Multireference configuration interaction study on spectroscopic properties of low-lying electronic states of As_2 molecule*

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The potential energy curves (PECs) of four electronic states ($X^1\Sigma_g^+$, $e^3\Delta_u$, $a^3\Sigma_u^-$, and $d^3\Pi_g$) of an As_2 molecule are investigated employing the complete active space self-consistent field (CASSCF) method followed by the valence internally contracted multireference configuration interaction (MRCI) approach in conjunction with the correlation-consistent aug-cc-pV5Z basis set. The effect on PECs by the relativistic correction is taken into account. The way to consider the relativistic correction is to employ the second-order Douglas-Kroll Hamiltonian approximation. The correction is made at the level of a cc-pV5Z basis set. The PECs of the electronic states involved are extrapolated to the complete basis set limit. With the PECs, the spectroscopic parameters (T_e, R_e, ω_e, $\omega_e x_e$, $\omega_e y_e$, α_e, β_e, γ_e, and B_e) of these electronic states are determined and compared in detail with those reported in the literature. Excellent agreement is found between the present results and the experimental data. The first 40 vibrational states are studied for each electronic state when the rotational quantum number J equals zero. In addition, the vibrational levels, inertial rotation and centrifugal distortion constants of $d^3\Pi_g$ electronic state are reported which are in excellent agreement with the available measurements. Comparison with the experimental data shows that the present results are both reliable and accurate.

Keywords: spectroscopic parameter, molecular constant, relativistic correction, extrapolation

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1. Introduction

The structures and spectra of metal dimmers and metal-like clusters have aroused considerable interest.[1,2] Such interest stems in part from the desire to characterize the properties of atoms on metal surfaces and understand a molecular level heterogeneous chemical catalysis and similar processes occurring on metal surfaces.[3] Arsenic is usually considered to be a nonmetallic element, but it possesses metal-like properties, such as a high conductivity. Therefore, the structure and spectrum of As_2 have been the subject of numerous investigations in the past several decades, both experimentally[4–17] and theoretically[18–33]

In experiment, the spectrum of As_2 molecule has been extensively investigated. An early spectrum was observed in 1934 by Gibson and Macfarlane[4] when ultraviolet light was absorbed by arsenic vapor. They detected about eighty band-heads between the wavelengths of 220 nm and 275 nm, and made an analysis of the vibrational levels. Almy and Kinzer,[5] Kinzer and Almy,[6] and Almy[7] studied the emission spectrum of As_2 in the ultraviolet region between 210 nm and 370 nm, and subsequently extended the region to 700 nm. Later, Mrozowski and Santaram[8] investigated the band spectra in a spectral range from 210 nm to 1000 nm with a medium-size spectrograph using a discharge tube developed for studies of forbidden lines. Donovan and Strachan[11] in 1971 observed the absorption spectra by the flash photolysis of AsH_3 and reported seven band systems. Dyke *et al.*[16] in 1986 recorded on the He (I) photoelectron spectra of the As_2 from heated solid arsenic and copper arsenide. Up to now, a number of band systems including $a \rightarrow X$, $d \rightarrow X$, $e \rightarrow X$, $A \rightarrow X$, $B \rightarrow X$, and $A \rightarrow a$ have been observed and rotational analysis has been carried out.[8–10,12–15,17]

In theory, early *ab initio* calculations were made in 1985 by Watanabe *et al.*,[18] who performed the spectroscopic parameter calculations for the ground state of As_2 using the model potential method. Up to now, a number of theoretical studies[19–33] have been made, and some spectroscopic parameters have been determined. Summarizing these theoretical results, we could find that the extracted spectroscopic properties from the investigations mainly focus on the ground state. Only two groups[32,33] reported on the results of $e^3\Delta_u$, $a^3\Sigma_u^-$, and $d^3\Pi_g$ electronic states, and their spectroscopic parameters[32,33] are far from the available measurements[3,7,8,10,14] in general, and the T_e of $d^3\Pi_g$ electronic state in particular. In addition, since the As_2 is a large molecule, the effect on spectroscopic properties by relativistic correction should be important. Of these investigations, only two groups[28,29] included the effect on spectroscopic parameters by the relativistic correction. Unfortunately, the two studies[28,29] determined the spectroscopic parameters only for ground state. Therefore, there is room for improvement by

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theory.

