Investigations of spectroscopic parameters and molecular constants for $X^1\Sigma_g^+$, $w^3\Delta_u$, and $W^1\Delta_u$ electronic states of P_2 molecule*

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The potential energy curves (PECs) of three low-lying electronic states ($X^1\Sigma_g^+$, $w^3\Delta_u$, and $W^1\Delta_u$) of P_2 molecule are investigated using the full valence complete active space self-consistent field (CASSCF) method followed by the highly accurate valence internally contracted multireference configuration interaction (MRCI) approach in conjunction with the correlation-consistent basis set in the valence range. The PECs of the electronic states involved are modified by the Davidson correction and extrapolated to the complete basis set (CBS) limit. With these PECs, the spectroscopic parameters of the three electronic states are determined and compared in detail with the experimental data. The comparison shows that excellent agreement exists between the present results and the available experimental data. The complete vibrational states are computed for the $w^3\Delta_u$ and $W^1\Delta_u$ electronic states when the rotational quantum number J equals zero and the vibrational level $G(v)$, the inertial rotation constant B_v, and the centrifugal distortion constant D_v of the first 30 vibrational states are reported, which accord well with the experimental data. The present results show that the two-point extrapolation scheme can obviously improve the quality of spectroscopic parameters and molecular constants.

Keywords: spectroscopic parameter, molecular constant, Davidson correction extrapolation

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1. Introduction

The study of structure and spectrum for molecules containing phosphorus has attracted much attention. The interest possibly arises from the contribution to the etching and epitaxial growth of phosphoruscontaining semiconductors.[1,2] As the simplest phosphoruscontaining molecule P_2 has received considerable attention and its molecular properties have been the subject of numerous investigations in the past several decades, both experimentally[3−16] and theoretically.[17−31]

In the experiment, the P_2 spectrum has been extensively investigated by using various methods and the spectroscopic parameters and the molecular constants have been determined by analysing the electronic, the vibrational, and the rotational spectra.[6−13] Of these experiments, the noteworthy one was carried out by Amiot *et al.*[13] in 1978. In their investigation, they recorded two new electronic systems ($b^3\Pi_g \rightarrow w^3\Delta_u$ and $A^1\Pi_g \rightarrow W^1\Delta_u$) and reported on the spectroscopic parameters and molecular constants of two new electronic states $w^3\Delta_u$ and $W^1\Delta_u$ for the first time. Based on the previous observations, some accurate spectroscopic parameters and molecular constants were compiled by Huber and Herzberg[14] prior to 1979. In theory, the first calculations were done as early as 1967 by Boyd and Lipscomb[17] who performed the self-consistent-field (SCF) calculations with basis sets of Slater orbitals. To date, a number of theoretical studies[18−31] have been performed and spectroscopic parameters have been determined. However, on the one hand, the theoretical work mainly focuses on the ground state and few studies are for evaluating the error by the method and basis sets. On the other hand, no theoretical investigation of the $w^3\Delta_u$ and $W^1\Delta_u$ excited electronic

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states can be found for the spectroscopic parameters (D_e, R_e, ω_e, $\omega_e x_e$, α_e, B_e). Therefore, in order to completely understand the spectroscopic and the molecular properties for P_2 molecule, it is an urgent task to perform high-level calculations for the $X^1\Sigma_g^+$, $w^3\Delta_u$, and $W^1\Delta_u$ electronic states.

The rest of this paper is organized as follows. First, the potential energy curves (PECs) for the low-lying electronic states ($X^1\Sigma_g^+$, $w^3\Delta_u$, and $W^1\Delta_u$) are calculated by the highly accurate valence internally contracted multireference configuration interaction (MRCI) approach[32] and the MRCI including Davidson correction (+Q) in combination with the correlation-consistent basis set, in the valence range. Then, the PECs of electronic states involved here are extrapolated to the complete basis set (CBS) limit based on the basis sets aug-cc-pV5Z and aug-cc-pV6Z. Finally, with these PECs of the P_2 molecule, the spectroscopic parameters and the vibrational manifolds are determined for all the electronic states when the rotational quantum number J is equal to zero ($J = 0$). This work is the first complete theoretical investigation on spectroscopic parameters and molecular constants of $w^3\Delta_u$ and $W^1\Delta_u$ electronic states for the P_2 molecule so far.

