A theoretical study on the electronically excited-state spectroscopic properties of phosphorus nitride

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ABSTRACT
The potential energy curves of 103 Ω states generated from the 39 Λ–S states of PN have been calculated using the internally contracted multireference configuration interaction method with the Davidson modification. Core-valence correlation and scalar relativistic corrections, as well as the basis-set extrapolation to the complete basis set limit are considered. The spin–orbit coupling is computed using the state interaction approach with the Breit-Pauli Hamiltonian. The spectroscopic parameters and molecular constants of bound and quasibound Λ–S and Ω states are evaluated. Our calculated spectroscopic results agree quite well with the available experimental data. The interactions among different electronic states in curve crossing regions have been discussed with the help of computed spin–orbit coupling matrix elements. The perturbations and predissociation phenomena of the A1 Π, b3 Π, D3 Δ, E3 Σ+, and 21 Π states and so on have been revealed.

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1. Introduction
Phosphorus plays an important role in biochemistry, being expected to be one of the candidates in star and meteorite evolution to provide the necessary life building material. Yet it is not a particularly prevalent element, with a cosmic abundance relative to hydrogen of P/H ∼ 2.8 × 10^-7 [1], less than that of many other third-row elements like Si and S. Thus, to date, only phosphorus mononitride, as the first phosphorus-bearing species, has been identified in interstellar medium and atmospheres [2–4]. Hence, spectral information of gas phase PN has attracted intense research interest over the past several decades.

Spectroscopic evidence for the gaseous PN molecule was first observed in laboratory by Curry et al. [5,6] in the early 1930s. From that time on, a number of experimental studies were performed for this molecule before 1979. Measurements of the radiofrequency [7], microwave
[8,9], fluorescence [10], photoelectron [11,12], and infrared spectrum [13] were recorded. The dissociation energy of the ground state was reported a couple of times [5,14–16]. Huber and Herzberg [17] summarised the spectroscopic properties of PN as of that time. Since then, the PN molecule has been the object of numerous experimental studies. Most spectroscopy experiments concentrated on the $A^1\Pi-X^1\Sigma^+$ [18–22], and $E^1\Sigma^+ - X^1\Sigma^+$ [23–25] band systems, the $X^1\Sigma^+$ [26–29], and several valence and Rydberg states [30–32]. Concerning the triplet states, the only transition observation was provided by Henshaw et al. [21], in which they tentatively identified the observed transition as the $3\Sigma^+ - X^1\Sigma^+$ transition. In contrast to the scarcity of information on most electronic states, the $X^1\Sigma^+$ and $A^1\Pi$ states remain well characterised experimentally. Only little spectroscopic data of a couple of triplet states, $e^2\Sigma^-$, $d^2\Delta$, $b^3\Pi$, have been approximately acquired by analysis of the perturbations of the vibrational levels of the $A^1\Pi$ state [20,22].

In theory, numerous ab-initio calculations have been performed on the electronic structure, spectroscopic parameters, and potential energy function of PN in the past several decades [33–51]. Of these theoretical studies, the early theoretical study was reported by Gottscho et al. [33] in 1978. Eight $\Lambda$–S electronic states were investigated using the self-consistent-field (SCF) method. Five years later, Grein and Kapur [34] calculated the potential energy curves (PECs) and spectroscopic parameters for the ground and eleven excited-states using the multireference single and double excitation configuration interaction (MRD-CI) method with Gaussian basis set. In the 1990s, a series of theoretical studies were performed by de Brouckere et al. [35–37], who calculated the PECs of the $X^1\Sigma^+$, $A^1\Pi$, and $D^1\Delta$ states using the same theoretical method as that of Grein and Kapur [34]. The rotational, rovibrational and transition properties of the $A^1\Pi-X^1\Sigma^+$ and $D^1\Delta-A^1\Pi$ band systems were determined. Recently, Abbiche et al. [38] studied the spectroscopic properties of the 27 $\Lambda$–$S$ states of PN using the variety of theoretical methods, including the explicitly correlated coupled cluster, complete active space self-consistent field, and multireference configuration interaction methods in combination with large correlation-consistent atomic orbitals basis sets AVQZ, AV5Z, and AV(5 + d)Z. The spectroscopic parameters of several states were determined, and the perturbations of the vibrational levels in the $A^1\Pi$ and $E^1\Sigma^+$ states were analyzed qualitatively. More recently, Qin et al. [39,40] performed a higher level calculation to investigate the transition properties of PN, in which the PECs of thirteen states were computed using the internally contracted multireference configuration interaction approach with the Davidson modification, core-valence and scalar relativistic corrections, as well as the basis-set extrapolation. The transition properties of fifteen band systems are predicted. Semenov et al. [41] made the PEC calculations for nine electronic states of PN using the icMRCI + Q/ECP10MWB method. The pure rotational ground state and rovibronic spectroscopy of $A^1\Pi-X^1\Sigma^+$ band system were evaluated.

Despite a lot of studies have been reported during the past several decades, our knowledge on PN is far from enough. Firstly, only the $X^1\Sigma^+$ and $A^1\Pi$ states remain the best characterised electronic states. Some of the published data for this molecule are contradictory or questionable. In particularly, the dissociation energy is still uncertain due to the lack of further measurements. Secondly, little is known about most of excited-states regardless of numerous spectroscopic studies. Thirdly, the complete picture of spin–orbit coupling in the electronic excited-states of PN is still lack, even if the spin–orbit interaction plays an important role in spectroscopy and dynamics of the light molecules that contain atoms of the first and second rows of the periodic table. No intact molecular property investigations can be found in the literature for the $\Omega$ states of PN. In addition, more information about the perturbations and predissociation mechanisms for this molecule is needed eagerly, which would help to determine the properties of the perturbing states accurately. So the spectroscopic properties of PN are worthy of further investigation theoretically.

In the present work, high-level ab-initio calculations including spin–orbit coupling effects have been made. The PECs of 39 $\Lambda$–$S$ states and 103 $\Omega$ states of PN will be present. Based on the computed PECs, the electronically excited-state properties and perturbations and predissociation mechanisms have been studied. The spectroscopic parameters of bound and quasibound states will be reported. Various curve crossings and perturbations will be revealed, and some predissociation pathways will be predicted with the help of the computed spin–orbit coupling matrix elements.

2. Computational methods

The present calculations are performed with the MOLPRO 2010 quantum chemistry package [52]. At a given internuclear distance, the molecule orbitals (MOs) of the ground state are calculated using the Hartree–Fock self-consistent field (HF) method at first. Then, the state-averaged complete active space self-consistent field (CASSCF) calculations are carried out using the HF orbitals as the starting guess values [53,54]. Next, utilising the CASSCF wavefunctions as reference, the energies
of each $\Lambda - S$ state are computed using the internally contracted multireference configuration interaction (icMRCI) approach [55,56] with the Davidson modification (+Q). In the CASSCF and subsequent icMRCI calculations, the $C_{2v}$ subgroup of the $C_{\infty v}$ point group is employed. Eight valence molecular orbitals (MOs), including $4a_1, 2b_1, $ and $2b_2$ symmetry MOs, are selected as the active space, which correspond to the atomic orbitals 3$s^3p$ of P and 2$s^2p$ of N. The rest of the inner electrons are kept frozen and not correlated. That is, the active space consists of ten electrons in eight molecular orbitals (referred to as CAS(10,8)).

The entirely uncontracted augmented correlation consistent polarised quintuple (aug-cc-pV5Z) and sextuple zeta (aug-cc-pV6Z) basis sets [57–59] are chosen to acquire the molecular energies. The energy extrapolation technique has been usually employed in high-level ab-initio calculations [60,61]. In our calculations, a two-point energy extrapolation scheme given by Muller et al. [62] is used. For two successive correlation-consistent basis sets, the energy extrapolation formula is written as,

$$\Delta E_{\text{total,}\infty} = \frac{\Delta E_{\text{total,n+1}}(n+1)^3 - \Delta E_{\text{total,n}}n^3}{(n+1)^3 - n^3}. \tag{1}$$

Here, $\Delta E_{\text{total,}\infty}$ is the total energy extrapolated to the complete basis set (CBS) limit. And $\Delta E_{\text{total,n}}$ and $\Delta E_{\text{total,n+1}}$ are the total energies obtained by the basis sets, aug-cc-pV$n$Z and aug-cc-pV$(n+1)$Z, respectively. Using the formula (1), the PEC of each state involved is extrapolated to the CBS limit using the aug-cc-pV5Z and aug-cc-pV6Z energies.

Scalar relativistic effect is taken into account through the third-order Douglas–Kroll–Hess (DKH) one-electron integrals [63,64] combined with the relativistic contracted basis set cc-pV5Z [65]. The difference between the icMRCI energy with and without DKH approximation forms the scalar relativistic contribution (denoted as DK). The core-valence correlation corrections are included in the molecular energies. At the icMRCI/aug-cc-pCV5Z level of theory [58], the difference between the core-valence correlation and the frozen-core approximation energies is calculated to estimate the core-valence contribution (denoted as CV). Only the two electrons in the 1$s$ inner shell of P atom are left uncorrected when we make the CV calculations for the PN molecule. The spin–orbit coupling effects are introduced using the state interaction approach with the full Breit-Pauli Hamiltonian [66] at the level of icMRCI theory in combination with all-electron aug-cc-pCVTZ (ACVTZ) [58] basis set.

The nuclear Schrödinger equation is solved using Le Roy’s Level program [67] to determine the spectroscopic parameters and molecular constants.

