Accurate *ab initio* study of low-lying electronic states of phosphorus nitride radical*

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This paper employs the highly accurate valence internally contracted multireference configuration interaction method to investigate the potential energy curves (PECs) for the ground state ($X^1\Sigma^+$) and two low-lying excited states ($A^1\Pi$ and $D^1\Delta$ of phosphorus nitride (PN) radical with the correlation-consistent basis set, aug-cc-pV6Z, in the valence range. Relativistic effects are considered in these calculations. The spectroscopic constants of the $X^1\Sigma^+$ and $A^1\Pi$ states are calculated based on the PECs, and the results are in good accord with the available experimental data. The first 30 vibrational states for the $X^1\Sigma^+$ state and the first 40 vibrational states for the$A^1\Pi$ state are determined when $J = 0$. For each vibrational state, molecular constants $G(\upsilon)$, $B(\upsilon)$ and $D(\upsilon)$ are also attained.

Keywords: PN radical, potential energy curves, spectroscopic constant, molecular constants
PACC: 3480, 3120C, 3520G

1. Introduction

Although phosphorus has a lower cosmic abundance, it is of interest due to its fundamental role in biological systems. The chemistry of small phosphorus-containing molecules has been widely investigated. One of the simplest phosphorus systems is phosphorus nitride (PN), which is the first phosphorus-containing molecule found in the interstellar medium.[1]

The electronic spectrum of PN radical was first investigated by Curry *et al.* in 1933[2] who reported the vibrational level with respect to the ground state up to the vibrational numbers υ=3. The spectrum was observed in the ultraviolet emission of an electric discharge through phosphorous and nitrogen.[3,4] The subject rested there until 1971 when Raymonda and Klemperer[5] reported the molecular beam electric resonance spectrum. Henceforth the PN radical became the subject of considerable work, both experimentally and theoretically. The study with respect to electronic spectrum of PN radical attracted considerable interests of experimentalists.[6−13] The latest experimental results of spectroscopic constants were given by Ahmad and Hamilton[14] using an Fourier transform infrared spectrometer. The photoelectron spectrum was recorded also,[15−17] which gives information on electronic structures of ions, and indirectly, on the electronic structure of PN radical. The contributions of Ghosh *et al.*[18] is particularly noteworthy because it provides the molecular constants in the ground state ($X^1\Sigma^+$) and the excited state ($A^1\Pi$) up to υ=11 when the rotational quantum number $J = 0$. After the first theoretical study was performed by Gottscho *et al.*,[19] who reported the results of *ab initio* calculations and semiempirical estimates based on the atomic spin-orbit splittings, a variety of theoretical methods were carried out on PN radical by a number of workers.[20−33] Most of the theoretical work on PN radical were confined to the study of the spectroscopic properties. Comparing with the experimental results, we find that not a theoretical information about vibrational manifolds of PN radical can be available, though these data are very useful in the ro-vibrational transition calculations.

For the $X^1\Sigma^+$ state, many of these properties have been observed experimentally, while for the $A^1\Pi$ state relatively few results are known. In comparison with them, the properties of $D^1\Delta$ state are unknown experimentally. This condition makes it possible to calibrate the theoretical methods using the available experimental data and to establish the likely reliability of the predicted values for properties which have

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not been measured experimentally.

The purpose of this work is twofold. First, we will obtain more high-quality theoretical values with respect to the $X^1\Sigma^+$ and $A^1\Pi$ states of PN radical. Second, we hope that the present experimentally unknown results of $D^1\Delta$ will offer reference for the future measurements or theoretical investgations.

