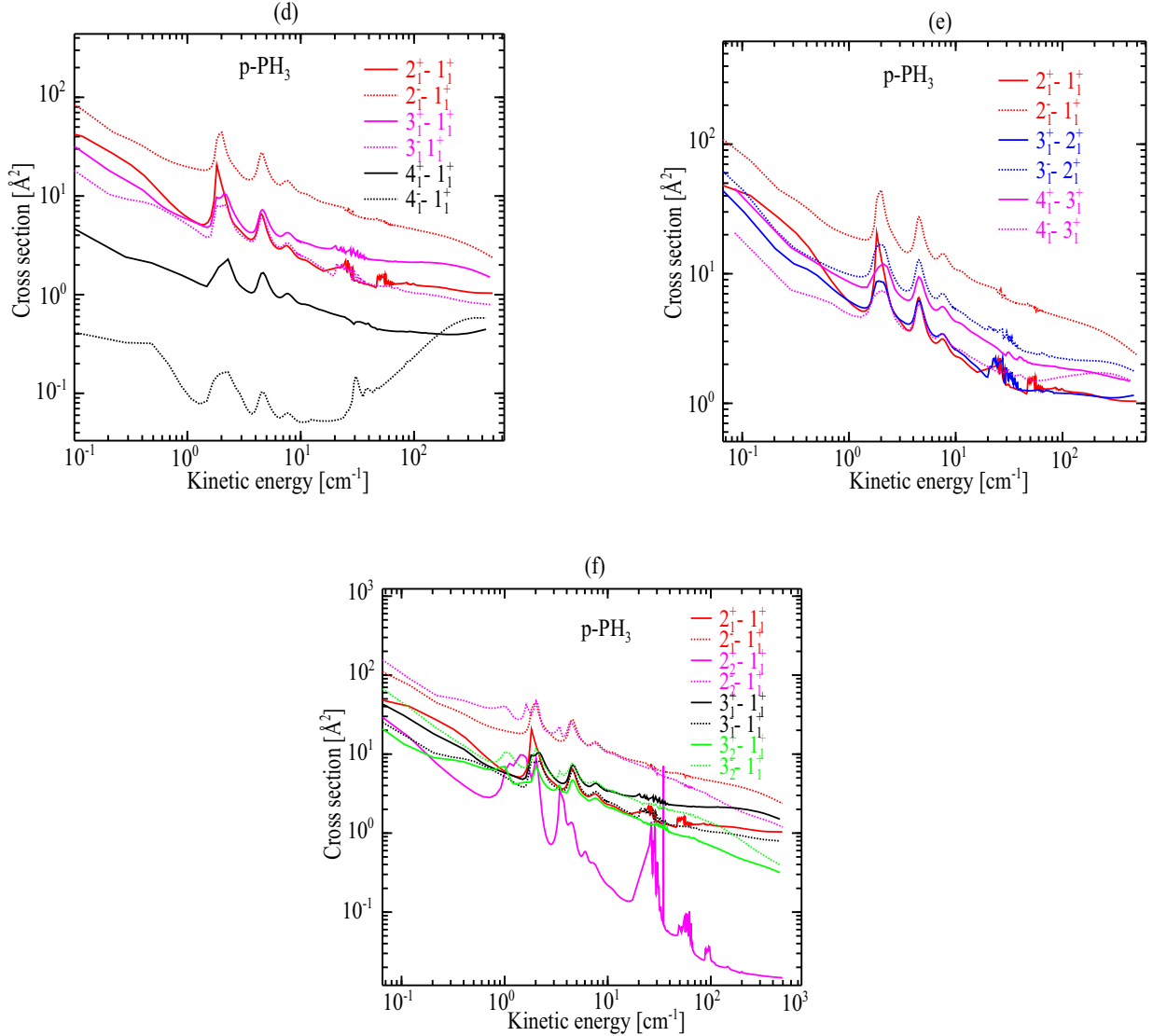
varied from  $9\text{--}1000\text{ cm}^{-1}$  ( $8.4\text{--}500\text{ cm}^{-1}$ ) for the scattering of  $o\text{-PH}_3$  ( $p\text{-PH}_3$ ). In order to converge cross-sections properly, we take all open channels into account by adding some closed channels for both ortho and para. The convergence tests showed that a rotational basis set including 97 levels for  $o\text{-PH}_3$  is large enough. The 97th level corresponds to  $j_{\text{max}} = 16$ . For  $p\text{-PH}_3$ , we considered a basis set of 152 levels, corresponding to  $j_{\text{max}} = 14$ .