### 3. Results and discussion

#### 3.1. PECs and spectroscopic properties of the $\Lambda - S$ states

Table 1 gives the dissociation relationships for all $\Lambda - S$ electronic states arising from the lowest six dissociation asymptotes of the PN molecule. Altogether, 39 $\Lambda - S$ electronic states of PN are investigated using the aforementioned methods, including four $\Lambda - S$ states correlating with the first dissociation channel $P(\Sigma^+_0) + N(\Delta^+_0)$, namely, one $1\Sigma^+$, one $3\Sigma^+$, one $5\Sigma^+$, and one $7\Sigma^+$ states; six $\Lambda - S$ states correlating with the second dissociation channel $P(2\Delta_u) + N(\Sigma^+_0)$, namely, one $3\Pi$, one $3\Sigma^+$, one $3\Delta$, one $5\Sigma^+$, one $5\Pi$, and one $5\Delta$ states; four $\Lambda - S$ states correlating with the third dissociation channel $P(2\Pi_u) + N(\Pi^+_0)$, namely, one $3\Sigma^-$, one $3\Pi$, one $5\Sigma^-$, and one $5\Pi$ states; six $\Lambda - S$ states correlating with the fourth dissociation channel $P(2\Sigma_u) + N(2\Delta_u)$, namely, one $3\Pi$, one $3\Sigma^+$, one $3\Delta$, one $5\Sigma^+$, one $5\Pi$, and one $5\Delta$ states; four $\Lambda - S$ states correlating with the fifth dissociation channel $P(2\Pi_u) + N(2\Pi_u)$, namely, one $3\Sigma^-$, one $3\Pi$, one $5\Sigma^-$, and one $5\Pi$ states; and fifteen singlet $\Lambda - S$ states correlating with the sixth dissociation channel $P(2\Sigma_u) + N(2\Pi_u)$, namely, three $1\Sigma^+$, two $1\Sigma^-$, four $1\Pi$, three $1\Delta$, one $1\Gamma$, and two $1\Phi$ states.

The calculated energy separations between each higher dissociation limit and the lowest one are summarised in Table 1 along with available literature results for comparison. The deviations between our computed energy separations and the experimental ones [68] are only 22.27, $-5.77$, $-0.87$, 47.34, and 200.04 cm$^{-1}$, respectively. While, the deviations between the theoretical [39] and the experimental ones [68] are 46.66, $-157.41$, $-131.5$, $58.89$, and 423.64 cm$^{-1}$, respectively. This indicates that our theoretical methods could describe the dissociation properties of PN more properly. The PECs of 39 $\Lambda - S$ states of PN are calculated for internuclear separation from 1.2 to 10.0 Å. For more clarity, we depict these curves in Figures 1–5 over a small range of distances. The PEC of ground state is plotted in all five figures for comparative purpose.

Summarising the characters of 39 $\Lambda - S$ states of PN, we can obtain the following results. (1) The $1^3\Sigma^+$, $2^3\Sigma^+$, $2^5\Sigma^-$, and $2^5\Pi$ states are bound or quasibound, and the other quintet and septet states are all repulsive in nature. Although the $4^3\Pi$ state has a shallow potential well induced by two avoided crossings with the neighbouring $3\Pi$ states, it could not support any vibration levels. (2) All singlet and triplet $\Lambda - S$ excited states are bound or quasibound states. (3) Some avoided crossings exist between the states of the same spin and spatial multiplicity, which make the PECs of several states unsmooth.
and several barriers formed, such as the $1^1\Phi$ and $2^1\Phi$, the $2^3\Sigma^+$ and $3^3\Sigma^+$ states and so on.

Based on the computed PECs, the ro-vibrational energy levels of bound and quasibound states are determined. It should be pointed out that the dissociation energies refer to the energy separation between the bottom of the potential well and its dissociation limit, whereas in the case of a quasibound state caused by the avoided crossing, refer to the energy separation between the bottom of the potential well and the top of the barrier.

For the convenience of comparison, we divide these states into three groups. The first group consists of the $X^1\Sigma^+$ and $A^1\Pi$ states, which remain the best characterised electronic states of PN experimentally. The second group contains nineteen states with $\Sigma$ and $\Delta$ symmetries, composed of the $a^3\Sigma^+$, $d^3\Delta$, $e^3\Sigma^-$, $C^1\Sigma^-$, $D^1\Delta$, $1^3\Sigma^+$, $2^3\Delta$, $E^1\Sigma^+$, $2^3\Sigma^+$, $2^3\Sigma^-$, $3^1\Sigma^+$, $2^3\Sigma^+$, $3^3\Sigma^+$, $2^1\Delta$, $4^1\Sigma^-$, $4^1\Sigma^+$, $3^1\Delta$, $1^1\Gamma$, and $2^5\Sigma^-$ states. The third one includes ten states with $\Pi$ and $\Phi$ symmetries, including the $b^3\Pi$, $1^3\Pi$, $2^3\Pi$, $3^3\Pi$, $2^1\Pi$, $4^3\Pi$, $1^1\Phi$, $3^1\Pi$, $4^1\Pi$, and $2^1\Phi$ states. For the states of the latter two groups, no spectroscopic measurements were performed, besides a few spectroscopic parameters of several states have been approximately determined through the perturbation observations of the $A^1\Pi$ and $E^1\Sigma^+$ states to date.

The main electronic configurations of all bound and quasibound states are abstracted from the MRCI/AV6Z

### Table 1. Dissociation relationships between the $\Lambda$–$S$ states and the atomic states of PN.

| Atomic state | $\Lambda$–$S$ state | This work | Exp.[68] | Cal.[34]$^a$ | Cal.[39]$^b$ | Cal.[38]$^c$ |
|--------------|----------------------|-----------|----------|-------------|-------------|-------------|
| P($2S_u$) + N($2S_u$) | $X^1\Sigma^+$, $1^3\Sigma^+$, $1^3\Sigma^+$, $1^3\Sigma^+$ | 0.00      | 0.00     | 0.00        | 0.00        | 0.00        |
| P($2D_u$) + N($2S_u$) | $1^1\Pi$, $1^3\Pi$, $1^3\Delta$, $2^3\Sigma^+$, $2^3\Sigma^+$, $1^3\Delta$ | 11390.10  | 11368.83 | 11719.23    | 11415.49    | 11986.20    |
| P($2P_u$) + N($4S_u$) | $1^3\Sigma^-$, $2^3\Pi$, $1^3\Sigma^-$, $2^3\Pi$ | 18729.59  | 18735.36 | 18577.95    | 18978.22    | 19686.37    |
| P($2S_u$) + N($4S_u$) | $3^3\Pi$, $2^1\Delta$, $3^3\Sigma^+$, $3^3\Sigma^+$, $3^3\Pi$, $2^3\Delta$ | 19227.95  | 19228.82 | 19097.32    | 19686.37    | 19686.37    |
| P($2D_u$) + N($4S_u$) | $2^3\Sigma^-$, $4^3\Pi$, $2^3\Sigma^-$, $4^3\Pi$ | 28886.46  | 28839.12 | 28780.23    | 28975.46    | 28975.46    |
| P($2S_u$) + N($4D_u$) | $2^1\Sigma^+$, $1^3\Pi$, $1^3\Delta$, $2^3\Pi$, $1^3\Sigma^+$, $1^3\Sigma^-$, $2^3\Delta$, $3^3\Pi$, $1^3\Phi$, $3^1\Delta$, $4^3\Pi$, $2^1\Phi$, $4^3\Sigma^+$, $2^3\Sigma^-$, $1^3\Pi$, $4^3\Sigma^+$, $5^3\Pi$, $3^3\Delta$, $6^3\Pi$, $5^3\Sigma^+$, $3^3\Sigma^-$, $4^3\Delta$, $7^3\Pi$, $1^3\Phi$, $5^3\Delta$, $8^3\Pi$, $2^3\Phi$, $6^3\Sigma^+$, $4^3\Sigma^-$, $1^3\Gamma$ | 30797.69  | 30597.65 | 31044.27    | 30174.01    | 31502.39    |

$^a$MRCI-Gaussian basis sets results.
$^b$MRCI/S6DKCV results.
$^c$MRCI/aV(5+d)Z results.

**Figure 1.** Potential energy curves of PN for the $X^1\Sigma^+$, five $1^1\Sigma$, three $1^3\Delta$, and one $1^1\Gamma$ states.

**Figure 2.** Potential energy curves of PN for the $X^1\Sigma^+$, four $1^1\Pi$, and two $1^3\Phi$ states.
wavefunctions near the equilibrium distance of each state, which are listed in Table S1 of the Supplementary materials for convenient discussion.

3.1.1. Spectroscopic parameters of the $X^1\Sigma^+$ and $A^1\Pi$ states

The computed spectroscopic parameters of the $X^1\Sigma^+$ and $A^1\Pi$ states of PN are summarised in Table 2 along with the available literature results for comparison.
Table 2. Our calculated spectroscopic parameters for the $X^1\Sigma^+$ and $A^1\Pi$ states along with available literature results.

|       | $\nu_1$/cm$^{-1}$ | $R_e$/Å  | $\omega_v$/cm$^{-1}$ | $\omega_{Xe}$/cm$^{-1}$ | $B_v$/cm$^{-1}$ | $10^4\omega_0$/cm$^{-1}$ | $D_v$/eV |
|-------|-------------------|----------|----------------------|------------------------|----------------|--------------------------|--------|
| $X^1\Sigma^+$ | 0.0 | 1.4915 | 1339.97 | 6.9923 | 0.7860 | 6.0862 | 6.3247 |
| Exp. [29] | 0.0 | 1.4907 | 1337.00 | 6.9164 | 0.7865 | 5.554 | 6.4396 |
| Exp. [28] | 0.0 | 1.4894 | 1336.95 | 6.8958 | 0.7865 | 5.5337 |
| Exp. [24] | 0.0 | 1.4910 | 1336.98 | 6.906 | 0.7863 | 5.31 | 6.21 |
| Exp. [20] | 0.0 | 1.491 | 1337.0 | 6.88 | 0.7865 | 5.54 | 6.538 |
| Exp. [18] | 0.0 | 1.491 | 1337.0 | 6.88 | 0.7865 | 5.538 |
| Exp. [17] | 0.0 | 1.4909 | 1337.24 | 6.983 | 0.7865 | 5.538 |
| Cal. [42] | 0.0 | 1.4927 | 1342.7 | 6.874 | 0.786 | 5.29 |
| Cal. [43] | 0.0 | 1.4984 | 1351.30 | 6.2587 |
| Cal. [44] | 0.0 | 1.4968 | 1336.2 | 6.6 |
| Cal. [29] | 0.0 | 1.4894 | 1352.2 | 6.58 | 0.7884 | 5.3630 | 6.3589 |
| Cal. [41] | 0.0 | 1.49 | 1303.23 | 0.78 | 6.5386 |
| Cal. [38] | 0.0 | 1.4977 | 1328.21 | 5.7768 | 0.7778 | 5.8 | 6.16 |
| Cal. [45] | 0.0 | 1.4948 | 1333.84 | 6.8373 | 0.7823 | 5.44 | 6.2792 |
| Cal. [40] | 0.0 | 1.492 | 1339.2 | 0.7853 |
| Cal. [39] | 0.0 | 1.4918 | 1339.61 | 6.594 | 0.7855 | 5.29 | 6.3795 |
| $A^1\Pi$ | 39652.5 | 1.5393 | 1104.29 | 7.2471 | 0.7320 | 7.1834 | 5.2242 |
| Exp. [20] | 39805.6 | 1.547 | 1103.0 | 7.25 | 0.7310 | 6.40 |
| Exp. [18] | 39805.9 | 1.547 | 1103.0 | 7.25 | 0.7310 | 6.41 |
| Exp. [17] | 39805.6 | 1.5467 | 1103.09 | 7.222 | 0.7307 | 6.63 | 5.1962 |
| Cal. [36] | 40007.6 | 1.5732 | 1066.3 | 10.72 | 0.7063 | 1.83 |
| Cal. [41] | 42143.7 | 1.56 | 1041.07 | 10.47 | 0.721 | 5.5669 |
| Cal. [38] | 40610.0 | 1.556 | 1078.42 | 7.3099 | 0.7213 | 4.9 | 5.039 |
| Cal. [45] | 40032.6 | 1.5501 | 1100.24 | 7.2185 | 0.7275 | 6.33 | 5.1245 |
| Cal. [39] | 40032.6 | 1.5501 | 1100.24 | 7.547 | 0.7306 | 7.47 | 5.0828 |
| Cal. [40] | 40637.7 | 1.548 | 1104.8 | 0.7306 |