2. Calculation details

The MRCI approach is a way to systematically include those configuration state functions (CSFs) that contribute most significantly to the correlation energy. The multireference treatment involves computing full valence, complete active space self-consistent field (CASSCF) wave functions and subsequently recovering dynamical correlation by means of internally contracted multireference configuration interaction calculations. That is to say, the full valence CASSCF is employed as the reference wavefunction for the MRCI calculations. The MRCI is a very robust method with a long tradition,[33−38] which unfortunately lacks size-extensivity. Therefore, several methods have been developed for the computation of size-extensivity corrections to MRCI.[39] The simplest one is the Davidson correction. In the present work, the MRCI mothod and MRCI method including the the Davidson correction (+Q) are used for the $X^1\Sigma_g^+$, $w^3\Delta_u$, and $W^1\Delta_u$ electronic states in conjunction with the correlation-consistent basis sets, aug-cc-pV6Z.

The calculations of potential energies are carried out in MOLPRO 2008.1 program package.[40] In the MOLPRO only the Abelian point group symmetry is used. For molecules with degenerate symmetry, an Abelian subgroup must be employed. That is, for the diatomic molecular such as P_2 with $D_{\infty h}$ symmetry, it will be substituted by D_{2h} symmetry with the order of the irreducible representations as $a_g/b_{3u}/b_{2u}/b_{1g}/b_{1u}/b_{2g}/b_{3g}/a_u$. Specifically, for the electronic states $X^1\Sigma_g^+$, $w^3\Delta_u$, and $W^1\Delta_u$ of P_2 molecule, eight molecular orbitals (MOs) are put into the active space, including two a_g's, one b_{3u}, one b_{2u}, two b_{1u}'s, one b_{2g}, and one b_{3g} symmetry MOs, which correspond to the 3s3p shells of the P atom. The rest of the electrons in the molecule are put into the closed-shell orbitals, including three a_g's, one b_{3u}, one b_{2u}, three b_{1u}'s, one b_{2g}, and one b_{3g} symmetry MOs. These MOs (five a_g's, two b_{3u}'s, two b_{2u}'s, five b_{1u}'s, two b_{2g}'s, and two b_{3g}'s) having been used, the PECs of the three electronic states obtained here are smooth.

In order to accurately determine the PECs, the interval used here is 0.02 nm for each electronic state. Only near the equilibrium position will the interval be 0.005 nm. The smaller step is adopted around the equilibrium position of each electronic state so that the properties of each PEC can be displayed more clearly.

With the aid of module VIBROT in the MOLCAS 7.4 program package,[41] the spectroscopic parameters and vibrational manifolds are evaluated for these three electronic states. In the module VIBROT, the potential is fitted to an analytical form by the cubic splines. The ro-vibrational Schrödinger equation is then solved by the Numerov's method for one vibrational state at a time and for a number of rotational quantum numbers as specified by the input, the spectroscopic parameters are determined by fitting the vibrational levels. The spectroscopic parameters obtained at the MRCI level and the MRCI+Q level here are given in Table 1.

To allow for extrapolation schemes it is mandatory to have a sequence of basis sets that converge uniformly to CBS. The correlation-consistent basis sets of Dunning and coworkers are chosen, since these basis sets provide a well-defined series and the calculated energies can be extrapolated to the CBS limit. The formula[39] of two-point extrapolation for electron correlation energy with two successive basis sets is as follows:

$$\Delta E_\infty = \frac{\Delta E_{X+1}(X+1)^3 - \Delta E_X X^3}{(X+1)^3 - X^3}, \qquad (1)$$

where ΔE is the electron correlation energy and X is the cardinal number of the basis set. The SCF refer-

ence energy and the correction energy have different convergence characteristics. In order to obtain the extrapolated total energies, the reference energy must be considered as well. Owing to the lack of accurate separate exponents for reference energy and electron correlation energy,[39] the same exponents in both cases are used in the present work and the total energies are extrapolated according to Eq. (1). It has been empirically found that the most reliable results[39] are obtained by two-point extrapolation. In this work, we use the correlation-consistent aug-cc-pV5Z and aug-cc-pV6Z to carry out the extrapolation. The extrapolation scheme is applied to energies only, and the spectroscopic parameters are also fitted by the same VIBROT program. These results are collected in Table 2.

3. Results and discussion

3.1. Spectroscopic parameters

Here, the effects on the spectroscopic parameters by the size-extensicity corrections and basis set size are discussed in detail. As very small quantities, the $\omega_e y_e$ and γ_e values which do not have a great influence on molecular constants are not contained in the following discussion.