2. Computational methods

The highly accurate valence internally contracted multireference configuration interaction (MRCI) approach[34] is employed to generate the potential energy curves (PECs) for the $X^1\Sigma^+$, $A^1\Pi$ and $D^1\Delta$ state in this work, which is a way to systematically include those configuration state functions that contribute most significantly to the correlation energy. It has been proved to be precise in treating small systems.[35−37] All the calculations are carried out with the full valence complete active space self-consistent field (CASSCF) method followed by the MRCI approach in MOLPRO 2008.1 program package[38] at the largest correlation-consistent basis set,[39,40] aug-cc-pV6Z, in the valence range. Thus, the full valence CASSCF is employed as the reference wavefunction for the MRCI calculations at the present investigation. Relativistic effects are considered in these calculations by the Douglas–Kroll relativistic one electron integrals.

The MOLPRO uses the Abelian point group symmetry only. For the PN radical with $C_{\infty v}$ symmetry, the Abelian point group symmetry, C_{2v} symmetry with the order of the irreducible representations as $a_1/b_1/b_2/a_2$, will be used. In detail, for the electronic states of PN, eight molecular orbitals (MOs) are put into the active space, here including four a_1, two b_1 and two b_2 symmetry MOs, which correspond to the $3s3p$ shell of P and the $2s2p$ shell of N atom. The rest of electrons in the PN are put into the closed-shell orbitals, here including four a_1, one b_1 and one b_2 symmetry MOs. Using these MOs (eight a_1, three b_1 and three b_2 and zero a_2), we find that the PECs of these electronic states calculated at the present MRCI/aug-cc-pV6Z level are smooth and convergent over the present internuclear separation range.

The PECs calculations are performed at 0.02 nm interval. However, the internuclear distance range which is limited by the convergence are different from state to state. For the $X^1\Sigma^+$ state, the energy scanning calculations are performed from about 0.05 to 175 nm. The same calculations are performed from about 0.05 to 190 nm for the $A^1\Pi$ state and from about 0.06 to 2.05 nm for the $D^1\Delta$ state. The smaller step 0.005 nm is adopted around the equilibrium positions so that the properties of the PECs are displayed more clearly.

In order to display the properties of the states more clearly, the spectroscopic constants are fitted with the aid of module VIBROT in Molcas program package[41] using the obtained PECs. At last, the molecular constants are also calculated with VIBROT.

3. Results and discussion

3.1. Spectroscopic parameters of PN radical

The spectroscopic paremeters at the MRCI/aug-cc-pV6Z level as well as experiments and other available theoretical calculations are listed in Table 1 for convenient comparison. Selected spectroscopic constants, dissociation energy, equilibrium distance, harmonic frequency, anharmonic constant, rotation constant and rigid-rotational factor, are respectively noted in standard notations as D_e, R_e, ω_e, $\omega_e\chi_e$, α_e, B_e.

For the $X^1\Sigma^+$ state, a number of theoretical investigations were made on the spectroscopic properties. Of these investigations, the earliest one was performed by Grein and Kapur[21] who used the configuration interaction (CI) method with a $(11s7p/6s4p)$ contracted Gaussian basis set augmented by two sets of d functions for P atom and a $(9s5p/4s2p)$ Gaussian basis set augmented by two sets of d functions for N atom. As tabulated in Table 1, their results are far from the experimental expectator R_e and B_e. Peterson and Woods[23] calculated partial spectroscopic constants (R_e, ω_e, $\omega_e\chi_e$, α_e) using the singles and doubles CI (SDCI) method. Their R_e is close to experiments while ω_e, $\omega_e\chi_e$ and α_e are far from them. Wong and Radom[24] performed the CASSCF/6-311G(MC)(d) calculations for PN radical. As can be seen in Table 1, their D_e, $\omega_e$and $\omega_e\chi_e$ values are poor in accuracy in comparison with the experiments. In the work of de Brouckère *et al.*,[26] multireference SDCI (MRSDCI) calculations were performed with an extended Gaussian basis set which is of approximately 'triple zeta' quality. The deviations for their $\omega_e\chi_e$ are up to 110.65% and 22.98% for α_e in comparison with the experiment.[2] Peterson and