$^a$Derived from $D_v = D_0 + \omega_v^2/2 - \omega_{Xe}^2/4$; $^b$CCSD(T)/7s7p4d3f for N and 7s7p4d4f for P; $^c$CCSD(T)/all-electron wCVDZ; $^d$CCSD(T)/aug-cc-pVXZ(x= T, Q, S); $^e$CCSD(T)/CBS+CV; $^f$MRCI+Q/ECP10MWB; $^g$MRCI/av(5$\sigma$+d)+D; $^h$MRCI/av6z; $^i$MRCI+Q/S6dcv; $^j$FCI/TZ.

[39] is 0.1134 eV smaller than the experimental value [17]. The present $T_e$ and $D_v$ values for the $A^1\Pi$ state are more accurate than those of previous theoretical studies.

Tables S2 and S3 of the Supplementary materials show the vibrational energy levels, rotational and centrifugal distortion constants of the $X^1\Sigma^+$ and $A^1\Pi$ states, respectively, as well as the available experimental and theoretical values [18,20,22,28,47] for comparison. It should be pointed out that the experimental energy levels [28] are computed using the spectroscopic parameters [28] and the zero-point energy [69]. Our molecular constants are in reasonable agreement with the available experimentally determined ones if existing. For example, for the $X^1\Sigma^+$ state, the largest errors of $G(v)$, $B_v$ and $D_v$ are 18 ($v = 11$), 0.00142 ($v = 6$), and 0.2227 ($v = 11$) cm$^{-1}$ deviated from the experimental values [18], while, for the $A^1\Pi$ state, the largest deviations of $G(v)$, $B_v$ and $D_v$ values are not more than 3.8, 0.0025, and 0.6 cm$^{-1}$ from the experimental values [20,22], respectively. We note that, our calculations indicate that the $A^1\Pi$ has a deep potential well with a depth of 42136.00 cm$^{-1}$ holding 55 vibrational levels. However, only the $A^1\Pi$ $v \leq 11$ vibrational levels have been recorded in experiment to date. In the energy range from 37700 to 80000 cm$^{-1}$, the $A^1\Pi$ PEC crosses with the PECs of many other excited states, and some correlate with different dissociation limits and have different spin multiplicities. In order to explore why the higher vibrational levels of $A^1\Pi$ cannot be observed in experiment, the couplings among the $A^1\Pi$ and other states will be discussed in detail in Section 3.3.

In general, a detailed comparison of the spectroscopic parameters and molecular constants of the $X^1\Sigma^+$ and $A^1\Pi$ states indicates that good agreement exists between the available experimental data and our calculations. It validates that our calculated results are of high quality. So, it is expected that we could present a more accurate prediction on the spectroscopic properties for higher excited states and some perturbations and predissociation phenomena of PN.

### 3.1.2. Spectroscopic parameters of the states with $\Sigma$, $\Delta$, and $\Gamma$ symmetries

The spectroscopic parameters of nineteen $\Lambda$–$S$ states with the $\Sigma$, $\Delta$ and $\Gamma$ symmetries are listed in Table 3 along with available literature results for comparison.

The first excited state of PN belongs to $^3\Sigma^+$ symmetry. This state is mainly described by the electronic configuration $5\sigma^26\sigma^27\sigma^22\pi^23\pi^1\Sigma^0$, arising from one-electron excitation $2\pi \rightarrow 3\pi$. Another configuration namely, $5\sigma^26\sigma^27\sigma^22\pi^13\pi^3\Sigma^0$ contributes to a small extent. It is a typical bound state with a well depth of 3.1049 eV. As shown in Table 3, our computed $T_e$, $\omega_v$, and $\omega_{Xe}$ values are in good agreement with the approximately experimental values [21], closer to the recent theoretical results [39], and prior to the theoretical results [38].

Similarly, the $d^1\Delta$, $e^1\Sigma^-$, $C^1\Sigma^-$, $D^1\Delta$, and $2^1\Delta$ states can be basically represented by one dominant configuration $5\sigma^26\sigma^27\sigma^22\pi^23\pi^1\Sigma^0$ mixed with another secondary configuration. The $d^1\Delta$ state is 33077.02 cm$^{-1}$ above the ground state. The $e^3\Sigma^-$ state is 5145.36 cm$^{-1}$
higher than the d3Δ state. Both d3Δ and e3Σ− states have deep potential wells and hold 58 and 60 vibrational levels with the well depths of 3.6582 and 3.9238 eV, respectively. For the e3Σ− state, our computed Rα, ωα, ωαXα, and Bε values deviate from the derived values from the observed perturbations of the A1Π state [20] by about 0.0094 Å, 5.81, 1.0617, and 0.292 cm−1, and respectively, which are in accord with the theoretical results [38,39]. Our calculated spectroscopic parameters for d3Δ do not agree with the derived values [20], but it is worth noting that our calculated spectroscopic parameters of d3Δ agree well with those predicted by Grein and Kapur [34], by Abbiche et al. [38], and by Qin et al. [39]. The C1Σ− and D1Δ states are also strong bound states holding 87 and 66 vibrational levels with the well depths of 5.4806 and 5.1078 eV, respectively. The D1Δ state is 1153.12 cm−1 above the A1Π state, which is in accord with the value of 1300 cm−1 given by Grein and Kapur [34], and...
larger internuclear distances it is also repulsive.

The \( ^2\Sigma^+ \) state has a long internuclear bond length of 2.8828 Å and a shallow potential well of 0.0486 eV holding 7 vibrational levels. It is mainly characterised by \( 5\sigma^26\sigma^22\pi^23\pi^28\sigma^0 \), \( 5\sigma^26\sigma^27\sigma^21\pi^33\pi^18\sigma^1 \), \( 5\sigma^26\sigma^27\sigma^21\pi^23\pi^28\sigma^1 \), and \( 5\sigma^26\sigma^27\sigma^21\pi^33\pi^38\sigma^0 \) configurations. Due to an avoided crossing with the next \( ^5\Sigma^- \) state, the \( ^2\Sigma^+ \) possesses a shallow potential well of 0.1310 eV holding only one vibrational level.

Regrettfully, no spectroscopic data for the \( ^2\Sigma^+ \), \( ^2\Delta \), \( ^2\Sigma^- \), \( ^4\Sigma^+ \), \( ^3\Delta \), and \( ^1\Gamma \) states can be compared with either experimentally or theoretically directly. In addition, there are 15 triplet states due to \( P(^2\Delta_u) + N(^2\Delta_u) \), but they are not computed and discussed in this work. While, this asymptotic limit is very close to \( P(^4\Sigma_u) + N(^2\Pi_u) \), therefore, the present results for the \( ^3\Sigma^+ \) state are not entirely reliable.

### 3.1.3. Spectroscopic parameters of the states with the \( \Pi \) and \( \Phi \) symmetries

We summarise the spectroscopic parameters of ten states with the \( \Pi \) and \( \Phi \) symmetries in Table 4 along with available literature results for comparison.

At equilibrium bond length, the \( ^b\Pi \) state is mainly characterised by the \( 5\sigma^26\sigma^27\sigma^21\pi^33\pi^18\sigma^0 \) configuration. However, two other configurations, \( 5\sigma^26\sigma^21\pi^32\pi^43\pi^18\sigma^0 \) and \( 5\sigma^26\sigma^27\sigma^21\pi^22\pi^23\pi^38\sigma^0 \) also contribute. The \( ^b\Pi \) state has a potential well with the depth of 3.5821 eV holding 35 vibrational states. Our calculated \( R_e \) of 1.5474 Å is nearly 0.06 Å larger than the estimated value of 1.49 Å from the observed perturbations of the \( ^1\Pi \) state [20], but closer to the theoretical values [34,38,39,41], while the computed \( \omega_e \) and \( T_e \) values of 1149.20 and 33596.74 cm\(^{-1} \) are more precise than previous investigations.

