

# *Ab initio* multi-reference configuration interaction of the low-lying states of the AsP molecule

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Received October 23, 2007

Nine low-lying electronic states of the AsP molecule, including  $\Sigma^+$ ,  $\Pi$ , and  $\Delta$  symmetries with singlet, triplet, and quintet spin multiplicities, are studied using multi-reference configuration interaction method. The potential energy curves and the spectroscopic constants of these nine states are determined, and compared with the experimental observed data as well as other theoretical works available at present. Three quintet states are reported for the first time. Furthermore, the analytical potential energy functions of these states are fitted using Murrell-Sorbie function and least square fitting method.

OCIS codes: 020.0020, 300.6390, 300.6360, 300.6210.

With the development of the calculation methods of the quantum chemistry, *ab initio* calculations can give more and more accurate potential energy curves (PEC) for diatomic molecules. Moreover, based on the PECs, one can determine the spectroscopic constants by solving the Schrödinger equation of nuclear motion. So it is an effective way to research the spectroscopic properties of diatomic molecules<sup>[1–6]</sup>.

The AsP molecule has been widely researched experimentally and theoretically. Both of the ground state and a number of low-lying states were reported. In 1969, Yee *et al.*<sup>[7]</sup> studied the emission spectrum of the AsP molecule. The spectroscopic constants of the ground state were reported in their work. The  $^1\Pi - X^1\Sigma^+$  transition system of AsP molecule was researched by Harding *et al.*<sup>[8]</sup>. In 1974, Gingerich *et al.*<sup>[9]</sup> measured the mass spectrometries of the AsP molecule and the BiP molecule. The dissociation energies of the ground state for the two molecules were reported. In 1982, Rajamanickam *et al.*<sup>[10]</sup> researched the dissociation energy of the ground state of the AsP molecule from a RKR-estimated potential curve. Then in 1986, Rasanen *et al.*<sup>[11]</sup> performed the laser induced fluorescence spectroscopy experiments on the AsP and SbP molecules. The excitation spectra of these two dimers were examined, some excited electronic transition were observed. Recently, Leung *et al.*<sup>[12]</sup> presented the rotational spectrum and hyperfine structure of arsenic monophosphide using Fourier-transform microwave spectrometer. Only Toscano *et al.*<sup>[13]</sup> reported a theoretical investigation performed with linear combination of Gaussian-type orbitals-model potential local spin density method (LCGTO-MP-LSD). The geometric and electronic structures of the ground and several excited states of some group VA dimmers (N<sub>2</sub>, P<sub>2</sub>, As<sub>2</sub>, SbP, PN, AsN, AsP, AsSb, SbN, and SbP) were reported in their work. However, limited by the density functional theory (DFT) calculation level, the spectroscopic constants of the excited states reported in their work are not in good agreement with the experimental results, with the percent error of the  $w_e$  of the four excited ( $^1\Pi$ ,  $^3\Sigma^+$ ,  $^3\Pi$ ,  $^3\Delta$ ) states all larger than 5% and the percent error for the  $T_e$  around 10%. Obviously, their results do not agree with exper-

imental data satisfactorily. More accurate theoretical study is still needed in order to understand the molecule completely. So in this paper, we carry out completely active space self-consistent field/multi-reference single and double configuration interaction (CASSCF/MRSDCI) computations on nine low-lying electronic states of the AsP molecule. The PECs and spectroscopic constants of these nine states are considered. The analytical potential energy functions (APEFs) of the states, which are necessary for dynamical calculations or determination of photoelectron spectra, are also the main objective.

CASSCF/multi-reference configuration interaction (MRCI) methods are used to compute the energy points of the nine states. The CASSCF<sup>[14,15]</sup> method is used to generate the initial orbitals for the MRSDCI<sup>[16,17]</sup> computations. Dunning's correlation consistent basis sets<sup>[18–22]</sup> (aug-cc-PVQZ) are selected to describe the orbitals of the two atoms [As: (22s, 17p, 13d, 3f, 2g)/[8s, 7p, 5d, 3f, 2g]; P: (17s, 12p, 4d, 3f, 2g)/[7s, 6p, 4d, 3f, 2g]]. Nine low-lying states of  $\Sigma^+$ ,  $\Pi$ , and  $\Delta$  symmetries with singlet, triplet, and quintet spin multiplicities are considered. Because of the limitation of the MOLPRO program package, all the calculations are carried out in  $C_{2v}$  symmetry with the order of the irreducible representations  $a_1/b_1/b_2/a_2$ . In the CASSCF and the subsequent MRCI calculation, eight MOs are put into active space, including four  $a_1$ , two  $b_1$ , two  $b_2$  symmetry MOs, which correspond to the 2s2p shells of the P atom and 4s4p shells of the As atom. The rest of the electrons are put into the closed-shell orbits — ten  $a_1$ , four  $b_1$ , four  $b_2$ , and one  $a_2$ . All of the calculations are performed with the MOLPRO 2002.6 program package<sup>[23]</sup> running on the Dawning-4000A computer<sup>[24]</sup> at Ludong University. The spectroscopic constants of the nine states are calculated using the PECs with the aid of module VIBROT in MOLCAS 5.4 program package<sup>[25]</sup>.