Table 1. Spectroscopic parameters obtained by MRCI and MRCI+Q methods for $P_2(X^1\Sigma_g^+)$, $P_2(w^3\Delta_u)$, and $P_2(W^1\Delta_u)$.

Source	T_e/eV	R_e/nm	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}	$10^3\omega_e y_e$/cm^{-1}	B_e/cm^{-1}	$10^3\alpha_e$/cm^{-1}	$10^6\gamma_e$/cm^{-1})
$X^1\Sigma_g^+$								
MRCI		0.19028	778.19	2.8390	14.433	0.3006	14551	1.8706
MRCI+Q		0.19037	775.80	2.8337	18.157	0.3004	1.4646	1.4197
Exp.[14]		0.18934	780.77	2.835	–	0.30362	149	–
$w^3\Delta_u$								
MRCI	3.0859	0.20735	587.73	2.4995	1.4862	0.2536	1.4366	0.6603
MRCI+Q	2.9774	0.20725	588.36	2.5134	2.9250	0.2535	1.4389	0.4396
Exp.[13]	3.0163	–	591.3	2.5	–	0.25604	1.409	–
$W^1\Delta_u$								
MRCI	4.0011	0.20462	622.66	2.3209	0.4986	0.2600	1.3636	0.7225
MRCI	3.8489	0.20450	624.65	2.3267	0.9535	0.2603	1.3585	0.8798
Exp.[13]	3.8555	–	627206	2.331	–	0.2628	14	–

Generally, we find that the total energies near the equilibrium position calculated by MRCI+Q method are always about 0.029 E_h lower than those obtained by MRCI for the three electronic states.

From Table 1, one can find that the Davidson modification lowers the excitation energies. For example, for the $w^3\Delta_u$ electronic state the T_e with the Davidson modification at AV6Z level is equal to 2.9774 eV, which deviates from the experimental data[13] only by 0.389 eV. Whereas the T_e value without the Davidson modification is 3.0859 eV, which deviates from the data[13] by 0.695 eV. It is clearly shown that the Davidson correction can obviously improve the T_e quality for the two excited electronic states.

The Davidson correction brings small changes for all of the R_e values. Such a modification shortens the R_e by 0.00010 nm and 0.00012 nm for the $w^3\Delta_u$ and $W^1\Delta_u$ and lengthens the R_e by 0.00009 nm for the $X^1\Sigma_g^+$ electronic state. For the $X^1\Sigma_g^+$ electronic state, the change makes the R_e closer to the experimental data.[14]

From Table 1, it is not difficult to see that the Davidson modification makes the ω_e and the $\omega_e x_e$ increase for $w^3\Delta_u$ and $W^1\Delta_u$ electronic states, whereas it makes the ω_e and the $\omega_e x_e$ decrease for the $X^1\Sigma_g^+$ electronic state. Specifically, the ω_e changes by adding the correction are 2.39, 0.63, and 1.99 cm^{-1}; the $\omega_e x_e$ changes are 0.0053, 0.0139, and 0.0058 cm^{-1} for the $X^1\Sigma_g^+$, the $w^3\Delta_u$, and the $W^1\Delta_u$ electronic states, respectively.

As for the other parameters B_e and α_e, the effect by the Davidson modification is very small. For example, the modification lowers the B_e by 0.0003 cm^{-1} for the $W^1\Delta_u$ and raises 0.0002, 0.0001 cm^{-1} for the $X^1\Sigma_g^+$ and the $w^3\Delta_u$ electronic states. This trend makes the B_e closer to the experimental data.[13,14]

On the whole, the Davidson correction brings about the obvious improvement of spectroscopic parameters for the three electronic states. A uniform trend is observed that the total energies near the equilibrium position decrease about 0.005 E_h with basis set increasing from the aug-cc-pV5Z to the 56-extrapolation at the level of either MRCI or MRCI+Q theory. All the spectroscopic parameters obtained by the extrapolation based on the AV5Z and AV6Z basis sets whether the Davidson correction is considered or not, are listed in Table 2. For simplicity, the following discussion in this section is based only on the results with the Davidson modification.

Table 2. Spectroscopic parameters obtained by the extrapolations for $P_2(X^1\Sigma_g^+)$, $P_2(w^3\Delta_u)$, and $P_2(W^1\Delta_u)$.