Dunning[29] used the CCSD(T) method and a series of standard correlation consistent basis sets, cc-pVnZ cc-pCVnZ and cc-pwCVnZ (n=D, T, Q and 5), to study the properties of PN radical Core-valence correlation effects were considered in their calculations and the best results with cc-pwCV5Z are listed in Table 1. It is not difficult to find that the value of D_e improved obviously. However, only D_e, R_e and ω_e were evaluated and ω_e is too large in comparison with the experimental results. Kemeny *et al.*[30] used the same method to calculate R_e, ω_e, $\omega_e\chi_e$ with cc-pV(Q+d)Z. Obviously, their $\omega_e\chi_e$ value is smaller than the experimental results. Recently, Cazzoli *et al.*[33] repeated the spectroscopic parameter calculations by the CCSD(T) theory with a series of correlation-consistent basis sets. The best favourable results were determined by extrapolation with the cc-pV(Q+d)Z and cc-pV(5+d)Z basis sets. Obviously, their ω_e value is larger than experimental result while $\omega_e\chi_e$ is smaller. More recently, Muniz and Jorge[32] carried out the Moller–Plesset second-order (MP2) calculations on D_e, R_e, ω_e with DZP, cc-pVDZ, ADZP and aug-cc-pVDZ sets, and their best results was obtained with aug-cc-pVDZ. However, their D_e and ω_e results deviated from the experimental value greatly. The MRCI method employed in this work was used by Woon and Dunning[28] with cc-pVDZ, cc-pVTZ, cc-pVQZ and cc-pV5Z ever. As tabulated in Table 1, their results are inferior to the present ones in comparison with the experiment.[2]

From Table 1, it is obvious that the results in this work are in excellent agreement with the available experimental data. For example, one can easily calculate that the spectroscopic parameters, D_e, R_e, ω_e and B_e, deviate from the experiments[2] only by 0.330%, 0.531%, 0.254% and 0.497%, respectively. Here, the deviations for $\omega_e\chi_e$ and α_e are somewhat large, but they are only 2.086% and 2.333%, respectively.

Table 1. Comparison of spectroscopic parameter among experiments and other available theoretical calculations for the PN radical at the MRCI/aug-cc-pV6Z level of theory.

source	D_e/cm^{-1}	R_e/nm	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}
$X^1\Sigma^+$						
This work	6.2792	0.14948	1333.84	6.83729	0.78230	0.00544
Exp. [2]	6.3	0.14869	1337.24	6.983	0.78621	0.00557
Exp. [6]	—	0.149086	1335.6	6.5	0.786489	—
Exp. [11]	—	0.149105	1336.98	6.906	0.78628	0.00531
Exp. [12]	—	0.1491	1337.0	6.88	0.78648	0.00554
Exp. [14]	—	—	1336.948	6.8958	0.7864844	0.0055337
Exp. [18]	—	—	1337.0	6.88	0.786486	0.005538
Theory [21]	5.49	0.1488	1400.6	9.33	0.789	0.0066
Theory [23]	—	0.14938	1367.0	6.36	—	0.005137
Theory [24]	5.172	0.1516	1299	7.5	0.76	0.0054
Theory [26]	—	0.15040	1358.4	14.71	0.7728	0.00685
Theory [28]	5.565	0.1496	1333.7	6.81	0.781	0.0054
Theory [29]	6.2587	0.14894	1351.30	—	—	—
Theory [30]	—	0.14968	1336.2	6.6	—	—
Theory [32]	5.70	0.1552	1363.5	—	—	—
Theory [33]	6.3589	0.14894	1352.2	6.58	0.788412	0.005363
A^1						
This work	5.1245	0.15501	1100.24	7.21846	0.727505	0.00633
Exp. [2]	5.1	0.15424	1103.09	7.222	0.73071	0.00663
Exp. [12]	—	0.1547	1103.0	7.25	0.7310	0.0064
Exp. [18]	—	—	1103.0	7.25	0.7310	0.00641
Theory [19]	—	0.1492	1380	21	0.785	0.01
Theory [21]	4.35	0.1566	1071.7	11.4	0.713	0.0075
Theory [27]	—	0.15732	1066.3	10.72	0.7063	0.00183
D^1						
This work	5.1522	0.16196	1002.269	4.28833	0.665056	0.00281
Theory [19]	—	0.1587	1190	5.7	0.692	0.004
Theory [21]	4.18	0.1622	967.9	1.97	0.664	0.0070
Theory [27]	—	0.16252	1105.7	16.17	0.6619	0.00298