The rest of this paper is organized as follows. First, the potential energy curves (PECs) of $X^1\Sigma_g^+$, $e^3\Delta_u$, $a^3\Sigma_u^-$, and $d^3\Pi_g$ electronic states of As_2 molecule are calculated by the complete active space self-consistent field (CASSCF) method followed by the valence internally contracted multireference configuration interaction (MRCI) approach[34,35]in combination with the correlation-consistent basis set[36]in the valence range. Then, the effect on PECs by the relativistic correction is taken into account, and the extrapolation to complete basis set (CBS) limit is carried out. Finally, with these PECs, the spectroscopic parameters and vibrational manifolds are evaluated for all the electronic states involved here when the rotational quantum number J is equal to zero ($J = 0$). The effect on the spectroscopic parameters by the relativistic correction and total-energy extrapolation are discussed in detail.

2. Computational details

The MRCI approach is a way to systematically include those configuration state functions (CSFs) that contribute most significantly to correlation energy. It has been proved to be precise in treating small systems.[37,38] The multireference treatment involves computing the CASSCF wave functions and subsequently recovering dynamical correlation by means of MRCI calculations. That is, the full valence CASSCF is used as reference wavefunction for the MRCI calculations. The correlation-consistent aug-cc-pV5Z (AV5Z) basis set, which means (26s, 17p, 13d, 3f, 2g, 1h) → (8s, 7p, 5d, 3f, 2g, 1h) for As atom, is used in the present work.

The present calculations of potential energies are carried out in the MOLPRO 2008.1 program package.[39] MOLPRO uses Abelian point group symmetry only. For molecules with degenerate symmetry, an Abelian subgroup must be used. That is, for the diatomic molecular such as As_2 with $D_{\infty h}$ symmetry, it will be substituted by D_{2h} symmetry with the order of the irreducible representations as $a_g/b_{3u}/b_{2u}/b_{1g}/b_{1u}/b_{2g}/b_{3g}/a_u$. In detail, for the electronic states $X^1\Sigma_g^+$, $e^3\Delta_u$, $a^3\Sigma_u^-$, and $d^3\Pi_g$ of As_2 molecule, eight molecular orbitals (MOs) are incorporated into the active space, including two a_g, one b_{3u}, one b_{2u}, two b_{1u}, one b_{2g}, and one b_{3g} symmetry MOs, which correspond to the 4s4p shells of As atom. The rest of the electrons in the molecule are placed into closed-shell orbitals, including seven a_g, three b_{3u}, three b_{2u}, one b_{1g}, seven b_{1u}, three b_{2g}, three b_{3g}, and one a_u symmetry MOs. Having these MOs (nine a_g, four b_{3u}, four b_{2u}, one b_{1g}, nine b_{1u}, four b_{2g}, four b_{3g}, and one a_u) used, the PECs of As_2 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. Here, 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 MOLCAS 7.4 program package,[40] the spectroscopic parameters and vibrational manifolds are evaluated for these electronic states. In the module VIBROT, the potential is fitted to an analytical form by cubic splines. The ro-vibrational Schrödinger equation is then solved by Numerov's method[41] for one vibrational state at a time and for a number of rotational quantum numbers as specified by input, and the spectroscopic parameters, such as excitation energy T_e, equilibrium distance R_e, harmonic frequency ω_e, anharmonic constant $\omega_e x_e$, and rotation constant factor B_e, are determined by fitting the vibrational levels. Here, the spectroscopic parameters obtained by the MRCI/AV5Z calculations are collected in Table 1.

Table 1. Effects of the relativistic correction on the spectroscopic parameters.