The calculated PECs of these nine states, including  $\Sigma^+$ ,  $\Pi$  and  $\Delta$  symmetries with singlet, triplet and quintet spin multiplicities, are presented in Fig. 1. The properties of the PEC of the  $^5\Delta$  state cannot be seen clearly from this figure. Actually, the  $^5\Delta$  state is a van der Waals state with a shallow potential well at about 0.5079 nm. We enlarge its PEC around the equilibrium bond length as

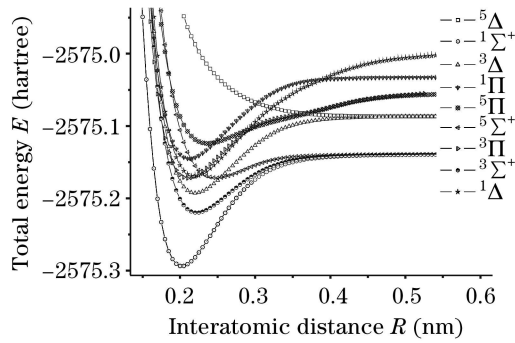


Fig. 1. Potential energy curves of the ground state and some low-lying states for the AsP molecule, and *ab initio* calculation at MRCI/aug-cc-PVQZ level.

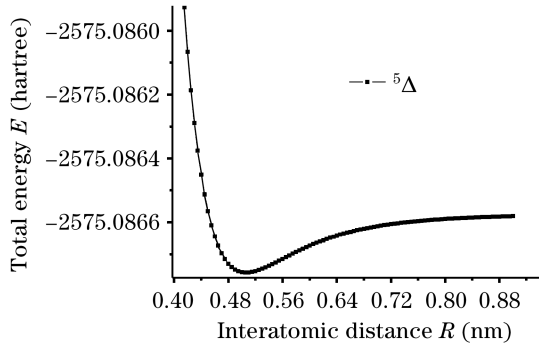


Fig. 2. Potential energy curves of the  $^5\Delta$  state for the AsP molecule, and *ab initio* calculation at MRCI/aug-cc-PVQZ level.

shown in Fig. 2. The calculated spectroscopic constants of the nine states compared with the previous theoretical and experimental data are listed in Table 1. It should be noted that the  $R_e$  and  $w_e$  of the ground state calculated at the LCGTO-MP-LSD level<sup>[13]</sup> are little bit better than the results obtained in this paper, but the calculated results of the excited states are much better than theirs. For example, for the four excited states ( $^1\Pi$ ,  $^3\Sigma^+$ ,  $^3\Pi$ ,  $^3\Delta$ ) comparing with experimental data, the percent error of the calculated vibrational constants  $w_e$  are only 0.8%, 2.7%, 2.3%, and 1.8%, respectively, while theirs are 5.8%, 8.4%, 11.4%, and 12.5%, respectively, which are much larger than ours. As for the ground state, although the percent errors of the calculated  $R_e$  and  $w_e$  are a little larger than Toscano's results, generally speaking, the spectroscopic constants for the ground state reported in the present work are in good agreement with the experimental data, corresponding to the percent error of  $w_e$ ,  $w_e x_e$ ,  $B_e$ ,  $\alpha_e$ , and  $D_e$  only 1.5%, 0.80%, 2.3%, 2.1%, and 3.3% respectively. The spectroscopic term  $T_e$  is an important parameter to identify the excited states. The calculated  $T_e$  together with experimental data and values in Ref. [13] are listed in Table 2. From it we can find that the calculated spectroscopic terms are in good agreement with the experimental data with the average deviation for the four states ( $^1\Pi$ ,  $^3\Sigma^+$ ,  $^3\Pi$ ,  $^3\Delta$ ) only  $274\text{ cm}^{-1}$  while  $2725\text{ cm}^{-1}$  in Ref. [13] which is ten times larger than ours. As for the  $^1\Delta$  state, there are no experimental reports, and its spectroscopic constants calculated with the two different methods deviate from each other obviously. The calculated  $T_e$  reported in Ref. [13] is  $4494\text{ cm}^{-1}$