Fig. 5 displays the variation of cross-sections for  $o\text{-PH}_3$  with respect to the kinetic energy. Fig. 5(a) depicts the  $j_0^+ \rightarrow 0_0^+$  transitions, Fig. 5(b) represents the transitions for which  $\{\Delta j, k, \epsilon\} = \{1, 0, +\}$  and Fig. 5(c) shows the  $j_k^\epsilon \rightarrow 0_0^+$  transitions. All these curves, except those associated with the  $4_0^+ \rightarrow 0_0^+$  and  $4_1^- \rightarrow 1_1^+$  transitions, are decreasing while increasing the kinetic energy. Below  $100\text{ cm}^{-1}$ , these cross-sections present both Feshbach and shape resonances. Such features were expected, as they were found in previous works, such as the one treating the collisional excitation of  $\text{NH}_3$  by atomic and molecular hydrogen (Bouhafs et al. 2017) and that investigating the collisions between  $\text{NH}_3$  and He (Machin & Roueff 2005). In fact, quasi-bound states occur when the He projectile is caught in the potential well, leading to Feshbach resonances. Regarding the shape resonances, they manifest

when tunnelling effects via the centrifugal energy barrier take place, forming quasi-bound states.

### 3.1.1 $o\text{-PH}_3$

Fig. 5(a) shows that the cross-sections of the  $2_0^+ \rightarrow 0_0^+$  and  $4_0^+ \rightarrow 0_0^+$  transitions are the strongest and weakest ones, respectively, in terms of magnitude, while an inversion occurs between the  $1_0^+ \rightarrow 0_0^+$  and  $3_0^+ \rightarrow 0_0^+$  transition cross-sections. Therefore, no selection rules can be associated with the parity of  $j$ . From Fig. 5(a) and (b), one can see that the magnitude of resonances decreases when  $j$  increases. Fig. 5(c) shows that the cross-sections of the  $3_3^- \rightarrow 0_0^+$  ( $4_3^- \rightarrow 0_0^+$ ) and  $3_3^- \rightarrow 0_0^+$  ( $4_3^- \rightarrow 0_0^+$ ) transitions are from either side of the  $3_0^+ \rightarrow 0_0^+$  ( $4_0^+ \rightarrow 0_0^+$ ) transition. Referring to each  $j_0^+ \rightarrow 0_0^+$ , the cross-sections of the  $j_3^- \rightarrow 0_0^+$  transitions are lifted, while those of the  $j_3^+ \rightarrow 0_0^+$  ones are shifted downward. Therefore, the propensity rule is in favour of symmetry (or parity) breaking, i.e.  $\Delta k = 3$  and  $j \rightarrow 0$ . In addition, each cross-section for the  $j_0^+ \rightarrow 0_0^+$  transition takes the shape of that of the  $j_3^- \rightarrow 0_0^+$  transition at low kinetic energy and then switches progressively to that of  $j_3^+ \rightarrow 0_0^+$ .



**Figure 6.** Inelastic cross-sections of p-PH<sub>3</sub> induced by collision with He versus kinetic energy; panels (a), (b) and (c) are for de-excitations involving selected low-lying rotational levels.

### 3.1.2 *p*-PH<sub>3</sub>

Fig. 6 displays the variation of cross-sections for p-PH<sub>3</sub> with respect to the kinetic energy. Fig. 6(a) shows that the magnitude of cross-sections decreases when  $j$  increases for the  $j_1^- \rightarrow 1_1^+$  transitions, while for the  $j_1^+ \rightarrow 1_1^+$  transitions no net dominance is observed. In Fig. 6(b), all cross-sections have almost the same shape, whatever the transition, with typically the same location of resonance peaks. Regarding the magnitudes, the transitions involving negative parities are stronger than the corresponding ones with positive parities, except for  $j = 4$ . For instance, the cross-section of  $2_1^- \rightarrow 1_1^+$  ( $4_1^+ \rightarrow 3_1^+$ ) transition outweighs that of  $2_1^+ \rightarrow 1_1^+$  ( $4_1^- \rightarrow 3_1^+$ ). Thus, one can state the predominance of parity breaking;  $\Delta k = 0$  and  $\Delta j = 1$  is lifted for higher  $j$  values. Fig. 6(c) is an extension of Fig. 6(b) to show the effect of the change of  $\Delta k$ . The previously highlighted behaviour persists, but for fixed  $j$  and  $\epsilon$ . The slight dominance of  $k = 2$  occurs only at low kinetic energy, then it reverses at higher energies (e.g. the  $2_1^- \rightarrow 1_1^+$  and  $2_2^- \rightarrow 1_1^+$  transitions).

In summary, we can conclude that no general propensity rule can be associated with the indexes  $j, k, \epsilon$ , in line with the already noticed behaviours of the radial coefficients (see Fig. 3).