Source	T_e/eV	R_e/nm	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}	$10^2\omega_e y_e$/cm^{-1}	B_e/cm^{-1}	$10^4\alpha_e$/cm^{-1}	$10^7\gamma_e$/cm^{-1}
$X^1\Sigma_g^+$								
AV5Z	0	0.21303	422.95	1.1128	1.5266	0.09916	3.1429	1.0233
+DK	0	0.21235	421.08	1.1278	1.3962	0.09980	3.2056	1.0224
Exp.[10]	0	0.2104	429.55	1.117		0.10179	3.33	
$e^3\Delta_u$								
AV5Z	2.4823	0.23124	324.71	0.8923	0.9054	0.08415	2.9978	0.2650
+DK	2.4916	0.23081	322.50	0.8846	0.9075	0.08446	3.0238	0.3815
Exp.[10]	2.4690		330.0	0.90				
$a^3\Sigma_u^-$								
AV5Z	3.0678	0.23023	333.20	0.8424	0.9711	0.08491	2.9145	0.3947
+DK	3.0725	0.22978	331.14	0.8353	0.9477	0.08523	2.9283	0.3659
Exp.[10]	3.0551	0.2279	337.0	0.83		0.08666	3.0	
$d^3\Pi_g$								
AV5Z	3.1386	0.22171	344.69	1.1894	0.8501	0.09156	3.7690	0.3442
+DK	3.1651	0.22128	340.59	1.1882	0.8199	0.09192	3.8332	0.4902
Exp.[10]	3.8209	0.2209	336.7	1.36		0.09222	3.3	

In order to evaluate the effect of the relativistic correction on spectroscopic parameters, we re-calculate the PECs of these electronic states over the present internuclear separations at the level of the cc-pV5Z basis set. Here, the way to consider the relativistic correction is to employ the second-order Douglas–Kroll Hamiltonian (DKH2) approximation.[42,43] Adding the relativistic correction results obtained at the level of cc-pV5Z basis set to the present AV5Z values (denoted as +DK), we obtain the PECs corrected by the relativistic effect for these electronic states. Here, the spectroscopic parameters are still evaluated by the VIBROT program in the MOLCAS 7.4 program package. These spectroscopic results are also collected in Table 1.

To allow for extrapolation schemes, it is mandatory to have a sequence of basis sets that converges uniformly to the CBS limit. The correlation-consistent basis sets of Dunning and coworkers[36] are chosen, since these basis sets provide a well-defined series and the calculated energies could be extrapolated to the CBS limit.

The total energy includes reference and electron-correlation energies. The electron-correlation energy could be extrapolated by the two-point extrapolation scheme. The formula[44] of two-point extrapolation with two successive basis sets is as follows:

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

where ΔE is the electron-correlation energy and X is the cardinal number of the basis set. For a given internuclear separation, ΔE_∞ is the correlation energy at the CBS limit, ΔE_X and ΔE_{X+1} are the correlation energies obtained at the correlation-consistent basis sets, ang-cc-pVXZ and ang-cc-pV $(X+1)Z$, respectively. To obtain the total extrapolated energies, the reference energy has to be considered as well. According to the suggestions given by Müller *et al.*,[44] the same exponents for reference and electron-correlation energy are used in the present work and the total energy is extrapolated according to Eq. (1). In the present work, we use the correlation-consistent basis sets, aug-cc-pVQZ (AVQZ) and AV5Z, to perform the present extrapolation scheme. The scheme is applied to energies only, and the spectroscopic parameters are still fitted by employing the same VIBROT program noted above. These spectroscopic results are also collected in Table 2.

Table 2. Spectroscopic parameters of the As_2 molecule, obtained by extrapolation.