The \( ^1\Pi \), \( ^2\Pi \), \( ^2\Pi \), and \( ^4\Pi \) states are mainly described by the \( 5\sigma^26\sigma^27\sigma^21\pi^33\pi^28\sigma^0 \) configuration as shown from Table S1 generating from the \( 7\sigma2\pi \rightarrow 3\pi^2 \) electronic excitation. Their excitation energies are 53131.96, 61015.48, 65280.75, and 66272.12 cm\(^{-1} \), respectively. And they have potential wells with the depths of 9262.47, 8732.56, 42096.34, and 13683.19 cm\(^{-1} \), holding 16, 20, 51, and 31 vibrational levels, respectively. Among these states, the existence of the \( ^2\Pi \) state has been experimentally demonstrated [25]. The approximate spectroscopic data for the \( ^2\Pi \) state are \( \omega_e = 600\text{ cm}^{-1} \), \( B_e = 0.55\text{ cm}^{-1} \), and \( T_e = 8.4\text{ eV} \) [30] derived from Verma and Ghosh’s experiment [25]. Our calculated values of \( \omega_e = 653.55\text{ cm}^{-1} \), \( B_e = 0.7355\text{ cm}^{-1} \), and \( T_e = 8.10\text{ eV} \) are consistent with the derived values [30] and the calculated results [38], but prior to the
Table 4. Our spectroscopic parameters for the Π and Φ states symmetries along with available literature results.

|   | $T_o$/cm$^{-1}$ | $R_o$/Å | $\omega_p$/cm$^{-1}$ | $\omega_p$E/cm$^{-1}$ | $B$/cm$^{-1}$ | $10^6\omega_e$/cm$^{-1}$ | $D_e$/eV |
|---|----------------|---------|----------------------|---------------------|--------------|-------------------------|---------|
| b$^1\Pi$ | 33596.74 | 1.5474 | 1149.10 | 11.7593 | 0.7267 | 5.5698 | 3.5716 |
| Exp. [20] | 33370.00 | 1.407 | 1150.0 | 8.00 | 0.78 | 5.00 | |
| Cal. [41]$^b$ | 35146.16 | 1.56 | 1070.81 | 0.71 | 4.1411 | |
| Cal. [38]$^b$ | 33843.01 | 1.555 | 1102.49 | 8.4532 | 0.7224 | 5.1 | 3.431 |
| Cal. [39]$^c$ | 33671.79 | 1.5449 | 1113.24 | 2.940 | 0.7330 | 7.34 | 3.6201 |
| 3$^1\Pi$ | 53131.96 | 1.7816 | 707.08 | 4.2039 | 0.5423 | 0.9551 | 1.1481 |
| Cal. [38]$^b$ | 53039.00 | 1.784 | 711.83 | 13.838 | 0.5486 | 6.7 | 1.047 |
| Cal. [39]$^c$ | 53760.81 | 1.7802 | 703.86 | 9.155 | 0.5513 | 4.97 | 1.1535 |
| 2$^1\Pi$ | 61015.48 | 1.7833 | 789.84 | 11.609 | 0.5167 | 14.788 | 1.0827 |
| Cal. [38]$^b$ | 60830.31 | 1.796 | 662.61 | 6.7232 | 0.5414 | 104.18 | 0.7419 |
| Cal. [38]$^b$ | 64592.04 | 1.6201 | 790.97 | 11.209 | 0.4709 | 104.18 | 0.7419 |
| 2$^3\Pi$ | 64846.95 | 1.664 | 419.90 | 65.323 | 0.6305 | 48.2 | 0.543 |
| Cal. [38]$^b$ | 65280.75 | 1.7336 | 653.55 | 0.7633 | 0.5790 | 0.7167 | 2.0967 |
| Exp. [30] | [67750.54] | [600] | [0.55] | | | | |
| Cal. [38]$^b$ | 65742.22 | 1.730 | 648.93 | 9.8053 | 0.5833 | 6.1 | 1.925 |
| Cal. [39]$^c$ | 65916.71 | 1.7650 | 733.20 | 17.515 | 0.7306 | 71.498 | 1.9892 |
| 4$^1\Pi$ | 66272.12 | 1.8017 | 700.84 | 0.8514 | 0.5031 | 9.3607 | 1.8302 |
| Cal. [38]$^b$ | 67347.27 | 1.699 | 581.54 | 10.349 | 0.6053 | 5.1 | 1.394 |
| 1$^1\Phi$ | 68307.97 | 1.6807 | 780.44 | 11.097 | 0.6192 | 10.145 | 1.8302 |
| 3$^1\Phi$ | 78275.19 | 1.9702 | 459.87 | 14.491 | 0.5324 | 21.368 | 0.4462 |
| 4$^1\Phi$ | 80019.13 | 1.8194 | 716.42 | 13.7455 | 0.4931 | 21.22 | 0.6284 |
| 2$^3\Phi$ | 85150.23 | 1.6343 | 1232.95 | 65.218 | 0.68423 | 34.92 | 0.7030 |

$^a$MRCI + Q/SCF10MWB.
$^b$MRCI/AV1Z.
$^c$MRCI + Q/56dkcv.

recent theoretical results [39]. However, any judgment should be withheld until the experimental values have been more firmly established. The spectroscopic parameters of the $1^3\Pi$ and $2^3\Pi$ states are also in accordance with the theoretical results [38,39]. However, for the $4^3\Pi$ state, our $R_o$, $\omega_p$ and $D_e$ values are somewhat larger than the corresponding computed results [38].

The rest five states, $3^3\Pi$, $1^1\Phi$, $3^1\Pi$, $4^1\Pi$, and $2^1\Phi$, lie 14761.64 cm$^{-1}$ above the ground state, and possess 11, 27, 11, 10, and 7 levels, respectively. These states exhibit strong multi-configurational characters due to avoided crossings with the adjacent states of the same symmetry and spin multiplicity. In detail, the avoided crossing between the $1^1\Phi$ and $2^1\Phi$ form a small barrier of 1297.16 cm$^{-1}$ higher than the dissociation asymptote and a potential well with depth of 14761.64 cm$^{-1}$ for the $1^1\Phi$ state, and produce a large barrier of 9104.36 cm$^{-1}$ higher than the dissociation asymptote and a shallow well with a depth of 5670.08 cm$^{-1}$ for the $2^1\Phi$ state. Similarly, the $3^3\Pi$ and $4^3\Pi$ states have flat potential wells with depths of 3599.38 and 5068.77 cm$^{-1}$, respectively due to avoided crossings with the neighbouring higher $2^3\Pi$ state. The barriers of the $3^3\Pi$ and $4^3\Pi$ PECs locate nearby $R = 2.7200$ and 2.4200 Å, and are 276.55 and 3380.43 cm$^{-1}$ higher than the dissociation asymptote, respectively. So the $\nu' = 11$ and 10 level appear to be the highest bound level supported by the $3^3\Pi$ and $4^3\Pi$ states, respectively.

Regrettfully, to our knowledge, spectroscopic information in the literature is lack for the $1^1\Phi$, $3^3\Pi$, $4^3\Pi$, and $2^1\Phi$ states either experimentally or theoretically. We expect our data reported here could be helpful for their definitive assignment, and may very well be corroborated by future experiments.

3.2. PECs and spectroscopic properties of Ω states

Table 5 shows the dissociation relationships for the possible Ω states and corresponding energy separations as well the experimental data [68].

When the spin–orbit coupling effects are taken into account, the first dissociation limit $P(1^3S_3/2) + N(4^3S_3/2)$ of PN does not split. The second, third, fourth and fifth dissociation limits split into two close dissociation asymptotes, $P(2^3D_3/2) + N(4^3S_3/2)$ and $P(2^3D_5/2) + N(4^3S_3/2)$, respectively. And the sixth dissociation channel splits into four close asymptotes, of which the $P(2^3D_3/2) + N(2^3D_3/2)$ is the lowest. The successively higher dissociation limits are $P(2^3D_3/2) + N(2^3D_5/2)$, $P(2^3D_5/2) + N(2^3D_5/2)$, respectively. Altogether, 103 Ω states generated from the 39 Λ–S states of PN are investigated, including eighteen states of $\Omega = 0^-$, nineteen states of $\Omega = 0^+$, twenty-seven states of $\Omega = 1$, twenty-one states of $\Omega = 2$, eleven states of $\Omega = 3$, three states of $\Omega = 4$, and four states of $\Omega = -1$. The PECs of all Ω states calculated here are plotted in Figure S1 of the Supplementary materials. In all case, the ground state $C^1\Sigma^+_g$ is shown for comparison.

Based on our calculations, the energy separations are 11381.62 ($4^3S_3/2-2^3D_3/2$ of P), 10.12 ($3^3D_5/2-2^3D_3/2$ of P),
Dissociation relationships of the $\Omega$ states of PN.

| Atomic state $(P + N)$ | $\Omega$ state | Relative energy/cm\(^{-1}\) |
|------------------------|----------------|-----------------------------|
| $^4S_{1/2} + ^5S_{1/2}$ | $3, 2, 2, 1, 1, 1, 0^+, 0^-, 0^+, 0^+$ | This work: 0.0 Exp. [68]: 0.0 |
| $^2D_{3/2} + ^5S_{1/2}$ | $3, 2, 2, 1, 1, 1, 0^+, 0^-, 0^+$ | 11381.62 11361.02 |
| $^2D_{5/2} + ^5S_{1/2}$ | $4, 3, 3, 2, 2, 2, 1, 1, 0^+, 0^-, 0^+, 0^+$ | 11391.74 11376.63 |
| $^2P_{1/2} + ^5S_{1/2}$ | $2, 1, 0^+, 0^+$ | 18735.42 18722.71 |
| $^2P_{3/2} + ^5S_{1/2}$ | $3, 2, 2, 1, 1, 0^+, 0^-, 0^+$ | 18748.80 18748.01 |
| $^2D_{3/2} + ^2D_{3/2}$ | $4, 3, 3, 2, 2, 2, 1, 1, 0^+, 0^-, 0^+, 0^+$ | 19264.02 19224.46 |
| $^2D_{3/2} + ^2D_{5/2}$ | $3, 2, 2, 1, 1, 0^+, 0^+$ | 19274.71 19233.18 |
| $^2D_{5/2} + ^2D_{5/2}$ | $2, 1, 0^+, 0^+$ | 28813.32 28838.92 |
| $^2D_{3/2} + ^2D_{5/2}$ | $4, 3, 3, 2, 2, 2, 1, 1, 0^+, 0^-, 0^+, 0^+$ | 28869.73 28839.31 |
| $^2D_{5/2} + ^2D_{5/2}$ | $4, 3, 3, 2, 2, 2, 1, 1, 0^+, 0^-, 0^+, 0^+$ | 30585.48 30594.20 |
| $^2D_{3/2} + ^2D_{3/2}$ | $3, 2, 2, 1, 1, 1, 0^+, 0^+$ | 30601.09 |
| $^2D_{5/2} + ^2D_{5/2}$ | $4, 3, 3, 2, 2, 2, 1, 1, 0^+, 0^-, 0^+, 0^+$ | 30609.81 |

Table 5: Dissociation relationships of the $\Omega$ states of PN.