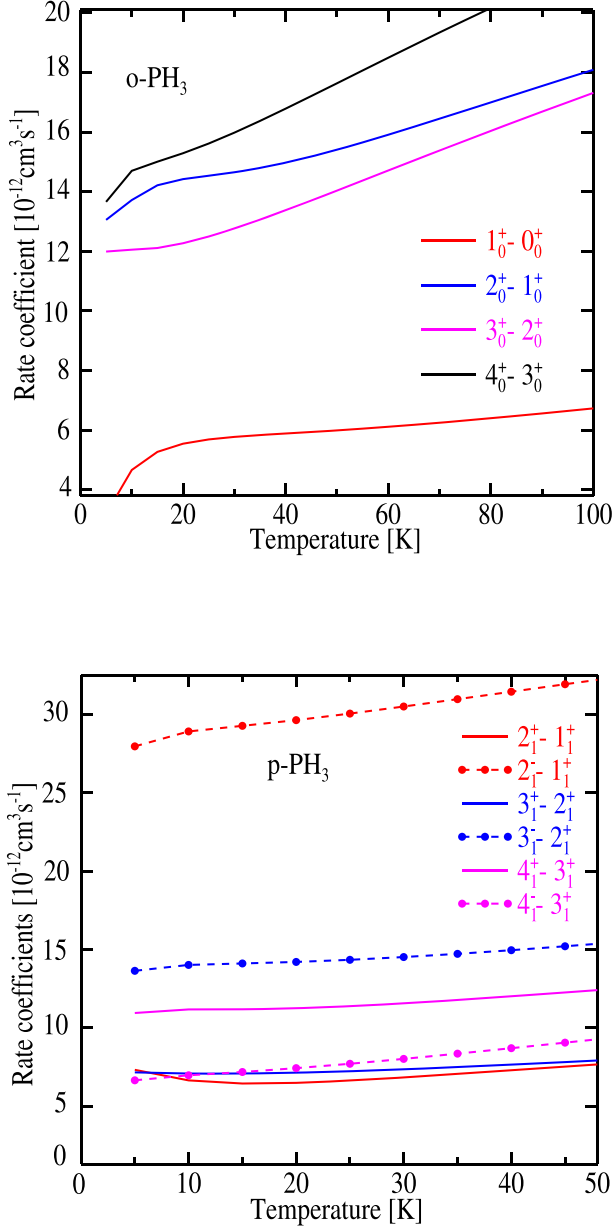
### 3.2 Rate coefficients

In order to deduce the rotational rate coefficients ( $R_{jk\epsilon \rightarrow j'k'\epsilon'}$ ) of both o-PH<sub>3</sub> and p-PH<sub>3</sub>, we averaged the cross-sections discussed above thermally using the Maxwell–Boltzmann velocity distribution:

$$R_{\alpha \rightarrow \alpha'}(T) = \left( \frac{8}{\pi \mu \beta} \right)^{1/2} \beta^2 \int_0^\infty E_c \sigma_{\alpha \rightarrow \alpha'}(E_c) e^{-\beta E_c} dE_c, \quad (4)$$

where the kinetic energy is denoted by  $E_c$ ,  $\beta$  stands for the reverse of  $(k_B \times T)$ , with  $k_B$  being the constant of Boltzmann, and  $\alpha$  refers to  $jk\epsilon$ .

The cross-sections of ortho-PH<sub>3</sub> covering the range 9–1000 cm<sup>-1</sup> allow us to generate the velocity coefficient for the transitions



**Figure 7.** Downward rotational rate coefficients of o-PH<sub>3</sub> (top panel) and p-PH<sub>3</sub> (bottom panel) induced by collision with He, as a function of the kinetic temperature.

between the 41 low-lying rotational levels [up to  $j_k = 10_0$ ] for temperatures up to 100 K. Similarly, the cross-sections of para-PH<sub>3</sub> covering the range 8.4–500 cm<sup>-1</sup> allow us to generate the velocity coefficient for the transitions between the 41 low-lying rotational levels [up to  $j_k = 7_1$ ] for temperatures up to 50 K.

Fig. 7 displays the variation of rate coefficients for the rotational excitation of o-PH<sub>3</sub> and p-PH<sub>3</sub> due to collisions with He as a function of the kinetic temperature. We represented only a few curves, as the patterns observed for the cross-sections persist here, whereas the full set of data is given in the Supplementary Material. Typically, for o-PH<sub>3</sub>, the top panel of Fig. 7 reproduces the behaviour observed in Fig. 5(b). The main difference consists of the dominance of the  $4_0^+ \rightarrow 3_0^+$  transition, which occurs for the whole temperature range, and no inversion is observed among the  $2_0^+ \rightarrow 1_0^+$  and  $3_0^+ \rightarrow 2_0^+$  transitions. Regarding p-PH<sub>3</sub>, the bottom panel of Fig. 7 confirms

**Table 2.** Comparison of PH<sub>3</sub> (this work) and NH<sub>3</sub> (Machin & Roueff 2005) rotational rate coefficients (in units of cm<sup>3</sup> s<sup>-1</sup>) at selected temperatures. The brackets stand for negative powers of ten.