Source	T_e/eV	R_e/nm	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}	$10^2\omega_e y_e$/cm^{-1}	B_e/cm^{-1}	$10^4\alpha_e$/cm^{-1}	$10^7\gamma_e$/cm^{-1}
$X^1\Sigma_g^+$								
AVQZ	0	0.21319	421.69	1.1179	1.5382	0.09901	3.1422	1.4394
AV5Z	0	0.21303	422.95	1.1128	1.5266	0.09916	3.1429	1.0233
Q5-ex	0	0.21286	424.31	1.1115	1.4877	0.09931	3.1172	0.6476
Q5-ex+DK	0	0.21218	422.42	1.1252	1.2008	0.09996	3.1656	1.3221
Exp.[10]	0	0.2104	429.55	1.117		0.10179	3.33	
$e^3\Delta_u$								
AVQZ	2.4734	0.23141	323.38	0.8918	0.9559	0.08403	3.0273	0.7450
AV5Z	2.4823	0.23124	324.71	0.8923	0.9054	0.08415	2.9978	0.2650
Q5-ex	2.4916	0.23106	326.13	0.9022	0.8024	0.08427	2.9954	0.6602
Q5-ex+DK	2.4931	0.23063	323.94	0.9001	0.7690	0.08459	2.9935	0.2002
Exp.[10]	2.4690		330.0	0.90				
$a^3\Sigma_u^-$								
AVQZ	3.0610	0.23038	322.04	0.8476	0.9669	0.08479	2.9383	0.4006
AV5Z	3.0678	0.23023	333.20	0.8424	0.9711	0.08491	2.9145	0.3947
Q5-ex	3.0751	0.23008	334.41	0.8374	0.9744	0.08502	2.8868	0.3821
Q5-ex+DK	3.0840	0.22963	332.33	0.8293	0.9535	0.08535	2.9031	
Exp.[10]	3.0551	0.2279	337.0	0.83		0.08666	3.0	0.3598
$d^3\Pi_g$								
AVQZ	3.1284	0.22192	343.25	1.2028	0.8336	0.09175	3.7467	0.4578
AV5Z	3.1386	0.22171	344.69	1.1894	0.8501	0.09156	3.7690	0.3442
Q5-ex	3.1494	0.22148	346.21	1.1774	0.8636	0.09175	3.7467	0.4578
Q5-ex+DK	3.1759	0.22104	342.13	1.1763	0.8317	0.09217	3.8099	0.4952
Exp.[10]	3.8209	0.2209	336.7	1.36		0.09222	3.3	

Note: (i) "Q5-ex" denotes the extrapolation based on AVQZ and AV5Z. (ii) "Q5+DK" refers to the extrapolation based on AVQZ+DK and AV5Z+DK

3. Results and discussion

3.1. Spectroscopic parameters

In this section, we discuss the effect of the relativistic correction on spectroscopic parameters in detail. Since the spectroscopic parameters $\omega_e y_e$ and γ_e are very small, here, we omit them in the following discussion.

With the relativistic correction added to the present MRCI/AV5Z results, the total energy of each electronic state is lowered by about $49.4E_h$ at the internuclear equilibrium separation.

From Table 1, it is not difficult to find that the relativistic correction makes all the T_e ascend In detail, the correction increases the T_e by 0.0093 eV, 0.0047 eV, and 0.0265 eV for the $e^3\Delta_u$, $a^3\Sigma_u^-$, and $d^3\Pi_g$ electronic states, respectively. Such a trend makes the T_e farther deviate from the experimental data[10] for all the electronic states. Similar to the T_e, the B_e and α_e values are also overestimated by such a correction. For the $X^1\Sigma_g^+$, $e^3\Delta_u$, $a^3\Sigma_u^-$, and $d^3\Pi_g$ electronic states, the shifts of B_e are 0.00064 cm^{-1}, 0.00031 cm^{-1}, 0.00032 cm^{-1}, 0.00036 cm^{-1} and the shifts of α_e are 0.00000627 cm^{-1}, 0.0000026 cm^{-1}, 0.00000138 cm^{-1}, and 0.00000642 cm^{-1}, respectively. As listed in Table 1, the trend makes the B_e and α_e values closer to the experimental data[10] for each electronic state compared with the results determined by the MRCI/AV5Z calculations.

On the contrary, the relativistic correction lowers the values of R_e and ω_e for all these electronic states. For the $X^1\Sigma_g^+$, $e^3\Delta_u$, $a^3\Sigma_u^-$, and $d^3\Pi_g$ electronic states, simple calculations indicate that the relativistic correction lowers the R_e by 0.00068 nm, 0.00043 nm, 0.00045 nm, and 0.00043 nm and lowers the ω_e by 1.87, 2.21, 2.06, and 4.10 cm^{-1}, respectively. As indicated in Table 1, such a trend makes the R_e closer to the experimental data[10] but makes the ω_e deviate farther from the experimental data[10] for each electronic state compared with the results determined by the MRCI calculations without the relativistic correction