Few theoretical investigations were made on the spectroscopic parameters for the $A^1\Pi$ and $D^1\Delta$ states. Of these investigations, the earliest one was performed by Gottscho *et al.*[19] However their results for $A^1\Pi$ state deviate from the experiment[2,12,18] greatly except R_e. Later, Grein and Kapur[21] calculated the spectroscopic parameters of the $A^1\Pi$ and $D^1\Delta$ states using the same method which had been used for the ground state. Obviously, for the $A^1\Pi$ state, their D_e value is too small while $\omega_e\chi_e$ value is too large in comparison with the experimental results. The MRSDCI method was carried out for these two low-lying states by de Brouckère *et al.*,[27] who obtained an improved value of $\omega_e\chi_e$ for the $A^1\Pi$ state. However, one can easily see that their ω_e and $\omega_e\chi_e$ are still larger than the experimental results.

From Table 1, it is obvious that the results in this work are in excellent agreement with the available experimental data. For example, one can easily calculate that the spectroscopic parameters, D_e, R_e, ω_e and B_e, deviate from the experiments[2] only by 0.330%, 0.531%, 0.254% and 0.497%, respectively. Here, the deviations for $\omega_e\chi_e$ and α_e are somewhat large, but they are only 2.086% and 2.333%, respectively.

Few theoretical investigations were made on the spectroscopic parameters for the $A^1\Pi$ and $D^1\Delta$ states. Of these investigations, the earliest one was performed by Gottscho *et al.*[19] However their results for $A^1\Pi$ state deviate from the experiment[2,12,18] greatly except R_e. Later, Grein and Kapur[21] calculated the spectroscopic parameters of the $A^1\Pi$ and $D^1\Delta$ states using the same method which had been used for the ground state. Obviously, for the $A^1\Pi$ state, their D_e value is too small while $\omega_e\chi_e$ value is too large in comparison with the experimental results. The MRSDCI method was carried out for these two low-lying states by de Brouckère *et al.*,[27] who obtained an improved value of $\omega_e\chi_e$ for the $A^1\Pi$ state. However, one can easily see that their ω_e and $\omega_e\chi_e$ are still larger than the experimental results.

As listed in Table 1, the spectroscopic parameters for the $A^1\Pi$ state in this work agree well with the available experiments. For example, the deviations of the D_e, R_e, ω_e, $\omega_e\chi_e$ and B_e α_e from the experiments[2] are only 0.480%, 0.499%, 0.258%, 0.0049 and 0.438%, respectively. As to α_e, our result is closer to the latest experiments,[12] the deviation is of only 1.093%.

To our knowledge, the experimental spectroscopic parameters of the $D^1\Delta$ state have not been reported in the literatures. We are unable to compare the present results with the experiments. Therefore only the present results together with available theoretical calculations are listed in Table 1. According to the discussion about the $A^1\Pi$ state, we can see that our method is superior to the previous methods[19,21,27] for the PN radical, so it is safe to say that our same calculations of the $D^1\Delta$ state are better than theirs. We hope that the present results can give reference for the future experimental and theoretical investigations.

From the above discussion, one can see that the present spectroscopic parameters based on the PECs are of high quality. So these PECs of PN radical are credible and can be used to find the molecular constants.