$18735.42 \ (^4S_{3/2} - ^2P_{1/2} \ of \ P), \ 13.38 \ (^2P_{3/2} - ^2P_{1/2} \ of \ P), \ 515.22 \ (^4S_{3/2} - ^2D_{5/2} \ of \ N), \ 10.69 \ (^2D_{3/2} - ^2D_{5/2} \ of \ N), \ 10064.52 \ (^2P_{1/2} - ^2P_{3/2} \ of \ N), \ and \ 0.39 \ (^2P_{1/2} - ^2P_{3/2} \ of \ N)$ cm\(^{-1}\), being in excellent agreement with the observed values of 11361.02, 15.51, 18722.71, 25.29, 476.45, 8.72, 10090.91, and 56.41 cm\(^{-1}\), respectively [68].

The spectroscopic parameters of bound and quasi-bound $\Omega$ states and the dominant $\Lambda$–$S$ compositions near the equilibrium bond distance of each state are listed in Table 6.

The $X^1\Sigma^+$ PEC do not cross with the PECs of other states, and the crossing point between the $a^3\Sigma^+$ and $b^3\Pi$ PECs is located at $R = 1.4016 \ \AA$, being away from the equilibrium internuclear distance of the $a^3\Sigma^+$ state. The PECs shape of the $\Omega$ states arising from the $X^1\Sigma^+$ and $a^3\Sigma^+$ states would not change evidently. Consequently, the lowest bound $\Omega$ states, $X^1\Sigma^+ + 1$, $a^3\Sigma^+ + 0$, and $a^3\Sigma^+$, have almost the same spectroscopic properties as the corresponding pure $\Lambda$–$S$ states.

The $b^3\Pi$ state crosses with the $d^3\Delta$ state near the bottoms of their potential wells, and its crossing points with the $e^3\Sigma^−, 1^5\Sigma^+$, and $1^7\Sigma^+$ states are far away from the equilibrium position of $d^3\Delta$. These states have the same $\Omega$ components as the $b^3\Pi$ and $d^3\Delta$ states. Due to the avoided crossing rule, the shapes of the $\Omega = 1$ and 2 components of the $b^3\Pi$ and $d^3\Delta$ states change greatly near their equilibrium distances, which has evident effects on their spectroscopic properties. For example, as shown in Table 6, for the $\Omega = 1$ and 2 components of the $b^3\Pi$ and $d^3\Delta$ states, the $R_c$ values become large, and the $D_e$ values decrease compared with the corresponding $\Lambda$–$S$ states. While, their $\omega_c$ values vary differently. The $\omega_c$ values of $d^3\Delta_1$ and $d^3\Delta_2$ decrease, whereas those of $b^3\Pi_1$ and $b^3\Pi_2$ increase. Except for the crossing point with the $b^3\Pi$ state, no other crossing points exist near the bottom of the $d^3\Delta$ state. Thus, the $d^3\Delta_1$ component has almost the same spectroscopic parameters as the $d^3\Delta$ state. And the crossing point between the $d^3\Delta$ and $1^7\Sigma^+$ states lies at about $R \sim 2.55 \ \AA$, far away from the equilibrium position of the $d^3\Delta$ state. Therefore, an avoided crossing between the $\Omega = 3$ components of the $d^3\Delta$ and $1^7\Sigma^+$ states makes the dissociation energy of $d^3\Delta$ smaller than that of the corresponding $\Lambda$–$S$ state. The avoided crossings with the $e^3\Sigma^–_{0+}, 1^5\Sigma^+_{0+}$, and $1^7\Sigma^+_{0−}$ states are far away from the bottom of the $b^3\Pi$ PEC, as a result of which the spectroscopic parameters of the $b^3\Pi_{0+}$ and $b^3\Pi_{0−}$ states are similar to those of the pure $\Lambda$–$S$ states, but their $D_e$ values become smaller than that of the $b^3\Pi$ state. Our spin–orbit splittings of the $b^3\Pi$ and $d^3\Delta$ states have been calculated to be 462.22 and 44.68 cm\(^{-1}\), respectively, being somewhat larger than the HF values [33] and the evaluated value from the perturbations on $A^1\Pi$ [20].

The $e^3\Sigma^−$ state splits into two components with the $e^3\Sigma^–_{1}$ lying below $e^3\Sigma^–_{0+}$ component. The computed fine structure splitting of the $e^3\Sigma^–$ state is only 4.61 cm\(^{-1}\). Since the avoided crossings with the $A^1\Pi, b^3\Pi, 1^5\Sigma^+$, and $1^7\Sigma^+$ states are far away from the $R_c$ of $e^3\Sigma^–$, the $R_c$ and $\omega_c$ values of two $\Omega$ states are similar to those of the $e^3\Sigma^–$ state. And the dissociation energies of two $\Omega$ states are smaller than that of the $e^3\Sigma^–$ state.

The spectroscopic parameters of the $C^1\Sigma^–_{0−}$ state are almost the same as the ones of the $C^1\Sigma^–$ state. While the avoided crossings with the $\Omega = 0^−$ components of the $1^5\Pi$ and $1^7\Sigma^+$ states are far from the $R_c$ of the $C^1\Sigma^–$ state, which decrease its dissociation energy greatly. The PEC of $A^1\Pi$ crosses with those of the $d^3\Delta, e^3\Sigma^–, 2^3\Delta, 1^5\Sigma^+, 1^5\Pi$, and $1^7\Sigma^+$ states. The PEC of $A^1\Pi$ changes greatly due to the avoided crossing with the $\Omega = 1$ components of above mentioned states, which makes the equilibrium bond length become longer, frequency increase, and dissociation energy decrease.

Because the $1^5\Sigma^+$ PEC crosses with the $A^1\Pi, D^1\Delta, e^3\Sigma^–$, and $d^3\Delta$ PECs, the PEC shapes of $\Omega = 0^+, 1$, and
Table 6. Our calculated spectroscopic parameters of the bound and quasibound Ω states of PN.

| Ω      | Te/cm−1 | Re Å | ωx/cm−1 | ωrx/ωx cm−1 | Dr/eV |
|--------|---------|------|---------|--------------|-------|
| X1Σ+0− | 0.0     | 1.4915 | 1339.98 | 6.9932       | 6.3246 |
| Exp. [29] | 0.0     | 1.4907 | 1337.00 | 6.9164       | 6.4396 |
| Exp. [17] | 0.0     | 1.49086 | 1337.24 | 6.983        | 6.3209 |
| a3Σ−1    | 25943.66 | 1.6517 | 934.98  | 6.4651       | 3.1050 |
| a3Σ−2    | 33073.73 | 1.6535 | 963.34  | 5.7023       | 2.8961 |
| b3Σ+2    | 33104.89 | 1.6397 | 840.84  | 1.6037       | 2.2130 |
| b3Σ+1    | 33108.41 | 1.6413 | 833.87  | 0.3886       | 2.1216 |
| b3Π+0    | 33502.36 | 1.5461 | 1149.17 | 7.8178       | 3.2613 |
| b3Π+1    | 33505.00 | 1.5474 | 1149.22 | 7.9594       | 2.1633 |
| b3Π0−1   | 33917.61 | 1.5802 | 1349.65 | 1.4521       | 2.7881 |
| b3Π0−2   | 33964.58 | 1.5764 | 1346.48 | 0.8557       | 2.7930 |
| e3Σ+0−1  | 38095.53 | 1.6270 | 984.32  | 29.653       | 3.0134 |
| e3Σ+0−2  | 38100.14 | 1.6276 | 989.62  | 7.7889       | 3.0238 |
| C1Σ+0−   | 38178.05 | 1.5907 | 1007.78 | 5.6096       | 3.0017 |
| A1Π+     | 39796.90 | 1.5606 | 1112.23 | 25.0013      | 2.8027 |
| Exp. [20] | 39805.64 | 1.547 | 1103.00 | 7.25         |
| Exp. [17] | 39805.60 | 1.5467 | 1103.09 | 7.22         |
| D1Δ          | 40814.82 | 1.5072 | 1045.88 | 32.086       | 2.6736 |
| t3Ω+1      | 43710.79 | 1.8466 | 1174.76 | 8.6622       | 2.3129 |
| t3Ω+2      | 45329.19 | 1.7491 | 1628.54 | 50.285       | 2.1152 |
| t3Ω+3      | 45741.37 | 1.7190 | 1897.91 | 81.077       | 2.0764 |
| t3Π1+1,2   | 50302.26 | 1.7816 | 705.61  | 20.542       | 0.9000 |
| t3Π1+2,3,4 | 57030.04 | 2.5234 | 926.16  | 57.175       | 0.6674 |
| t3Π2+1     | 53098.38 | 1.7815 | 702.79  | 3.6819       | 1.1582 |
| t3Π0+1     | 53132.39 | 1.7816 | 716.08  | 9.3035       | 1.2176 |
| t3Π0+2     | 53162.46 | 1.7814 | 705.66  | 11.549       | 1.2146 |
| t3Π0+3     | 53164.00 | 1.7817 | 703.91  | 3.4975       | 1.1561 |
| t3Π0−0     | 53194.29 | 1.7815 | 706.39  | 3.8501       | 1.1463 |
| t3Δ0+1     | 54438.27 | 1.9142 | 709.67  | 14.873       | 0.9858 |
| t3Δ0+2,1   | 54400.30 | 1.8866 | 989.26  | 10.677       | 1.3700 |
| t3Δ0−1,2   | 60568.41 | 2.3563 | 894.53  | 68.344       | 0.2955 |
| t3Δ0−2     | 54438.27 | 1.9142 | 709.67  | 14.873       | 0.9858 |
| E1Σ+0−1    | 54918.04 | 1.8644 | 691.77  | 10.068       | 1.3167 |
| E1Σ+0−2    | 54918.04 | 1.8644 | 691.77  | 10.068       | 1.3167 |

2 components of 1Σ+ change greatly, which make their Rs shorten, and ωx and Dr values increase greatly.

The 1Π1 state separates into six components with Ω = −1, 0+, 0, 1, 2, and 3 with the spin–orbit interactions. Since the 1Π1 PEC crosses with the 1Σ+ and 2Δ PECs far away from it equilibrium distance, the Rs and ωx values of Ω = −1, 0+, 0, 1, 2, and 3, and the first well of Ω = 3 components are quite close to that of the 15Π1 state, while the Dr values of Ω = 0+ and 1 components are slightly larger than that of the corresponding Λ–S state. The second potential well of the 1Π1 state is located at R = 2.5334 Å, which is 3957.78 cm−1 higher than the first one with a depth of 5382.94 cm−1. The 23Δ state splits into three components with a separation of 45.87 cm−1 in an inverted order. The 23Δ state crosses with the 15Π state near its equilibrium internuclear separation. Hence, the PECs of three components of 23Δ change greatly, which make the spectroscopic parameters of all three components change greatly. And the 23Δ2 state possesses two potential wells located at 1.8865 and 2.3563 Å with depths of 11049.79 and 2383.37 cm−1, respectively.