The effect of the relativistic correction on $\omega_e x_e$ is not systematic: the $\omega_e x_e$ values decrease for the $e^3\Delta_u$ and $a^3\Sigma_u^-$, whereas increase for $X^1\Sigma_g^+$ and $d^3\Pi_g$ electronic states. The changes of $\omega_e x_e$ are 0.0150 cm^{-1}, 0.0077 cm^{-1}, 0.0071 cm^{-1}, and 0.0012 cm^{-1} for the $X^1\Sigma_g^+$, $e^3\Delta_u$, $a^3\Sigma_u^-$, and $d^3\Pi_g$ electronic states, respectively.

On the whole, the relativistic correction has a rather large effect on the spectroscopic parameters, such as R_e, $\omega_e x_e$, B_e, and α_e, and makes them closer to the observations for most electronic states. But for the T_e and ω_e, such a correction makes them slightly deviate farther from the experimental data.

We extrapolate the total energy of each energy point on PECs to the CBS limit. A uniform trend is observed for all electronic states that the total energies near equilibrium position reduce about $0.008E_h$ by the extrapolation (from the AVQZ to the Q5-extrapolation).

Table 2 shows the spectroscopic parameters obtained by extrapolation. By comparing the extrapolation results without the relativistic correction with the MRCI/AV5Z results, we can draw the following conclusions. (i) The extrapolation raises the T_e, ω_e, and B_e for all the electronic states. The shifts of T_e are 0.0093 eV, 0.0073 eV, and 0.0108 eV for the $e^3\Delta_u$, $a^3\Sigma_u^-$, and $d^3\Pi_g$ electronic states, the shifts of ω_e are 1.36 cm^{-1}, 1.42 cm^{-1}, 1.21 cm^{-1}, and 1.52 cm^{-1} and the shifts of B_e are 0.00015 cm^{-1}, 0.00012 cm^{-1}, 0.00011 cm^{-1}, and 0.00019 cm^{-1} for the $X^1\Sigma_g^+$, $e^3\Delta_u$, $a^3\Sigma_u^-$, and $d^3\Pi_g$ electronic states, respectively. (ii) In opposition to the trends of T_e, ω_e, and B_e, the extrapolation lowers the R_e and α_e for each electronic state. For example, the extrapolation reduces the R_e by 0.00017 nm, 0.00018 nm, 0.00015 nm, and 0.00023 nm, and lowers the α_e by 0.00000257 cm^{-1}, 0.00000024 cm^{-1}, 0.00000307 cm^{-1}, and 0.00000223 cm^{-1} for the $X^1\Sigma_g^+$, $e^3\Delta_u$, $a^3\Sigma_u^-$, and $d^3\Pi_g$ electronic states, respectively. (iii) As to the $\omega_e x_e$, the extrapolation lowers it by 0.0013 cm^{-1} , 0.0050 cm^{-1} , and 0.0120 cm^{-1} for the $X^1\Sigma_g^+$, $a^3\Sigma_u^-$, and $d^3\Pi_g$, and raises it by 0.0099 cm^{-1} for the $e^3\Delta_u$ electronic state. Obviously, the quality of almost all the spectroscopic parameters is improved by the extrapolation compared with corresponding results at the MRCI/AV5Zlevel.

Similar to Refs. [32] and [33], Tables 1 and 2 show that the T_e value of $d^3\Pi_g$ electronic state determined here is also far from the experimental data.[10] To obtain reliable T_e results, more approaches have been used here. These methods, including the coupled clusters with single and double substitutions corrected for the effect of triple excitations [CCSD(T)], MR averaged-coupled-pair functional (MR-ACPF), and MR averaged quadratic coupled cluster (MR-AQCC), are used together with the AV5Z basis set. These results obtained by the MRCI/AV5Z calculations are collected in Table 3. Form Table 3, we can see that these methods give the T_e values with almost same quality, though these values are still far form the experimental data.[10]

In the following discussion, we employ the spectroscopic results obtained by the MRCI/ Q5-ex+DK calculations for comparison. These results are collected in Table 4 together with the RKR data and other theoretical results for convenient comparison.