Source	T_e/eV	R_e/nm	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}	$10^3\omega_e y_e$/cm^{-1}	B_e/cm^{-1}	$10^3\alpha_e$/cm^{-1}	$10^6\gamma_e$/cm^{-1}
$X^1\Sigma_g^+$								
MRCI								
AV5Z		0.19042	776.22	2.8360	14.186	0.3002	1.4554	1.7785
AV6Z		0.19028	778.19	2.8390	14.433	0.3006	14551	1.8706
56-ex		0.19009	780.81	2.8481	14.084	0.3012	1.4546	1.5607
MRCI+Q								
AV5Z		0.19049	773.79	2.8403	15.758	0.3000	1.4627	1.9284
AV6Z		0.19037	775.80	2.8337	18.157	0.3004	1.4646	1.4197
56-ex		0.19014	778.57	2.8211	21.732	0.3011	1.4672	1.7104
Exp.[14]		0.18934	780.77	2.835	–	0.30362	149	–
$w^3\Delta_u$								
MRCI								
AV5Z	3.0780	0.20752	586.27	2.5061	2.1889	0.2529	1.4338	1.0329
Av6Z	3.0859	0.20735	587.73	2.4995	1.4862	0.2536	1.4366	0.6603
56-ex	3.0969	0.20712	589.47	2.5063	2.9201	0.2539	1.4378	0.6767
MRCI+Q								
AV5Z	2.9691	0.20743	586.92	2.5151	2.7679	0.2531	1.4365	0.7409
AV6Z	2.9774	0.20725	588.36	2.5134	2.9250	0.2535	1.4389	0.4396
56-ex	2.9888	0.20698	590.30	2.4961	1.1000	0.2541	1.4393	0.5911
Exp.[13]	3.0163	–	591.3	2.5	–	0.25604	1.409	–
$W^1\Delta_u$								
MRCI								
AV5Z	3.9968	0.20478	621.38	2.3207	0.5729	0.2596	1.3608	0.5225
AV6Z	4.0011	0.20462	622.66	2.3209	2.3209	0.2600	1.3636	0.7225
56-ex	4.0070	0.20441	624.45	2.3233	0.4866	0.2605	1.3675	0.9764
MRCI+Q								
AV5Z	3.8445	0.20467	623.28	2.3287	0.1242	0.2598	1.3576	0.7043
AV6Z	3.8489	0.20450	624.65	2.3267	0.9535	0.2603	1.3585	0.8798
56-ex	3.8552	0.20428	626.54	2.3260	0.6589	0.2608	1.3651	0.8651
Exp.[13]	3.8555	–	627206	2.331	–	0.2628	14	–

Note: "AV5Z" denotes aug-cc-pV5Z. "AV6Z" represents aug-cc-pV6Z. "56-ex" denotes extrapolation based on AV5Z and AV6Z.

As listed in Table 2, the extrapolation makes the T_e values generally increase and become nearer to the data[13] for the two excited states. For example, for the $W^1\Delta_u$ electronic state, the T_e values increase from 3.8445 eV to 3.8552 eV with the basis set increasing from the AV5Z to the 56-extrapolation and the corresponding deviation from the experimental data[13] changes from 0.011 eV to 0.0003 eV.

For all the three electronic states, the extrapolation shortens the R_e values compared with the results based on the AV5Z and AV6Z. Specifically, the changes from the results at the AV5Z level to the 56-

extrapolation are 0.00035, 0.00045, 0.00039 nm for the $X^1\Sigma_g^+$, the $w^3\Delta_u$, and the $W^1\Delta_u$ electronic states, respectively. For the $X^1\Sigma_g^+$ electronic state, this trend makes the R_e closer to the data.[14]

Similar to the trend of T_e values, the trend exists which raises the values of ω_e, B_e, and α_e for all three electronic states at the CBS limit. Specifically, compared with the results at the AV5Z level, the extrapolation raises the ω_e by 4.78, 3.38, and 3.26 cm^{-1}, the B_e by 0.0011, 0.001, and 0.001 cm^{-1}, raises the α_e by 0.0000045, 0.0000028, and 0.0000075 cm^{-1}, for the $X^1\Sigma_g^+$, the $w^3\Delta_u$, and the $W^1\Delta_u$ electronic states, respectively. As indicated in Table 2, the extrapolation makes the values of ω_e, B_e, and α_e closer to the experimental data.[13,14] For example, for the $w^3\Delta_u$ electronic state, the ω_e obtained by the extrapolation is equal to 590.30 cm^{-1}, which deviates from the experimental data[13] only by 1.0 cm^{-1}. Whereas the ω_e value at the aug-cc-pV5Z level is 586.92 cm^{-1} which deviates from the data[13] by 4.38 cm^{-1}.