| Initial levels |     |            | Final levels |      |             | $T = 50$ K        |                   | $T = 100$ K       |                   |
|----------------|-----|------------|--------------|------|-------------|-------------------|-------------------|-------------------|-------------------|
| $j$            | $k$ | $\epsilon$ | $j'$         | $k'$ | $\epsilon'$ | o-PH <sub>3</sub> | o-NH <sub>3</sub> | o-PH <sub>3</sub> | o-NH <sub>3</sub> |
| 1              | 0   | +          | 0            | 0    | +           | 5.99(12)          | 2.72(12)          | 6.73(12)          | 4.65(12)          |
| 2              | 0   | +          | 0            | 0    | +           | 2.09(11)          | 1.37(11)          | 2.34(11)          | 1.72(11)          |
| 2              | 0   | +          | 1            | 0    | +           | 1.54(11)          | 0.59(11)          | 1.81(11)          | 0.88(11)          |
| 3              | 3   | -          | 0            | 0    | +           | 1.43(11)          | 1.19(11)          | 1.34(11)          | 1.45(11)          |
| 3              | 3   | -          | 2            | 0    | +           | 3.20(11)          | 1.61(11)          | 3.21(11)          | 2.36(11)          |
| 3              | 3   | +          | 0            | 0    | +           | 3.70(13)          | 0.11(13)          | 2.80(13)          | 0.14(13)          |
| 3              | 3   | +          | 2            | 0    | +           | 2.24(11)          | 0.23(11)          | 2.15(11)          | 0.45(11)          |
| 4              | 0   | +          | 3            | 0    | +           | 1.76(11)          | 0.66(11)          | 2.17(11)          | 0.98(11)          |
| 4              | 0   | +          | 0            | 0    | +           | 6.82(13)          | 1.76(13)          | 1.66(12)          | 3.61(13)          |
| 4              | 3   | +          | 0            | 0    | +           | 7.40(14)          | 1.51(14)          | 1.00(13)          | 0.25(13)          |

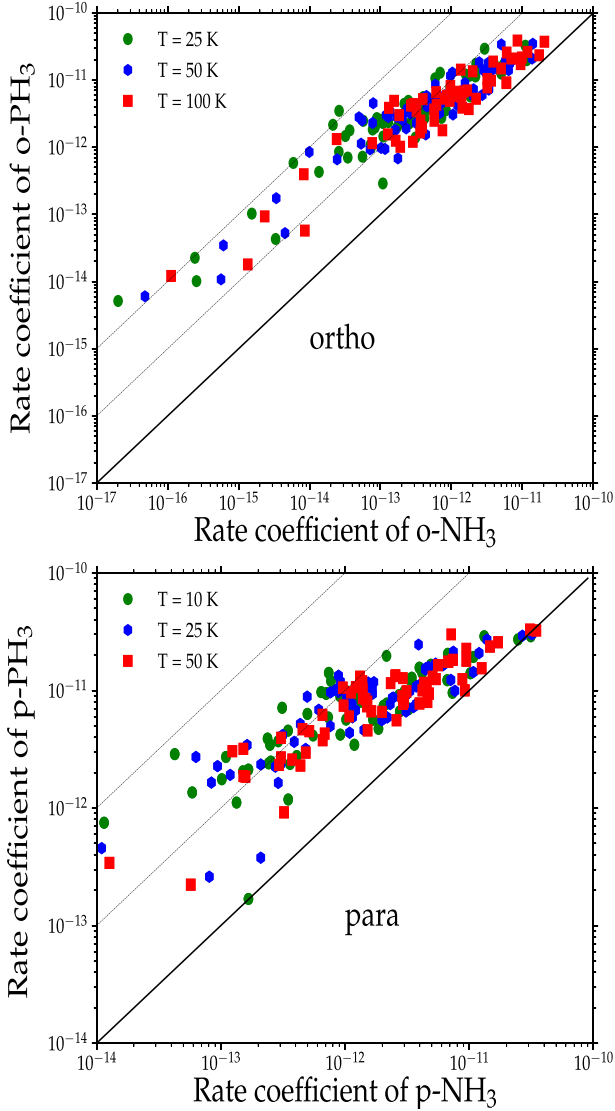
  

|     |     |            |      |      |             | $T = 25$ K        |                   | $T = 50$ K        |                   |
|-----|-----|------------|------|------|-------------|-------------------|-------------------|-------------------|-------------------|
| $j$ | $k$ | $\epsilon$ | $j'$ | $k'$ | $\epsilon'$ | p-PH <sub>3</sub> | p-NH <sub>3</sub> | p-PH <sub>3</sub> | p-NH <sub>3</sub> |
| 2   | 2   | +          | 1    | 1    | +           | 2.61(13)          | 0.81(13)          | 2.23(13)          | 0.54(13)          |
| 2   | 2   | -          | 1    | 1    | +           | 2.70(11)          | 1.39(11)          | 2.57(11)          | 1.70(11)          |
| 2   | 1   | +          | 1    | 1    | +           | 6.63(12)          | 3.10(12)          | 7.76(12)          | 3.98(12)          |
| 2   | 1   | -          | 1    | 1    | +           | 3.01(11)          | 3.20(11)          | 3.24(11)          | 3.47(11)          |
| 3   | 2   | +          | 1    | 1    | +           | 5.60(12)          | 1.98(12)          | 5.58(12)          | 2.60(12)          |
| 3   | 2   | -          | 1    | 1    | +           | 9.75(12)          | 0.19(12)          | 1.02(11)          | 0.14(11)          |
| 3   | 1   | +          | 2    | 1    | +           | 7.23(12)          | 3.56(12)          | 7.98(12)          | 4.61(12)          |
| 3   | 1   | -          | 2    | 1    | +           | 1.43(11)          | 1.08(11)          | 1.55(11)          | 1.26(11)          |
| 4   | 1   | +          | 3    | 1    | +           | 1.14(11)          | 0.41(11)          | 1.25(11)          | 0.54(11)          |
| 4   | 1   | -          | 3    | 1    | +           | 7.71(12)          | 3.77(12)          | 9.41(12)          | 0.52(12)          |