3.2. Molecular constants of PN radical

Based on the interaction potential of the PN radical. We determine the first 30 vibrational states for the $X^1\Sigma^+$ state and the first 40 vibrational states for the $A^1\Pi$ state when $J = 0$ with the aid of module VIBROT in Molcas program package. For each vibrational state, vibrational level, inertial rotation constant and centrifugal distortion constant are attained. Here, the vibrational level, inertial rotation and centrifugal distortion constants are noted in standard notations $G(\upsilon)$, $B(\upsilon)$ and $D(\upsilon)$ respectively.

The first 30 vibrational levels for the $X^1\Sigma^+$ state when $J = 0$ are tabulated in Table 2 together with $B(\upsilon)$ and $D(\upsilon)$. In experiment, only $B(\upsilon)$ and $D(\upsilon)$ values of the partial vibrational levels can be found in the literatures[2,18] to our knowledge. These $B(\upsilon)$ and $D(\upsilon)$ values have been collected in Table 2. From Table 2, it is not difficult to find that the present results conform almost perfectly to the available measurements. The deviations from the latest experiments[18] are of only 0.528%, 0.520%, 0.513% for the $B(\upsilon)$ at $\upsilon = 0$, 1 and 2, respectively. It is also easy to obtain the deviations for the $D(\upsilon)$ from the experiment[18] which are of only 1.272%, 0.982%, 0.024% at $\upsilon = 0$, 1 and 2, respectively.

The first 40 vibrational levels for the $A^1\Pi$ state when $J = 0$ are tabulated in Table 3 together with $B(\upsilon)$ and $D(\upsilon)$ as well as the available experiments. The largest deviations from the latest experiments[13] do not exceed 0.478% for the $B(\upsilon)$. We did not compare the $D(\upsilon)$ with experiments because the variation of experimental $D(\upsilon)$ is rather erratic.

Table 2. Comparison of molecular constants with experiments for the $X^1\Sigma^+$ state when $J = 0$ at the MRCI/ aug-cc-pV6Z level of theory.

v	$G(v)/\mathrm{cm}^{-1}$	$B(v)/\mathrm{cm}^{-1}$			$10^6 D(v)/\mathrm{cm}^{-1}$	
	this work	this work	Exp. [2]	Exp. [18]	this work	Exp. [18]
0	664.58	0.779573	0.78340	0.78371567	1.07781	1.0917
1	1983.85	0.774114	0.77790	0.77816569	1.08068	1.0914
2	3289.82	0.768631	0.77226	0.772600010	1.08326	1.083
3	4582.40	0.763130	0.76671	0.767021110	1.08659	1.093
4	5861.48	0.757618		0.7614285	1.09076	1.109
5	7126.96	0.752104		0.755629	1.09550	1.11
6	8378.72	0.746571		0.750329	1.09934	1.11
7	9616.66	0.741017		0.744444	1.10383	1.12
8	10840.68	0.735436		0.738848	1.10743	1.12
9	12050.66	0.729821		0.733106	1.11104	1.22
10	13246.51	0.724167		0.72791	1.11461	1.02
11	14428.11	0.718478		0.72271	1.11879	1.02
12	15595.36	0.712753		1.12418		
13	16748.16	0.706998		1.13053		
14	17886.39	0.701215		1.13828		
15	19009.95	0.695404		1.14726		
16	20118.73	0.689564		1.15711		
17	21212.64	0.683694		1.16816		
18	22291.55	0.677788		1.18024		
19	23355.37	0.671844		1.19321		
20	24403.99	0.665857		1.20708		
21	25437.29	0.659816		1.22147		
22	26455.19	0.653716		1.23628		
23	27457.56	0.647547		1.25178		
24	28444.31	0.641298		1.26786		
25	29415.33	0.634962		1.28472		
26	30370.51	0.628530		1.30282		
27	31309.74	0.621991		1.32210		
28	32232.92	0.615335		1.34266		
29	33139.94	0.608551		1.36496		