The effect on $\omega_e x_e$ by the basis set size is also systematic. The extrapolation lowers the $\omega_e x_e$ values for each electronic state compared with the results at the AV5Z and AV6Z levels. For example, the changes from the results at the AV5Z level to the 56-extrapolation are 0.0192, 0.0190, 0.0027 cm^{-1} for the $X^1\Sigma_g^+$, $w^3\Delta_u$, and $W^1\Delta_u$ electronic states, respectively.

Obviously, the extrapolation makes the results closer to the experimental data than those obtained at the AV5Z and AV6Z levels. Therefore, we select the present results at MRCI+Q/56-extrapolation level to compare with the experimental data in the following discussion. For the convenient comparison with our results, other theoretical results and the experimental data are also presented in Table 3. A number of theoretical studies[18−31] have been performed on the ground state for the P_2. Of these investigations, three groups[22,23,27] only evaluated two spectroscopic parameters, R_e and ω_e. As can be seen in Table 3, their results are inferior to ours compared with the experimental data[14] as a whole. For example, Muniz and Jorge[23] carried out the Moller–Plesset second-order (MP2) calculations with DZP, cc-pVDZ, ADZP, and aug-cc-pVDZ sets. Their best results were obtained with aug-cc-pVDZ and their ω_e is too large compared with the experimental data.[14]

Table 3. Comparisons of spectroscopic parameters between available measurements and other calculations for $P_2(X^1\Sigma_g^+)$, $P_2(w^3\Delta_u)$, and $P_2(W^1\Delta_u)$.

Source	T_e/eV	R_e/nm	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}	$10^3\omega_e y_e$/cm^{-1}	B_e/cm^{-1}	$10^3\alpha_e$/cm^{-1}	$10^6\gamma_e$/cm^{-1}
$X^1\Sigma_g^+$								
This Work		0.19014	778.57	2.8211	21.732	0.3011	1.4672	1.7104
Exp.[7]		0.18931	780.89	2.820	–	0.30359	1477	–
Exp.[9]		–	780.89	2.820	–	–	–	–
Exp.[10]		–	780.76	2.835	–	0.30356	143	–
Exp.[14]		0.18934	780.77	2.835	–	0.30362	149	–
Theory[22]		0.1899	785.5	–	–	–	–	–
Theory[23]		0.1952	819.8	–	–	–	–	–
Theory[25]		0.1905	–	–	–	–	–	–
Theory[27]		0.1898	908	–	–	–	–	–
Theory[29]		0.1921	755	3.69	–	0.295	–	–
Theory[30]		0.1901	779	–	–	–	–	–
Theory[31]		0.19194	770.3	3.09	–	0.2955	1.44	–
$w^3\Delta_u$								
This work	2.9888	0.20698	590.30	2.4961	1.1000	0.2541	1.4393	0.5911
Exp.[13]	3.0163	–	591.3	2.5	–	0.25604	1.409	–
$W^1\Delta_u$								
This work	3.8552	0.20428	626.54	2.3260	0.6589	0.2608	1.3651	0.8651
Exp.[13]	3.8555	–	627206	2.331	–	0.2628	14	–

Note: Ref. [22]: CCSD(T)/cc-pwCV5Z; Ref. [23]: MP2/aug-cc-pVDZ; Ref. [25]: SCF/3d2f1g; Ref. [27]: MP3/6-31G*; Ref. [30]: MRCI/CBS limit; Ref. [31]: MRCI+Q/aug-cc-pVQZ".

In 1991 Widmark *et al.*[29] used the MRCI+Q method with atomic natural orbital (ANO) basis set to investigate the spectroscopic properties of P_2. As can been seen in Table 3, their results are still far from the experimental data.[14] Later Woon and Dunning[30] performed the benchmark calculations on P_2 employing the contracted MRCI and MRCI+Q methods with the correlation-consistent basis sets. Their favourable results obtained by the extrapolation with the MRCI method are listed in Table 3. Unfortunately they evaluated only the two parameters R_e and ω_e.