the dominance in favour of the de-excitations for which the parity is broken,  $\Delta k = 0$  and  $j \leq 3 \rightarrow j'$ , as can be seen in panel (e) of Fig. 5.

It is worth noting that the rate coefficients of NH<sub>3</sub> induced by collisions with helium (Machin & Roueff 2005), supplemented by those due to para-H<sub>2</sub> impact (Rist et al. 1993), were used to model the PH<sub>3</sub> abundance in astrophysical media. In this realm, comparing our data on PH<sub>3</sub>-He with those of Machin & Roueff (2005) on NH<sub>3</sub>-He is a clue to settle the validity of using rate coefficients of isoelectronic molecules instead. For this purpose, Table 2 compares the PH<sub>3</sub> rate coefficients computed in this work with those of NH<sub>3</sub> (Machin & Roueff 2005). This table shows that large differences between both sets of data are observed for both ortho and para, especially for  $j \geq 3$ . For  $\Delta j = 1$  (as in the observed transitions,  $1_0^+ \rightarrow 0_0^+$ ,  $2_0^+ \rightarrow 1_0^+$  and  $2_1^\epsilon \rightarrow 1_1^\epsilon$ ), we noticed agreement within a factor of  $\sim 2.5$ . In order to have a global view of the comparison, in Fig. 8 we plot the rate coefficients of PH<sub>3</sub> as a function of those of NH<sub>3</sub>. For both ortho and para, the data reported by Machin & Roueff (2005) are smaller than the values computed in this work. At low temperature, the rate coefficients of NH<sub>3</sub> can drop down to a factor of two orders of magnitude lower than those of PH<sub>3</sub>. This discrepancy decreases as the temperature increases, which suggests a better agreement at higher temperatures ( $T \geq 300$ ). Although PH<sub>3</sub> is observed in a relatively hot environment (e.g. the carbon star envelopes IRC+10216 and CRL2688), using the rate coefficients of NH<sub>3</sub> to model its abundance will lead to an underestimation of its density. Consequently, this may lead to misunderstandings in phosphorous chemistry, as phosphine is likely one of the main phosphorous reservoirs in space. Otherwise, the observed lines suggest that phosphine can be formed anywhere in a disc of radius  $100R_*$  around the centre of the star (Agúndez et al. 2014). Hence, PH<sub>3</sub> can eventually be observed in warm/cold media, where the use of NH<sub>3</sub> rate coefficients would yield underestimation of the abundance of phosphine by a factor larger than one order of magnitude. Consequently, the present data should be used, rather than those of NH<sub>3</sub>, for more reliable determination of the PH<sub>3</sub> abundances in space.





**Figure 8.** Comparison of the  $\text{PH}_3$  rate coefficients (in  $\text{cm}^3\text{s}^{-1}$ ) with those of  $\text{NH}_3$ . With respect to the diagonal, the first dashed line represents a factor of one order of magnitude and the second dashed line stands for a factor of two orders of magnitude.

#### 4 CONCLUSION

We carried out the construction of a highly accurate 3D-PES for the  $\text{PH}_3\text{-He}$  interacting system. This 3D-PES was mapped in Jacobi coordinates and computed at the CCSD(T)/aug-cc-pVQZ+bf level of theory. The interaction among helium and phosphine is quite anisotropic and presents one single potential well of  $34.92\text{ cm}^{-1}$  at  $R = 6.75\text{ bohr}$ ,  $\theta = 90^\circ$  for  $\Phi = 60^\circ$  and  $\Phi = 180^\circ$ . Then, an analytical expansion of this 3D-PES was derived. These electronic structure computations were followed by computations of state-to-state inelastic cross-sections of rotational (de-)excitation of ortho- and para-phosphine, induced by collision with helium. This is done using a quantum mechanical treatment, by means of the close-coupling approach. These data were then thermally averaged according to the Maxwell-Boltzmann kinetic energy distribution, leading to record rate coefficients up to (100 K) 50 K for the (41) 42 low-lying rotational levels of (o- $\text{PH}_3$ ) p- $\text{PH}_3$ . No general propensity rules are found for either p- $\text{PH}_3$  or o- $\text{PH}_3$ .