**Table 1. Spectroscopic Constants of the Nine States of AsP Compared with Previous Experimental and Theoretical Data**

State	$R_e$ (nm)	$w_e$ ( $\text{cm}^{-1}$ )	$w_e x_e$ ( $\text{cm}^{-1}$ )	$w_e y_e$ ( $\text{cm}^{-1}$ )	$B_e$ ( $\text{cm}^{-1}$ )	$\alpha_e$ ( $\text{cm}^{-1}$ )	$\gamma_e$ ( $\text{cm}^{-1}$ )	$D_e$ ( $\text{cm}^{-1}$ )	$\beta_e$ ( $\text{cm}^{-1}$ )
$X^1\Sigma$									
Present	0.2023	594.9	1.895	$0.6442 \times 10^{-2}$	0.1878	$7.821 \times 10^{-4}$	$7.684 \times 10^{-7}$	$7.483 \times 10^{-8}$	$2.723 \times 10^{-10}$
Experiment	0.1999 <sup>a</sup>	604 <sup>a</sup>	1.98 <sup>a</sup>		0.1925 <sup>a</sup>	$8.0 \times 10^{-4a}$		$7.8 \times 10^{-8a}$	
Toscano's	0.1985	603	1.88 <sup>b</sup>		0.19240 <sup>c</sup>	$7.992 \times 10^{-4c}$		$7.2383 \times 10^{-8c}$	
$^1\Pi$									
Present	0.2124	470.9	1.873	$0.2498 \times 10^{-2}$	0.1704	$8.859 \times 10^{-4}$	$7.272 \times 10^{-7}$	$8.924 \times 10^{-8}$	$3.269 \times 10^{-10}$
Experiment	0.210 <sup>a</sup>	475 <sup>a</sup>	2.12 <sup>a</sup>		0.17441 <sup>a</sup>	$9.0 \times 10^{-4a}$		$1.1 \times 10^{-7a}$	
Toscano's	0.2090	503	1.64 <sup>b</sup>						
$^1\Delta$									
Present	0.2189	466.6	1.511	$0.6737 \times 10^{-3}$	0.1605	$7.166 \times 10^{-4}$	$3.444 \times 10^{-7}$	$7.599 \times 10^{-8}$	$1.159 \times 10^{-10}$
Toscano's	0.2150	478							
$^3\Sigma^+$									
Present	0.2221	427.6	1.898	$0.2924 \times 10^{-3}$	0.1558	$8.238 \times 10^{-4}$	$2.735 \times 10^{-6}$	$8.271 \times 10^{-8}$	$5.295 \times 10^{-10}$
Experiment		439.7 <sup>b</sup>	1.904 <sup>b</sup>						
Toscano's	0.2123	476							
$^3\Pi$									
Present	0.21066	486.5	2.117	$1.602 \times 10^{-3}$	0.1733	$9.134 \times 10^{-4}$	$1.595 \times 10^{-6}$	$8.793 \times 10^{-8}$	$5.486 \times 10^{-10}$
Experiment		475.5 <sup>b</sup>	2.12 <sup>b</sup>						
Toscano's		544							
$^3\Delta$									
Present	0.2201	452.4	1.618	$3.081 \times 10^{-3}$	0.1588	$7.538 \times 10^{-4}$	$0.8497 \times 10^{-6}$	$7.823 \times 10^{-8}$	$2.287 \times 10^{-10}$
Experiment		461 <sup>b</sup>	1.63 <sup>b</sup>						
Toscano's	0.2133	519							
$^5\Sigma^+$									
Present	0.2481	305.500	0.919	$0.784 \times 10^{-1}$	0.125	$9.051 \times 10^{-4}$	$3.051 \times 10^{-6}$	$7.923 \times 10^{-8}$	$2.061 \times 10^{-9}$
$^5\Pi$									
Present	0.2366	311.0	2.002	$0.1352 \times 10^{-1}$	0.1374	$9.737 \times 10^{-4}$	$7.578 \times 10^{-6}$	$1.003 \times 10^{-7}$	$1.716 \times 10^{-9}$
$^5\Delta$									
Present	0.5079	7638.4	24.61	3.373	$0.2984 \times 10^{-1}$	$0.3118 \times 10^{-4}$	$6.597 \times 10^{-7}$	$4.924 \times 10^{-12}$	$1.129 \times 10^{-12}$

<sup>a</sup>Data from Ref. [7], <sup>b</sup>data from Ref. [11], <sup>c</sup>data from Ref. [13].