The E1Σ+0− PEC does not cross with the other Ω PECs of the same symmetry near the equilibrium distance, which makes no influence on its Te, Rs, and ωx. While, the avoided crossing with the 25Σ+0− state at long internuclear distance makes the Dr value of E1Σ+0− decrease.

The energy separations of the Ω components of the b3Π, d3Σ−, 15Π, 25Σ+, and 23Δ states are significant, hence, the spin–orbit coupling effects should not be neglected when analyzing the spectroscopic properties of these states.

In the energy range of 60000–90000 cm−1, there are many curve crossings between the Λ–S states, and when the spin–orbit coupling effects are considered, various avoided crossings would be come into being. The PECs of Ω states in this region are much more complex than the lower energy regions due to the avoided crossing rule. And some Ω states have two or more shallow potential wells. The depths of these wells are rather small, and some of them even cannot support one vibrational level. The spectra of PN in this energy range will be very diffuse and hard to be observed in experiment.
We have tabulated the \( G(\nu), B(\nu), \) and \( D(\nu) \) results of the \( X^1 \Sigma^+ \) and \( A^1 \Pi_1 \) states in Table S4 of Supplementary materials in order to facilitate comparison. As shown in Tables S2–S4, we find that the effects of spin–orbit coupling on molecular constants of \( X^1 \Sigma^+ \) and \( A^1 \Pi_1 \) states are small. For example, for the \( X^1 \Sigma^+ \) states, the largest contributions of spin–orbit coupling on the \( G(\nu), B(\nu), \) and \( D(\nu) \) are equal to 12.48 cm\(^{-1}\) at \( \nu = 4 \), and \(-3.5089 \times 10^{-7} \) cm\(^{-1}\) at \( \nu = 1 \), respectively. For the \( A^1 \Pi_1 \) state, the largest contributions of spin–orbit coupling on \( G(\nu), B(\nu), \) and \( D(\nu) \) are only 0.30 cm\(^{-1}\) at \( \nu = 19 \), 0.000003 cm\(^{-1}\) at \( \nu = 11 \), and 7.2110 \times 10^{-8} \) cm\(^{-1}\) at \( \nu = 1 \), respectively. Comparing with the experiments, excellent agreement can be found between the present \( G(\nu), B(\nu), \) and \( D(\nu) \) and the measurements for the \( X^1 \Sigma^+ \) and \( A^1 \Pi_1 \) states. For example, for the \( X^1 \Sigma^+ \) state, the largest deviation from the experimental data is only \(-15.09 \) (0.10%) \[18\] and \(-13.65 \) (0.09%) cm\(^{-1}\) \[28\] when \( \nu = 11 \). Similarly, for the \( A^1 \Pi_1 \) state, the largest deviations between our calculations and the experimental ones are only 3.71 cm\(^{-1}\) (0.08%) for the \( G(\nu) \) at \( \nu = 4 \) \[20\] and \(-0.0024 \) cm\(^{-1}\) (0.33%) for the \( B(\nu) \) at \( \nu = 1 \) \[20\], respectively. The present molecular constants for the \( X^1 \Sigma^+ \) and \( A^1 \Pi_1 \) states are accurate and reliable.

### 3.3. Curve crossings and perturbations

A larger number of excited states of PN lie in a small range as shown in Tables 2–4. Their PECs are therefore close together with numerous crossings occurring. We depict the amplified views of the curve crossing regions in Figure 6. This high density should favour their mutual interactions and some of them involve states of different spin multiplicities and symmetries, which makes the analysis of the observed rovibrational resolved spectra quite difficult. Thus, an accurate ab-initio calculation is definitely helpful to explain the experimentally observed perturbations and identify the possibly predissociation phenomena. We have calculated the spin–orbit coupling matrix elements of interacting states in the crossing regions from the Cartesian components of the Breit-Pauli operator to determine the coupling strength. Figure S2 displays the evolution of the absolute values of spin–orbit matrix elements as functions of internuclear distances. The definitions of the schematic representation for the spin–orbit matrix elements used in these figures are given in Table S5 of Supplementary materials.

As shown in Figure 6(a), in the energy range of 35000–45000 cm\(^{-1}\) with \( R = 1.2–1.8 \) Å, the potential wells of the \( A^1 \Pi_1 \) state and the \( d^3 \Delta, e^3 \Sigma^-, C^1 \Sigma^- \), and \( D^1 \Delta \) states have overlaps, and the crossing points of their PECs are at \( R = 1.4136, 1.5415, 1.5325, 1.6598, \) and 1.7644 Å, respectively, near the bottom of the \( A^1 \Pi_1 \) state. The \( A^1 \Pi_1 \) state is 1478.38, 1552.78, and 6575.46 cm\(^{-1}\) higher than the \( C^1 \Sigma^- \), \( e^3 \Sigma^- \), and \( d^3 \Delta \) states, respectively, and 1153.12 cm\(^{-1}\) lower than the \( D^1 \Delta \) state as shown in Tables 2 and 3. The lowest vibrational levels of \( A^1 \Pi_1 \) would be perturbed by those of the \( d^3 \Delta \), \( e^3 \Sigma^- \), \( C^1 \Sigma^- \), and \( D^1 \Delta \) states due to the vibronic coupling. Our calculations indicate that the \( A^1 \Pi_1 \) \( \nu' = 3 \) level would be perturbed by the \( d^3 \Delta \) \( \nu' = 10 \) and 11 levels, the \( A^1 \Pi_1 \) \( \nu' = 2 \) levels would be perturbed simultaneously by two different states, i.e. the \( e^3 \Sigma^- \) \( \nu' = 2 \) and 3 levels and the \( D^1 \Delta \) \( \nu' = 0 \) and 1 levels, and the \( A^1 \Pi_1 \) \( \nu' = 0 \) and 1 levels would perturb the \( C^1 \Sigma^- \) \( \nu' = 1 \) and 2 levels. These conclusions are in good accord with the observations of Saraswathy et al. \[18,20\], Le Floch et al. \[22\] and de Brouckère et al. \[37\]. Nevertheless, Abbiche et al. \[38\] predicted that the \( A^1 \Pi_1 \) \( \nu' = 1 \) level is perturbed simultaneously by the \( e^3 \Sigma^- \) \( \nu' = 9 \) level, the \( b^3 \Pi \) the \( \nu' = 5 \) level, the \( d^3 \Delta \) the \( \nu' = 10 \) level, and

![Figure 6](image_url)  
Figure 6. Amplified views of the curve crossing regions (a) between the singlet and triplet \( \Delta-S \) states; (b) between the triplet, quintet and septet \( \Delta-S \) states.
the C1Σ− ν′ = 4 level, which is significantly different from our conclusions. The absolute values of our computed spin–orbit matrix elements for (A1Π−d3Δ) and (A1Π−e3Σ−) are 14.59 and 13.98 cm−1 at the crossing points, respectively. On the one hand, these crossings lie in the potential wells of the d3Δ and e3Σ− states. On the other hand, their spin–orbit interactions are weak. Thus, the spin–orbit couplings between the A1Π state and the d3Δ and e3Σ− states could not induce certain predissociations, but enhance the perturbations on the lower vibrational spectrum of the A1Π state. In addition, the attractive sides of the A1Π and a3Σ+ PECs crosses at R = 1.2893 Å, in between the A1Π ν′ = 16 and 17 levels. The absolute value of the spin–orbit coupling matrix element for (A1Π−a3Σ+) is only 6.33 cm−1 at the crossing point, which is insignificant and could be negligible.

In the energy range of 50000–80000 cm−1 within 1.8–3.1 Å, the E1Σ+, 23Δ, 23Π, 23Σ−, 23Σ+, 33Σ+, 33Π, and 43Π states cross with the A1Π state at R = 2.0329, 1.9852, 2.3328, 2.3600, 2.3199, 2.5416, 2.4287, and 3.0656 Å, respectively. The E1Σ+ state is 15264.46 cm−1 higher than the A1Π state. Thus, the A1Π ν′ ≥ 17 vibrational levels would be perturbed by those of the E1Σ+ state due to the vibronic coupling. The potential wells of the A1Π state and those of the 23Δ, 23Π, and 23Σ− states have overlaps, and their crossing points lie in between the A1Π ν′ = 14 and 15 levels (or the A1Π ν′ = 0 level); in between the A1Π ν′ = 31 and 32 levels (or in the 23Π ν′ = 11 and 12 levels); and in between the A1Π ν′ = 33 and 34 levels (or in the 23Σ− ν′ = 10 and 11 levels). These crossing points are all located in the potential wells of the 23Δ, 23Π, and 23Σ− states. So the predissociation pathways A1Π → 23Δ, 23Π, and 23Σ− would not be open. However, the computed spin–orbit couplings for (A1Π−23Δ), (A1Π−23Π), and (A1Π−23Σ−) are 26.74, 43.34, and 11.91 cm−1 at their crossings, respectively, which indicates that the effects of spin–orbit coupling should not be neglected. Thus, when the spin–orbit coupling is taken into account, the curve crossing between the 23Δ and A1Π states becomes an avoided crossing between the 23Δ1 and A1Π1 states, which is located near the A1Π1 ν′ = 14 vibrational level.

In the vicinity of the avoided crossing between the 23Δ and A1Π1 PECs, the electronic wave functions of them mix together, and thus their spectra would become diffuse. The same case could be said for the 23Π and 23Σ− states. The A1Π PEC crosses with the repulsive sides of the 23Σ+, 33Σ+, 33Π, and 43Π PECs. And the absolute values of our computed spin–orbit–matrix elements are 12.43, 46.62, 23.57, and 28.13 cm−1 for (A1Π−23Σ+), (A1Π−33Σ+), (A1Π−33Π), and (A1Π−43Π) at the crossing points, respectively. Hence, several weak predissociation pathways could be provided for the A1Π state, such as A1Π ν′ ≥ 29 vibrational levels via 23Σ+, ν′ ≥ 33 levels via 33Π, ν′ ≥ 38 levels via 33Σ+, and ν′ ≥ 51 levels via 43Π.