In 1994, de Brouckère *et al.*[31] employed the MRCI+Q calculations on P_2 using the aug-cc-pVQZ basis set. As listed in Table 3, their results greatly deviate from the available experimental data. For example, the deviations of their R_e and ω_e from the experimental data in Ref. [12] are 0.00263 cm^{-1} and 10.59 cm^{-1}, respectively.

As can be seen in Table 3, it is not difficult to find that the present spectroscopic results for the $X^1\Sigma_g^+$ electronic state are more accurate and complete than those obtained by previous theoretical calculations. For example, one can easily obtain the spectroscopic parameters, R_e ω_e, $\omega_e x_e$, and B_e, which deviate from the experiments[14] only by 0.42%, 0.28%, 0.49%, and 0.82%, respectively. Here, the deviation for α_e is somewhat large, but it is only 1.53%.

To our knowledge, there have been no theoretical spectroscopic parameters available in the literature for the $w^3\Delta_u$ and $W^1\Delta_u$ electronic states. This work is the first theoretical calculations for this electronic state to this day. From Table 1, excellent agreement can be found between the Rydberg–Klein–Rees (RKR) data and the present ones. For example for the $w^3\Delta_u$ electronic state, the values of T_e, ω_e, $\omega_e x_e$, and B_e deviate from the experimental data[13] only by 0.91%, 0.16%, 0.15%, and 0.75%, respectively; and for the $w^1\Delta_u$ electronic state, the values of T_e, ω_e, $\omega_e x_e$, and B_e deviate from the experimental data[13] only by 0.9007%, 0.10%, 0.21%, and 0.76%, respectively. Similar to the case of $X^1\Sigma_g^+$ electronic state, the deviations of α_e for the $w^3\Delta_u$ and $W^1\Delta_u$ are somewhat large, but they are only 2.15% and 2.49% respectively.

3.2. Vibrational manifolds

Using the PECs obtained by the extropalation based on the AV5Z and AV6Z basis set with the MRCI+Q approach, we determine the vibrational levels, inertial rotation constants, and centrifugal distortion constants of the $X^1\Sigma_g^+$, the $w^3\Delta_u$, and the $w^1\Delta_u$ electronic states. Owing to the length limitations of this article, we list only the first 30 vibrational states for the $w^3\Delta_u$ and $W^1\Delta_u$ electronic states when $J = 0$ in Tables 4 and 5, respectively.

Table 4. Comparisons of vibrational levels and molecular constants between the present results and experimental data for $P_2(w^3\Delta_u)$ when $J = 0$.

v	$G(v)/cm^{-1}$	B_v/cm^{-1}		$10^7 D_v/cm^{-1}$		v	$G(v)/cm^{-1}$	B_v/cm^{-1}	$10^7 D_v/cm^{-1}$
	This work	This work	Exp.[13]	This work	Exp.[13]		This work	This work	This work
	294.01	0.253406	0.255334	1.89284	1.923	15	8526.42	0.231653	1.98158
1	878.32	0.251965	0.253926	1.89698	1.967	16	9033.78	0.230186	1.99031
2	2601.34	0.250523		1.90126		17	9535.83	0.228716	2.00032
3	2032.00	0.249080		1.90570		18	10032.5	0.227242	2.01021
4	2601.34	0.247637		1.91026		19	10523.9	0.225764	2.02047
5	3165.63	0.246192		1.91528		20	11009.9	0.224284	2.03096
6	3724.86	0.244746		1.92051		21	11490.4	0.222799	2.04258
7	4279.01	0.243298		1.92571		22	11965.6	0.221310	2.05515
8	4828.05	0.241849		1.93200		23	12435.2	0.219815	2.06882
9	5371.97	0.240399		1.93754		24	12899.4	0.218313	2.08296
10	5910.73	0.238946		1.94407		25	13358.1	0.216806	2.09799
11	6444.31	0.237492		1.95075		26	13811.3	0.215292	2.11393
12	6972.69	0.236036		1.95838		27	14259.0	0.213770	2.13105
13	7495.86	0.234577		1.96542		28	14701.1	0.212241	2.14945
14	8013.77	0.233117		1.97318		29	15137.6	0.210703	2.16907

Only one study[13] has reported on the vibrational manifolds of the $w^3\Delta_u$ and the $W^1\Delta_u$ electronic states. For convenient comparison with the present results, we list these data[13] in Tables 4 and 5, respectively. For the $w^3\Delta_u$ electronic state, from Table 4, a good agreement can be found between those experimental data and the present ones. For example for the B_υ, the present results are lower than the experimental data[13] only by 0.75% and 0.77% when $\upsilon = 0$ and $\upsilon = 1$, respectively and for the D_υ, the present results deviate from the experimental data[13] are also only 1.56% and 3.55% when $\upsilon = 0$ and $\upsilon = 1$, respectively. Because the D_υ is a very small quantity, as a whole, such deviations are indeed not large.