Table 3. Comparison of molecular constants with experiments for the $A^1\Pi$ state when $J = 0$ at the MRCI/aug-cc-pV6Z level of theory.

v	$G(v)/\mathrm{cm}^{-1}$	$B(v)/\mathrm{cm}^{-1}$				$10^6 D(v)/\mathrm{cm}^{-1}$		
	this work	this work	Exp. [2]	Exp. [13]	Exp. [18]	this work	Exp. [13]	Exp. [18]
0	548.46	0.724343	0.72740	0.727744	0.727926	1.27591	1.273	1.424
1	1634.56	0.718011	0.72077	0.721382	0.72140	1.28088	1.302	1.453
2	2706.29	0.711676		0.715094	0.715005	1.28581	1.215	0.92
3	3763.71	0.705337		0.707404	0.70653	1.29076	1.082	0.85
4	4806.89	0.698995			0.701718	1.29558		1.3717
5	5835.92	0.692652			0.695544	1.30058		1.4010
6	6850.87	0.686308			0.689036	1.30517		1.546
7	7851.80	0.679958			0.68013	1.30976		1.24
8	8838.80	0.673614			0.675938	1.31514		1.5015
9	9811.93	0.667269			0.66921	1.31949		1.549
10	10771.27	0.660924			0.66201	1.32439		0.8120
11	11716.88	0.654577				1.32910		
12	12648.85	0.648237				1.33426		
13	13567.25	0.641902				1.33959		

Table 3. (*Continued*).

v	$G(v)/\mathrm{cm}^{-1}$	$B(v)/\mathrm{cm}^{-1}$				$10^6 D(v)/\mathrm{cm}^{-1}$		
	this work	this work	Exp. [2]	Exp. [13]	Exp. [18]	this work	Exp. [13]	Exp. [18]
14	14472.15	0.635575				1.34505		
15	15363.62	0.629253				1.35095		
16	16241.74	0.622936				1.35649		
17	17106.58	0.616626				1.36227		
18	17958.21	0.610322				1.36793		
19	18796.70	0.604028				1.37371		
20	19622.14	0.597742				1.37954		
21	20434.58	0.591465				1.38497		
22	21234.11	0.585201				1.39041		
23	22020.80	0.578950				1.39553		
24	22794.72	0.572714				1.40073		
25	23555.94	0.566491				1.40613		
26	24304.54	0.560280				1.41167		
27	25040.59	0.554080				1.41796		
28	25764.16	0.547885				1.42476		
29	26475.33	0.541694				1.43248		
30	27174.17	0.535500				1.44135		
31	27860.75	0.529298				1.45128		
32	28535.14	0.523082				1.46268		
33	29197.43	0.516843				1.47584		
34	29847.67	0.510574				1.49131		
35	30485.96	0.504263				1.50956		
36	31112.35	0.497897				1.53118		
37	31726.92	0.491459				1.55667		
38	32329.74	0.484931				1.58682		
39	32920.89	0.478292				1.62234		

4. Conclusions

In this paper, we have investigated the PECs, spectroscopic parameters of the ground $X^1\Sigma^+$ state and the low-lying $A^1\Pi$ excited state of PN radical by using the MRCI theory in combination with a very large correlation-consistent basis set, aug-cc-pV6Z, in the valence range. Relativistic effects have been considered in the calculation process. It is exciting to find that the computational spectroscopic parameters are in agreement with the available experiments. The other excited state $D^1\Delta$, which is unknown experimentally, has also been studied. The results can offer reference for the future measurements or theoretical investigations. With the PECs obtained at the MRCI/aug-cc-pV6Z level, the first 30 vibrational states for the $X^1\Sigma^+$ state and the first 40 vibrational states for the $A^1\Pi$ state when $J = 0$ have been obtained with the aid of Molcas program package. For each vibrational state, vibrational level, inertial rotation constant and centrifugal distortion constant are attained. Comparison with the available experiments shows that our work gives the satisfactory results.

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