Base on the discussion above, we can conclude that the perturbations of the lower vibrational levels (ν = 0–3) of A1Π to be the result of the interaction with the adjacent singlet and triplet states, such as the d3Δ, e3Σ−, C1Σ+, and D1Δ states. The 23Δ, 23Π, E1Σ+, and 23Σ− states are identified here to be perturbing states of the higher ν′ ≥ 14 vibrational levels of A1Π state. Meanwhile, the higher vibrational levels of the A1Π state is predissociative, mainly coming from the spin–orbit couplings with the 23Σ+, 33Σ+, 33Π, and 43Π states. For these reasons mentioned above, we could conclude that the ν′ ≥ 14 vibrational levels of the A1Π state are hard to detect.

The D1Δ state crosses with the 23Δ, 23Σ+, 33Σ+, 23Π, 33Π, 43Π, 23Σ−, and E1Σ+ states at R = 2.0067, 2.3332, 2.5517, 2.3546, 2.4298, 3.2996, 2.3854, and 2.0931 Å, respectively, in the region from 54000 to 72000 cm−1. The D1Δ–23Σ+, D1Δ–33Σ+, and D1Δ–23Σ− transitions are forbidden. The spin–orbit couplings between them are all equal to zero. The interactions between D1Δ–33Π and D1Δ–43Π are extremely weak and could be negligible. The absolute values of our computed spin–orbit–matrix elements for (D1Δ–23Δ) and (D1Δ–23Π) are 108.35 and 59.78 cm−1 at the crossing points, and the latter is in accord with the value of 58.95 cm−1 for (D1Δ–23Π) reported by Abbiche et al. [38]. Because these crossing points are all in the potential wells of the 23Δ and 23Π states, the D1Δ (ν′ ≥ 14) → 23Δ and D1Δ (ν′ ≥ 30) → 23Π predissociation pathways would not be open. However, the spin–orbit interactions between the D1Δ state and the 23Δ and 23Π state are significant, the strong spin–orbit couplings will make the PECs and spectroscopic parameters of Ω = 2 components of the D1Δ, 23Δ, and 23Π states change greatly as can be seen from Figure S1 and Table 6. The D1Δ and E1Σ+ PECs have overlaps, thus, the ν′ ≥ 14 vibrational levels of D1Δ would be perturbed by those of the E1Σ+ state.

Besides crossing with the D1Δ and A1Π states, the E1Σ+ state also crosses with the 23Δ, 23Π, 33Π, 43Π, and 23Σ− states at R = 1.7801, 2.5873, 2.6224, 3.5837, and 3.0879 Å, with the 23Σ− state twice at R = 1.5085 and 2.4451 Å, and with the 33Σ− state at R = 2.7018 Å, respectively. The E1Σ+ ν′ = 0 and 1 vibrational levels would be perturbed by the 23Δ ν′ = 1 and 2 levels due to the vibronic coupling. The 23Π state is 6098.52 cm−1 higher than the E1Σ+ state, and the potential well of the former is basically in that of the latter. Thus, the E1Σ+ ν′ ≥ 10 vibrational levels could be perturbed by those of the 23Π state, and the strong spin–orbit coupling between the E1Σ+ and 23Π states would enhance...
this perturbation. This is essentially in agreement with the measurement reported by Coquart and Prudhomme [23], who observed twelve vibrational levels of the E1Σ+ state. Our calculations indicate the absolute value of our calculated spin–orbit matrix element for (E1Σ+−3ΣΠ) is 19.89 cm−1 at the crossing point, which is in accord with the reported value by Abbiche et al. [38], and the spin–orbit interactions between the E1Σ+ state and the 4ΣΠ and 2ΣΣ− states are insignificant and could be negligible. The E1Σ+, 2ΣΣ+ states are extremely small and are insignificant. The 2ΣΣ+ state crosses with the 3ΣΣ+ state twice at R = 1.6727 and 2.0335 Å, respectively. The absolute value of our computed spin–orbit matrix element for (2ΣΣ+−3ΣΠ) is equal to 54.80 cm−1 at the crossing point. Thus, the 2ΣΣ+ state could predissociate via the 3ΣΣ+ state. While, the spin–orbit interactions between the 2ΣΣ+ state and the 2ΣΣ−, 3ΣΣ−, and 4ΣΠ states are extremely small and are insignificant. The 2ΣΣ+ state crosses with the 3ΣΣ+ state twice at R = 1.5634 and 2.3673 Å, and with the 2Δ state at R = 1.7952 Å. The 2ΣΣ+ state and 2 vibrational levels would be perturbed by the 3ΣΣ+ state. The 2ΣΣ+ state crosses with the 3ΣΣ+ state twice at R = 1.5634 and 2.3673 Å, and with the 2Δ state at R = 1.7952 Å. The 2ΣΣ+ state and 2 vibrational levels would be perturbed by the 3ΣΣ+ state. Therefore, the 2ΣΣ+ state does not cross with the 1Φ and 3ΣΠ states, while, the potential well of the 2ΣΣ+ state is located in that of the 3ΣΠ state. Thus, the absolute values of our computed spin–orbit matrix elements for (2ΣΣ+−3ΣΠ) are 6.98/5.67, 9.70, and 104.86 cm−1 at their crossing points. The spin–orbit interactions between the 2ΣΣ+ state and the 2ΣΣ+ and 3ΣΣ− states are insignificant. The 2Δ state lies in that of the 3ΣΠ state, and the potential well of the 1Φ state lies in that of the 2ΣΣ+ state. Therefore, the 2ΣΣ+ state would be perturbed by those of the 1Φ state due to the vibronic coupling. The 2ΣΣ+ state would be perturbed by the 3ΣΠ state due to the Coriolis coupling.

As shown in Figure 6(b), the b3Π PEC crosses with the PECs of the a3Σ+, d3Δ, 15Σ+, and e3Σ− states at R = 1.4016, 1.5683, 1.8608, and 1.8722 Å, respectively. The absolute values of our computed spin–orbit matrix elements are 16.78, 13.44, 16.43 and 17.31 cm−1 for the (a3Σ+−b3Π), (d3Δ−b3Π), (e3Σ−−b3Π) and (b3Π−15Σ+) states, respectively, at their curve crossing points. The absolute value of our computed spin–orbit matrix element for (b3Δ−b3Π) at the crossing point is slightly smaller than 20 cm−1 reported by Abbiche et al. [38]. Thus, these weak perturbations on the b3Π state would be negligible. The b3Π state would be perturbed by the 15Σ+ state at R = 2.3673 Å, and with the 21Σ+ and 10 levels by the 15Σ+ state. The 21Σ+ state would be perturbed by those of the 31Σ+ state. The computed spectroscopic parameters and molecular constants of bound states match the available experimental data very well. Various curve crossings related to the A1Π, b3Π, D1Δ, E1Σ+, and 2ΣΣ+ states, and so on are analyzed, and several possible predissociation pathways have been predicted with the help of the calculated spin–orbit coupling matrix elements. We propose that the d3Δ, e3Σ+, C1Σ−, and D1Δ states are responsible for the perturbations of the A1Π state due to the vibronic coupling. The a3Σ+, d3Δ, E1Σ+, and 2ΣΣ− states are perturbing states of the A1Π state due to vibronic and spin–orbit couplings.
This induces the $\nu' \geq 14$ vibrational levels of the $A^1\Pi$ state are hard to detect. Meanwhile, several weak predissociation pathways could provide for the higher vibrational levels of the $A^1\Pi$ state via the $2^3\Sigma^+, 3^3\Sigma^+, 3^3\Pi$, and $4^3\Pi$ states. The $2^3\Sigma^+$ and $2^3\Delta$ states are the perturbing states of the lower vibrational levels of the $E^1\Sigma^+$ state due to the vibronic coupling, and the higher vibrational levels of the $E^1\Sigma^+$ state would be perturbed due to the strong spin–orbit interaction with the $2^3\Sigma$ state. We hope that future improvements in experimental techniques will be able to verify these predictions.