The rate coefficients computed in this work were compared with those of Machin & Roueff (2005) for the  $\text{NH}_3\text{-He}$  system, which is used to estimate the abundances of phosphine. Large differences are noticed, especially at low temperatures. Therefore, the results obtained in this work may be of great help to the astrophysical community, in order to model the physical conditions of media where phosphine was observed. Indeed, exact knowledge of the  $\text{PH}_3$  abundance may be a clue to constrain the chemistry of interstellar phosphorus. In addition, the present data may help in the identification of  $\text{PH}_3$  in astrophysical media where other P-containing molecules were detected, e.g. in massive dense cores (Fontani et al. 2016) or the Galactic Centre (Rivilla et al. 2018).

#### ACKNOWLEDGEMENTS

The authors acknowledge the Programme National ‘Physique et Chimie du Milieu Interstellaire’ (PCMI) of Centre National de la Recherche Scientifique (CNRS).

#### DATA AVAILABILITY

Collision rates are available in the Supplementary Material. The strongest inelastic transitions are of the order of  $10^{-11}$ ; we considered as significant only values of rates that are greater than  $1 \times 10^{-14}$ . Values that are less than  $1 \times 10^{-14}$  are considered significantly zero.

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## SUPPORTING INFORMATION

Supplementary data are available at *MNRAS* online.

**Table S1:** Rotational levels of ortho-PH<sub>3</sub>.

**Table S2:** Rotational levels of para-PH<sub>3</sub>.

**Table S3:** Rate coefficients (in units of cm<sup>3</sup> s<sup>-1</sup>, given as  $A(B) = A \times 10^{-B}$ ) of ortho-PH<sub>3</sub> induced by collision with He as a function of the kinetic temperature, where (II), IF corresponds to (Initial), Final–Index).

**Table S4:** Rate coefficients (in units of cm<sup>3</sup> s<sup>-1</sup>, given as  $A(B) = A \times 10^{-B}$ ) of ortho-PH<sub>3</sub> induced by collision with He as a function of the kinetic temperature, where (II), IF corresponds to (Initial), Final–Index).

**Table S5:** Rate coefficients (in units of cm<sup>3</sup> s<sup>-1</sup>, given as  $A(B) = A \times 10^{-B}$ ) of para-PH<sub>3</sub> induced by collision with He as a function of the kinetic temperature, where (II), IF corresponds to (Initial), Final–Index).

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# List of astronomical key words (Updated on 2020 January)

This list is common to *Monthly Notices of the Royal Astronomical Society*, *Astronomy and Astrophysics*, and *The Astrophysical Journal*. In order to ease the search, the key words are subdivided into broad categories. No more than *six* subcategories altogether should be listed for a paper.

The subcategories in boldface containing the word ‘individual’ are intended for use with specific astronomical objects; these should never be used alone, but always in combination with the most common names for the astronomical objects in question. Note that each object counts as one subcategory within the allowed limit of six.

The parts of the key words in italics are for reference only and should be omitted when the keywords are entered on the manuscript.

## **General**

editorials, notices  
errata, addenda  
extraterrestrial intelligence  
history and philosophy of astronomy  
miscellaneous  
obituaries, biographies  
publications, bibliography  
sociology of astronomy  
standards

## **Physical data and processes**

acceleration of particles  
accretion, accretion discs  
asteroseismology  
astrobiology  
astrochemistry  
astroparticle physics  
atomic data  
atomic processes  
black hole physics  
chaos  
conduction  
convection  
dense matter  
diffusion  
dynamo  
elementary particles  
equation of state  
gravitation  
gravitational lensing: micro  
gravitational lensing: strong  
gravitational lensing: weak  
gravitational waves  
hydrodynamics  
instabilities  
line: formation  
line: identification  
line: profiles  
magnetic fields  
magnetic reconnection  
(*magnetohydrodynamics*) MHD  
masers  
molecular data  
molecular processes  
neutrinos  
nuclear reactions, nucleosynthesis, abundances  
opacity  
plasmas  
polarization

radiation: dynamics  
radiation mechanisms: general  
radiation mechanisms: non-thermal  
radiation mechanisms: thermal  
radiative transfer  
relativistic processes  
scattering  
shock waves  
solid state: refractory  
solid state: volatile  
turbulence  
waves

## **Astronomical instrumentation, methods and techniques**

atmospheric effects  
balloons  
instrumentation: adaptive optics  
instrumentation: detectors  
instrumentation: high angular resolution  
instrumentation: interferometers  
instrumentation: miscellaneous  
instrumentation: photometers  
instrumentation: polarimeters  
instrumentation: spectrographs  
light pollution  
methods: analytical  
methods: data analysis  
methods: laboratory: atomic  
methods: laboratory: molecular  
methods: laboratory: solid state  
methods: miscellaneous  
methods: numerical  
methods: observational  
methods: statistical  
site testing  
space vehicles  
space vehicles: instruments  
techniques: high angular resolution  
techniques: image processing  
techniques: imaging spectroscopy  
techniques: interferometric  
techniques: miscellaneous  
techniques: photometric  
techniques: polarimetric  
techniques: radar astronomy  
techniques: radial velocities  
techniques: spectroscopic  
telescopes

## **Astronomical data bases**

astronomical data bases: miscellaneous  
atlases  
catalogues  
surveys  
virtual observatory tools