**Table 2. Spectroscopic Terms of the Nine States of AsP Compared with Previous Experimental and Theoretical Data**

	$X^1\Sigma^+$	$^3\Sigma^+$	$^3\Delta$	$^3\Pi$	$^1\Pi$	$^1\Delta$	$^5\Sigma^+$	$^5\Pi$	$^5\Delta$
Present	0	16219	22105	26668	32624	27201	26749	37240	45403
Toscano's	0	19621	23989	24189	28545	31695	—	—	—
Experiment <sup>[11]</sup>	0	16418	21714	25969	32417				
					32353 <sup>[7]</sup>				

larger than the value in the present study. According to the discussions above, we think that values in Ref. [13] for this state should be imprecise. So we can conclude that the LCGTO-MP-LSD computations cannot precisely enough to give the properties of the excited states for the AsP molecule while the MRCI calculations can. No data on quintet state are available from the previous experimental and theoretical studies up to now. The calculated spectroscopic constants and spectroscopic terms  $T_e$  of the three states are only provided in Tables 1 and 2, respectively.

In some calculations, for example, to determine dynamical process or photoelectron spectrum, APEFs of the PECs are more convenient. So, based on the PECs obtained from *ab initio* calculations, we fit the APEFs of these nine states with the Murrell-Sorbie (MS) function which can perfectly reproduce the PECs of the bounding diatomic molecules<sup>[24–26]</sup>. The common MS function<sup>[27]</sup> can be written as

$$V(\rho) = -D_e \left( 1 + \sum_{i=1}^n a_i \rho^i \right) \exp(-a_1 \rho), \quad (1)$$

where  $\rho = R - R_e$ ,  $R$  and  $R_e$  stand for the interatomic distance and the equilibrium bond length, respectively.  $D_e$  is the dissociation energy. We employ  $n = 9$  for the fitting action of these five states. Usually the parameters  $D_e$  and  $R_e$  are fixed as dissociation energy and equilibrium bond length respectively, but in this work they are treated as fitting parameters equally in order to get the more accurate fitting results. To judge the quality of the fitting results, we calculate their root mean square (RMS) errors. The RMS function can be expressed as

$$\text{RMS} = \frac{1}{n} \sqrt{\sum_{i=1}^n (V_{\text{MS}}(i) - V_{ab \text{ initio}}(i))^2}, \quad (2)$$

where  $V_{ab \text{ initio}}(i)$  is the  $i$ th energy of the *ab initio* calculation and  $V_{\text{MS}}(i)$  is the corresponding fitting value. The fitted parameters of APEFs are not listed out for simplicity. The calculated RMS values of the eight bound states are only 1.4, 0.89, 1.62, 2.61, 6.0, 2.3, 4.3, and 1.6  $\text{cm}^{-1}$ , respectively, which are much smaller than the chemical accuracy of 349.7  $\text{cm}^{-1}$ . The  $^5\Delta$  state is identified as a van der Waals state because of its large bond length and small dissociation energy. The calculated RMS value of this state is only 0.0059  $\text{cm}^{-1}$ . So we can conclude that the MS function can accurately reproduce PECs of the bound states as well as that of the van der Waals states.

In summary, we present the theoretical study on the potential energy curves, spectroscopic constants, and APEFs of nine states of the AsP molecule. The calculated results are in good agreement with the experimental

data available at present. So, for the three quintet states with no experimental measurement and theoretical studies, the spectroscopic constants reported in this paper can be a helpful reference for the future researches. It is found that the MRCI method with aug-cc-PVQZ basis set can accurately describe the properties of both the ground state and the excited states while the previous theoretical LCGTO-MP-LSD method only can give reliable results for the ground state. All of these nine states are fitted to APEFs with the MS function. Small RMS values for all of these states show that the MS function can accurately reproduce the PECs of not only the general bound states but also the van der Waals states.

This work was supported by the National Natural Science Foundation of China under Grant No. 10674114. C. Yang is the author to whom the correspondence should be addressed, his e-mail address is yangchuanlu@126.com.

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