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**References**

[1] N. Grevesse and A.J. Sauval, Space Sci. Rev. 85, 161 (1998). doi:10.1023/A:1005161325181
[2] L.M. Ziurys, Astrophys. J. 321, L81 (1987). doi:10.1086/185010
[3] T. Yamaguchi, S. Takano, N. Sakai, T. Sakai, S.-Y. Liu, Y.-N. Su, H. Hirano, S. Takakawa, Y. Aikawa, H. Nomura and S. Yamamoto, Publ. Astron. Soc. Japan. 63, L37 (2011). doi:10.1093/pasj/63.5.L37
[4] F. Fontani, V.M. Rivilla, P. Caselli, A. Vasyunin and A. Palau, Astrophys. J. Lett. 822, L30 (2016). doi:10.3847/2041-8205/822/2/L30
[5] J. Curry, L. Herzberg and G. Herzberg, J. Chem. Phys. 1, 749 (1933). doi:10.1063/1.1749238
[6] J. Curry, L. Herzberg and G. Herzberg, Z. Phys. 86, 348 (1933). doi:10.1007/BF01330645
[7] J. Raymonda and W. Klemperer, J. Chem. Phys. 55, 232 (1971). doi:10.1063/1.1675513
[8] F.C. Wyse, E.L. Manson and W. Gordy, J. Chem. Phys. 57, 1106 (1972). doi:10.1063/1.1678365
[9] J. Hoefi, E. Tiemann and T. Törring, Z. Naturforsch. A. 27, 703 (1972). doi:10.1515/zna-1972-0424
[10] M.B. Moeller and S.J. Silvers, Chem. Phys. Lett. 19, 78 (1973). doi:10.1016/0009-2614(73)87067-8
[11] M. Wu and T.P. Fehlin, Chem. Phys. Lett. 36, 114 (1975). doi:10.1016/0009-2614(75)85700-9
[12] D.K. Bulgin, J.M. Dyke and A. Morris, J. Chem. Soc. Faraday Trans. 2. 73, 983 (1977). doi:10.1039/F29777300983
[13] R.M. Atkins and P.L. Timms, Spectrochimica Acta A 33, 853 (1977). doi:10.1016/0584-8539(77)80083-4
[14] E.O. Huffman, G. Tarbutton, K.L. Elmore, W.E. Cate, H.K. Walters Jr and G.V. Elmore, J. Am. Chem. Soc. 76, 6239 (1954). doi:10.1021/ja01653a006
[15] O.M. Uy, E.J. Kohl and K.D. Carlson, J. Phys. Chem. 72, 1611 (1968). doi:10.1021/jc00851a037
[16] K.A. Gingerich, J. Phys. Chem. 73, 2734 (1969). doi:10.1021/jc00842a047
[17] K.P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure, Constants of Diatomic Molecules, vol. IV (Van Nostrand–Reinhold Press, New York, 1979).
[18] S.N. Ghosh, R.D. Verma and J. Vanderlinde, Can. J. Phys. 59, 1640 (1981). doi:10.1139/p81-216
[19] P. Saraswathy and G. Krishnamurthy, Pramana 23, 665 (1984). doi:10.1007/BF02846689
[20] P. Saraswathy and G. Krishnamurthy, Pramana – J. Phys. 29, 53 (1987). doi:10.1007/BF02845678
[21] T.L. Henshaw, M.A. MacDonald, D.H. Stedman and R.D. Coombe, J. Phys. Chem. 91, 2838 (1987). doi:10.1021/j100295a037
[22] A.C. Le Floch, F. Melen, I. Dubois and H. Bredohl, J. Mol. Spectrosc. 176, 75 (1996). doi:10.1006/jmsp.1996.0063
[23] B. Coquart and J.C. Prudhomme, J. Phys. B: At. Mol. Phys. 13, 2251 (1980). doi:10.1088/0022-3700/13/11/016
[24] B. Coquart and J.C. Prudhomme, J. Mol. Spectrosc. 87, 75 (1981). doi:10.1016/0022-2852(81)90084-9
[25] R.D. Verma and S.N. Ghosh, J. Phys. B: At. Mol. Phys. 17, 3529 (1984). doi:10.1086/0022-3700/17/17/022
[26] A.G. Maki and F.F. Lovas, J. Mol. Spectrosc. 85, 368 (1981). doi:10.1016/0022-2852(81)90209-5
[27] R. Ahlrichs, M. Bär, H.S. Plitt and H. Schnöckel, Chem. Phys. Lett. 161, 179 (1989). doi:10.1016/0009-2614(89)85053-5
[28] I.K. Ahmad and P.A. Hamilton, J. Mol. Spectrosc. 169, 286 (1995). doi:10.1006/jmsp.1995.1022
[29] G. Cazzoli, L. Cludi and C. Puzzarini, J. Mol. Struct. 780-781, 260 (2006). doi:10.1016/j.molstruc.2005.07.010
[30] R.D. Verma, S.N. Ghosh and Z. Iqbal, J. Phys. B: At. Mol. Phys. 20, 3961 (1987). doi:10.1088/0022-3700/20/16/009
[31] H. Bredohl, I. Dubois, D. Macau–Hercot, F. Remy, J. Breton and J.M. Esteve, J. Mol. Spectrosc. 156, 292 (1992). doi:10.1016/0022-2852(92)90232-D
[32] H. Bredohl, J. Breton, I. Dubois, A. Elaïfi, J.M. Esteve, D. Macau–Hercot, F. Remy, A. Saouli and E. Somé, J. Mol. Spectrosc. 171, 125 (1995). doi:10.1006/jmsp.1995.1106
[33] R.A. Gottschos, R.W. Field and H. Lefebvre–Brion, J. Mol. Spectrosc. 70, 420 (1978). doi:10.1016/0022-2852(78)90180-7
[34] F. Grein and A. Kapur, J. Mol. Spectrosc. 99, 25 (1983). doi:10.1016/0022-2852(83)90289-8
[35] G. de Brouckère, D. Feller, J.A. Koot and G. Berthier, J. Phys. B: At. Mol. Opt. Phys. 25, 4433 (1992). doi:10.1088/0953-4075/25/21/011
[36] G. de Brouckère, D. Feller and J.A. Koot, J. Phys. B: At. Mol. Opt. Phys. 26, 1915 (1993). doi:10.1088/0953-4075/26/13/014
[37] G. de Brouckère, D. Feller, A.C.L. Floch, F. Melen, I. Dubois and H. Bredhol, J. Phys. B: At. Mol. Opt. Phys. 29, 6069 (1996). doi:10.1088/0953-4075/29/24/013
[38] K. Abbiche, M. Salah, K. Marakchi, O.K. Kabbaj and N. Komia, Mol. Phys. 112, 117 (2014). doi:10.1080/00268976.2013.804216

[39] Z. Qin, J.M. Zhao and L.H. Liu, J. Quant. Spectrosc. Radiat. Transfer. 227, 47 (2019). doi:10.1016/j.jqsrt.2019.02.002

[40] Z. Qin, T. Bai and L.H. Liu, Chem. Phys. Lett. 782, 139028 (2021). doi:10.1016/j.cplett.2021.139028

[41] M. Semenov, N. El–Kork, S.N. Yurchenko and J. Tennyson, Phys. Chem. Chem. Phys. 23, 22057 (2021). doi:10.1039/D1CP02537F

[42] G.L. Gutsev, P. Jena and R.J. Bartlett, Phys. Rev. A. 58, 4972 (1998). doi:10.1103/PhysRevA.58.4972

[43] K.A. Peterson and T.H. Dunning, Jr, J. Chem. Phys. 117, 10548 (2002). doi:10.1063/1.1520138

[44] A.E. Kemeny, J.S. Francisco, D.A. Dixon and D. Feller, J. Chem. Phys. 118, 8290 (2003). doi:10.1063/1.1565317

[45] J.M. Wang, J.F. Sun and D.H. Shi, B. Chin. Phys. 19, 113404 (2010). doi:10.1088/1674-1056/19/11/113404

[46] R. Glaser, C.J. Horan and P.E. Haney, J. Phys. Chem. 97, 1835 (1993). doi:10.1021/j100111a020

[47] L. Yorke, S.N. Yurchenko, L. Lodi and J. Tennyson, MNRAS. 445, 1383 (2014). doi:10.1093/mnras/stu1854

[48] R.B. Viana, P.S.S. Pereira, L.G.M. Macedo and A.S. Pimentel, Chem. Phys. 363, 49 (2009). doi:10.1016/j.chemphys.2009.07.008

[49] S. Coriani, D. Marchesan, J. Gauss, C. Hättig, T. Helgaker and P. Jorgensen, J. Chem. Phys. 123, 184107 (2005). doi:10.1063/1.204387

[50] T. Kupka, M. Leszczyska, K. Ejsmont, A. Mnich, M. Broda, K. Thangavel and J. Kaminský, Int. J. Quantum Chem. 119, e26032 (2019). doi:10.1002/qua.26032

[51] C.E. Cotton, J.S. Francisco and A.O. Mitrushchenkov, J. Chem. Phys. 138, 074314 (2013). doi:10.1063/1.4790604

[52] H.–J. Werner, P.J. Knowles, R. Lindh, F.R. Manby, M. Schütz, P. Celani, T. Korona, A. Mitrushchenkov, G. Rauhut, T.B. Adler, R.D. Amos, A. Bernhardsson, A. Berning, D.L. Cooper, M.J.O. Deegan, A.J. Dobbyn, F. Eckert, E. Goll, C. Hampel, G. Hetzer, T. Hrenar, G. Knizia, C. Köppi, Y. Liu, A.W. Lloyd, R.A. Mata, A.J. May, S.J. Mcnicholas, W. Meyer, M.E. Mura, A. Nicklass, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, U. Schumann, H. Stoll, A.J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, and A. Wolf, MOLPRO, verion 2010.1, a package of ab initio programs, see http://www.molpro.net (2010).

[53] H.J. Werner and P.J. Knowles, J. Chem. Phys. 82, 3503 (1985). doi:10.1063/1.448627

[54] P.J. Knowles and H.J. Werner, Chem. Phys. Lett. 115, 259 (1985). doi:10.1016/0009-2614(85)80025-7

[55] H.J. Werner and P.J. Knowles, J. Chem. Phys. 89, 5803 (1988). doi:10.1063/1.455556

[56] P.J. Knowles and H.J. Werner, Chem. Phys. Lett. 145, 514 (1988). doi:10.1016/0009-2614(88)87412-8

[57] T.V. Van Mourik, A.K. Wilson and T.H. Dunning, Jr, Mol. Phys. 96, 529 (1999). doi:10.1080/00268979909482990

[58] D.E. Woon and T.H. Dunning, Jr, Mol. Phys. 98, 1358 (1999). doi:10.1080/00268979909482990

[59] D.E. Woon and T.H. Dunning, Jr, Mol. Phys. 101, 8877 (1999). doi:10.1080/00268979909482990

[60] H. Liu, D.H. Shi, J.F. Sun and Z.L. Zhu, Spectrochim. Acta A: Mol. Biomol. Spectrosc. 168, 148 (2019). doi:10.1007/s10633-019-01051-0

[61] H. Liu, D.H. Shi, J.F. Sun and Z.L. Zhu, Mol. Phys. 115, 714 (2017). doi:10.1080/00268979709482990

[62] T. Muller, M. Dallos, H. Lischa, Z. Dubrovay and P.G. Szalay, Theor. Chem. Acc. 105, 227 (2001). doi:10.1007/s002140000210

[63] M. Reiher and A. Wolf, J. Chem. Phys. 121, 10945 (2004). doi:10.1063/1.1818681

[64] A. Wolf and M. Reiher, J. Chem. Phys. 124, 64102 (2006). doi:10.1063/1.2161179

[65] W.A. de Jong, R.J. Harrison and D.A. Dixon, J. Chem. Phys. 114, 48 (2001). doi:10.1063/1.1329891

[66] A. Berning, M. Schweizer, H–J Werner, P.J. Knowles and P. Palmieri, Mol. Phys. 98, 1823 (2000). doi:10.1080/0026897009483386

[67] R.J. Le Roy, LEVEL 7.7: A computer program for solving the radial Schrödinger equation for bound and quasi-bound levels, University of Waterloo: Chemical Physics Research Report No. CP–661 (2005).

[68] NIST. https://www.nist.gov/pml/atomic-spectra-database.

[69] K.K. Irikura, J. Phys. Chem. Ref. Data. 36, 389 (2007). doi:10.1063/1.2436891