## **Software**

software: data analysis  
software: development  
software: documentation  
software: public release  
software: simulations

## **Astrometry and celestial mechanics**

astrometry  
celestial mechanics  
eclipses  
ephemerides  
occultations  
parallaxes  
proper motions  
reference systems  
time

## **The Sun**

Sun: abundances  
Sun: activity  
Sun: atmosphere  
Sun: chromosphere  
Sun: corona  
Sun: coronal mass ejections (CMEs)  
Sun: evolution  
Sun: faculae, plages  
Sun: filaments, prominences  
Sun: flares  
Sun: fundamental parameters  
Sun: general  
Sun: granulation  
Sun: helioseismology  
Sun: heliosphere  
Sun: infrared  
Sun: interior  
Sun: magnetic fields  
Sun: oscillations  
Sun: particle emission  
Sun: photosphere  
Sun: radio radiation  
Sun: rotation  
(*Sun:*) solar–terrestrial relations  
(*Sun:*) solar wind  
(*Sun:*) sunspots  
Sun: transition region  
Sun: UV radiation  
Sun: X-rays, gamma-rays

## **Planetary systems**

comets: general

## **comets: individual: . . .**

Earth  
interplanetary medium  
Kuiper belt: general

## **Kuiper belt objects: individual: . . .**

meteorites, meteors, meteoroids

minor planets, asteroids: general

## **minor planets, asteroids: individual: . . .**

Moon  
Oort Cloud  
planets and satellites: atmospheres  
planets and satellites: aurorae  
planets and satellites: composition  
planets and satellites: detection  
planets and satellites: dynamical evolution and stability  
planets and satellites: formation  
planets and satellites: fundamental parameters  
planets and satellites: gaseous planets  
planets and satellites: general

## **planets and satellites: individual: . . .**

planets and satellites: interiors  
planets and satellites: magnetic fields  
planets and satellites: oceans  
planets and satellites: physical evolution  
planets and satellites: rings  
planets and satellites: surfaces  
planets and satellites: tectonics  
planets and satellites: terrestrial planets  
planet–disc interactions  
planet–star interactions  
protoplanetary discs  
zodiacal dust

## **Stars**

stars: abundances  
stars: activity  
stars: AGB and post-AGB  
stars: atmospheres  
(*stars:*) binaries (*including multiple*): close  
(*stars:*) binaries: eclipsing  
(*stars:*) binaries: general  
(*stars:*) binaries: spectroscopic  
(*stars:*) binaries: symbiotic  
(*stars:*) binaries: visual  
stars: black holes  
(*stars:*) blue stragglers  
(*stars:*) brown dwarfs  
stars: carbon  
stars: chemically peculiar  
stars: chromospheres  
(*stars:*) circumstellar matter  
stars: coronae  
stars: distances  
stars: dwarf novae  
stars: early-type  
stars: emission-line, Be  
stars: evolution  
stars: flare  
stars: formation  
stars: fundamental parameters  
(*stars:*) gamma-ray burst: general  
(*stars:*) **gamma-ray burst: individual: . . .**  
stars: general  
(*stars:*) Hertzsprung–Russell and colour–magnitude diagrams  
stars: horizontal branch  
stars: imaging  
**stars: individual: . . .**  
stars: interiors

stars: jets  
 stars: kinematics and dynamics  
 stars: late-type  
 stars: low-mass  
 stars: luminosity function, mass function  
 stars: magnetars  
 stars: magnetic field  
 stars: massive  
 stars: mass-loss  
 stars: neutron  
 (*stars:*) novae, cataclysmic variables  
 stars: oscillations (*including pulsations*)  
 stars: peculiar (*except chemically peculiar*)  
 (*stars:*) planetary systems  
 stars: Population II  
 stars: Population III  
 stars: pre-main-sequence  
 stars: protostars  
 (*stars:*) pulsars: general  
 (*stars:*) **pulsars: individual: . . .**  
 stars: rotation  
 stars: solar-type  
 (*stars:*) starspots  
 stars: statistics  
 (*stars:*) subdwarfs  
 (*stars:*) supergiants  
 (*stars:*) supernovae: general  
 (*stars:*) **supernovae: individual: . . .**  
 stars: variables: Cepheids  
 stars: variables: Scuti  
 stars: variables: general  
 stars: variables: RR Lyrae  
 stars: variables: S Doradus  
 stars: variables: T Tauri, Herbig Ae/Be  
 (*stars:*) white dwarfs  
 stars: winds, outflows  
 stars: Wolf–Rayet

### **Interstellar medium (ISM), nebulae**

ISM: abundances  
 ISM: atoms  
 ISM: bubbles  
 ISM: clouds  
 (*ISM:*) cosmic rays  
 (*ISM:*) dust, extinction  
 ISM: evolution  
 ISM: general  
 (*ISM:*) HII regions  
 (*ISM:*) Herbig–Haro objects