As shown in Table 5, one can easily find that the present results of the $w^1\Delta_u$ electronic state are still in excellent agreement with the available measurements. For example, the present values of B_υ deviate from the RKR data[13] by only 0.74%, 0.72%, and 0.75% when $\upsilon = 0$, 1 and 2, respectively. As for the D_υ, as a very small quantity a good agreement also exists between previous measurements[13] and the present ones. Therefore, the present investigations are reliable.

Table 5. Comparisons of vibrational levels and molecular constants between the present results and experimental data for $P_2(W^1\Delta_u)$ when $J = 0$.

υ	$G(\upsilon)/\mathrm{cm}^{-1}$	$B_\upsilon/\mathrm{cm}^{-1}$		$10^7 D_\upsilon/\mathrm{cm}^{-1}$		υ	$G(\upsilon)/\mathrm{cm}^{-1}$	$B_\upsilon/\mathrm{cm}^{-1}$	$10^7 D_\upsilon/\mathrm{cm}^{-1}$
	This work	This work	Exp.[13]	This work	Exp.[13]		This work	This work	This work
	313.01	0.260157	0.2621	2.20809	2.3	15	9129.77	0.238794	2.00253
1	935.73	0.258798	0.2607	1.81107	2.3	16	9673.21	0.237148	2.03505
2	1553.93	0.257443	0.2594	1.81264	2.2	17	10210.5	0.235511	2.06698
3	2167.51	0.256083		1.81296		18	10741.5	0.233893	2.09435
4	2776.36	0.254721		1.81294		19	11266.1	0.232298	2.12036
5	3380.36	0.253367		1.81764		20	11784.2	0.230720	2.14268
6	3979.41	0.252021		1.82535		21	12295.7	0.229158	2.15458
7	4573.40	0.250678		1.83170		22	12800.5	0.227610	2.15847
8	5162.22	0.249339		1.82849		23	13298.4	0.226065	2.15041
9	5745.75	0.248009		1.82084		24	13789.4	0.224522	2.13039
10	6323.88	0.246665		1.82643		25	14273.4	0.222971	2.10312
11	6896.51	0.245254		1.86201		26	14750.2	0.221415	2.06604
12	7463.53	0.243729		1.91653		27	15219.7	0.219847	2.02707
13	8024.82	0.242106		1.95951		28	15681.8	0.218274	1.98301
14	8580.27	0.240447		1.98117		29	16136.5	0.216693	1.94069

Unfortunately, no experiments can be found in the literature about the $G(\upsilon)$ of both the excited states. Thus, we cannot make any direct comparison between them. However, according to the excellent agreement between the present spectroscopic parameters and the available measurements, we have reasons to believe that the results collected in Tables 4 and 5 are reliable and accurate. And the present work is the first complete theoretical investigations on the spectroscopic parameters and molecular constants of the $w^3\Delta_u$, and $W^1\Delta_u$ excited electronic states with respect to the P_2 molecule to this day.

4. Conclusions

In this paper, the PECs of three electronic states ($X^1\Sigma_g^+$, $w^3\Delta_u$, and $W^1\Delta_u$) of the P_2 molecule are studied using the MRCI theory in combination with the correlation-consistent basis set, aug-cc-pV5Z and aug-cc-pV6Z, in the valence range. The effect on PECs by the Davidson modification is taken into consideration. Then, the PECs are extrapolated to the CBS limit by the two-point total-energy extrapolation formula. With these PECs, the spectroscopic parameters are determined, and are in excellent agreement with the available experimental data. Using the PECs determined by the extrapolation at the MRCI+Q level of theory, we compute the complete vibrational states for the $w^3\Delta_u$ and $W^1\Delta_u$ electronic states when $J = 0$. For each vibrational state of both the states, we determine the vibrational level, the initial rotation constant, and the centrifugal distortion constant when $J = 0$. The present results show that the two-point total-energy extrapolation used here can obviously improve the quality of spectroscopic parameters and

molecular constants.

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