### **ISM: individual objects: . . .**

(*except planetary nebulae*)  
 ISM: jets and outflows  
 ISM: kinematics and dynamics  
 ISM: lines and bands  
 ISM: magnetic fields  
 ISM: molecules  
 (*ISM:*) photodissociation region (PDR)  
 (*ISM:*) planetary nebulae: general  
 (*ISM:*) **planetary nebulae: individual: . . .**  
 ISM: structure  
 ISM: supernova remnants

### **The Galaxy**

Galaxy: abundances  
 Galaxy: bulge  
 Galaxy: centre  
 Galaxy: disc  
 Galaxy: evolution  
 Galaxy: formation  
 Galaxy: fundamental parameters  
 Galaxy: general  
 (*Galaxy:*) globular clusters: general  
 (*Galaxy:*) **globular clusters: individual: . . .**  
 Galaxy: halo  
 Galaxy: kinematics and dynamics  
 (*Galaxy:*) local interstellar matter  
 Galaxy: nucleus  
 (*Galaxy:*) open clusters and associations: general  
 (*Galaxy:*) **open clusters and associations: individual: . . .**  
 (*Galaxy:*) solar neighbourhood  
 Galaxy: stellar content  
 Galaxy: structure

### **Galaxies**

galaxies: abundances  
 galaxies: active  
 galaxies: bar  
 (*galaxies:*) BL Lacertae objects: general  
 (*galaxies:*) **BL Lacertae objects: individual: . . .**  
 galaxies: bulges  
 galaxies: clusters: general  
**galaxies: clusters: individual: . . .**  
 galaxies: clusters: intracluster medium  
 galaxies: disc  
 galaxies: distances and redshifts  
 galaxies: dwarf  
 galaxies: elliptical and lenticular, cD  
 galaxies: evolution  
 galaxies: formation  
 galaxies: fundamental parameters  
 galaxies: general  
 galaxies: groups: general

### **galaxies: groups: individual: . . .**

galaxies: haloes  
 galaxies: high-redshift

### **galaxies: individual: . . .**

galaxies: interactions  
 (*galaxies:*) intergalactic medium  
 galaxies: irregular  
 galaxies: ISM  
 galaxies: jets  
 galaxies: kinematics and dynamics  
 (*galaxies:*) Local Group  
 galaxies: luminosity function, mass function  
 (*galaxies:*) Magellanic Clouds  
 galaxies: magnetic fields  
 galaxies: nuclei  
 galaxies: peculiar  
 galaxies: photometry  
 (*galaxies:*) quasars: absorption lines  
 (*galaxies:*) quasars: emission lines  
 (*galaxies:*) quasars: general

*(galaxies:)* **quasars: individual: . . .**  
*(galaxies:)* quasars: supermassive black holes  
galaxies: Seyfert  
galaxies: spiral  
galaxies: starburst  
galaxies: star clusters: general

**galaxies: star clusters: individual: . . .**  
galaxies: star formation  
galaxies: statistics  
galaxies: stellar content  
galaxies: structure

### **Cosmology**

*(cosmology:)* cosmic background radiation  
*(cosmology:)* cosmological parameters  
*(cosmology:)* dark ages, reionization, first stars  
*(cosmology:)* dark energy  
*(cosmology:)* dark matter  
*(cosmology:)* diffuse radiation  
*(cosmology:)* distance scale  
*(cosmology:)* early Universe  
*(cosmology:)* inflation  
*(cosmology:)* large-scale structure of Universe  
cosmology: miscellaneous  
cosmology: observations  
*(cosmology:)* primordial nucleosynthesis  
cosmology: theory

### **Resolved and unresolved sources as a function of wavelength**

gamma-rays: diffuse background  
gamma-rays: galaxies  
gamma-rays: galaxies: clusters  
gamma-rays: general  
gamma-rays: ISM  
gamma-rays: stars  
infrared: diffuse background  
infrared: galaxies  
infrared: general  
infrared: ISM  
infrared: planetary systems  
infrared: stars  
radio continuum: galaxies  
radio continuum: general  
radio continuum: ISM  
radio continuum: planetary systems  
radio continuum: stars  
radio continuum: transients  
radio lines: galaxies  
radio lines: general  
radio lines: ISM  
radio lines: planetary systems  
radio lines: stars  
submillimetre: diffuse background  
submillimetre: galaxies  
submillimetre: general  
submillimetre: ISM  
submillimetre: planetary systems  
submillimetre: stars  
ultraviolet: galaxies

ultraviolet: general  
ultraviolet: ISM  
ultraviolet: planetary systems  
ultraviolet: stars  
X-rays: binaries  
X-rays: bursts  
X-rays: diffuse background  
X-rays: galaxies  
X-rays: galaxies: clusters  
X-rays: general  
**X-rays: individual: . . .**  
X-rays: ISM  
X-rays: stars

### **Transients**

*(transients:)* black hole mergers  
*(transients:)* black hole - neutron star mergers  
*(transients:)* fast radio bursts  
*(transients:)* gamma-ray bursts  
*(transients:)* neutron star mergers  
transients: novae  
transients: supernovae  
transients: tidal disruption events