To date, a number of theoretical investigations have been made on the spectroscopic parameters of As_2 molecule. Of these investigations, three studies[18,20,25] used the *ab initio* model potential method to investigate the ground-state properties. For example, Watanabe *et al.*[18] in 1985 made the Hartree–Fock–Roothaan calculation on the ground state with a valence basis set determined for an As atom. Huzinaga *et al.*[20] employed the *ab initio* core model potential method and the valence basis set to perform the potential calculations. Katsuki[25] used the model potential method with the basis function (43211/4211/3) for the valence orbitals of an As atom and (4322/422/3) for the core orbitals to carry out the PEC. However, these model potential calculations did not yield sufficiently accurate spectroscopic parameters. As shown in Table 4, their ω_e values are overestimated compared with the experimental results.[10]

Table 3. Spectroscopic parameters of the $d^3\Pi_g$ electronic state, obtained from different approaches.

Source	T_e/eV	R_e/nm	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}	$10^2\omega_e y_e$/cm^{-1}	B_e/cm^{-1}	$10^4\alpha_e$/cm^{-1}	$10^7\gamma_e$/cm^{-1}
MRCI	3.1386	0.22171	344.69	1.1894	0.8501	0.09156	3.7690	0.3442
MR-ACPF	3.0684	0.21184	343.81	1.1697	0.4068	0.09143	3.6910	0.5955
MR-AQCC	3.0891	0.22180	344.16	1.1825	0.7224	0.09147	3.6956	0.4326
UCCSD(T)	3.0606	0.22130	350.38	1.0813	0.9446	0.09188	3.5563	0.9167
Exp.[10]	3.8209	0.2209	336.7	1.36		0.09222	3.3	

Table 4. Comparisons of spectroscopic parameters between our data and other measurements and calculations for As_2 ($X^1\Sigma_g^+$, $e^3\Delta_u$, $a^3\Sigma_u^-$, and $d^3\Pi_g$).

Source	T_e/eV	R_e/nm	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}	$10^2\omega_e y_e$/cm^{-1}	B_e/cm^{-1}	$10^4\alpha_e$/cm^{-1}	$10^7\gamma_e$/cm^{-1}
$X^1\Sigma_g^+$								
This work	0	0.21218	422.42	1.1252	1.2008	0.09996	3.1656	1.3221
Exp. [3]	0	0.21026	429.5	1.12				
Exp. [7]	0		429.4					
Exp. [8]	0		430.3	1.2				
Exp. [10]	0	0.2104	429.55	1.117		0.10179	3.33	
Exp. [14]	0		428.96	1.068		0.10205	3.27	
Theory[18]	0	0.2138	453			0.0984		
Theory[20]	0	0.2146	454					
Theory[21]	0	0.2107	447					
Theory[22]	0	0.2120	426					
Theory[23]	0	0.2110	476					
Theory[24]	0	0.2058	423					
Theory[25]	0	0.2142	449					
Theory[26]	0	0.2170	393					
Theory[27]	0	0.2116	431					
Theory[28]	0	0.21098	432.1					
Theory[29]	0	0.21185	428.9					
Theory[30]	0	0.2117	429					
Theory[31]	0	0.2133	417					
Theory[32]	0	0.2164	394					
Theory[33]	0	0.2085	446					
$e^3\Delta_u$								
This work	2.4931	0.23063	323.94	0.9001	0.7690	0.08459	2.9935	0.2002
Exp. [10]	2.4690		330.0	0.90				
Theory[32]	2.4767	0.2357	324					
Theory[33]	2.5913	0.2271	340					
$a^3\Sigma_u^-$								
This work	3.0840	0.22963	332.33	0.8293	0.9535	0.08535	2.9031	0.3598
Exp. [8]	3.0555	—-	337	0.83				
Exp. [10]	3.0551	0.2279	337.0	0.83		0.08666	3.0	
Theory[32]	3.2739	0.2345	341					
$d^3\Pi_g$								
This work	3.1759	0.22104	342.13	1.1763	0.8317	0.09217	3.8099	0.4952
Exp.[10]	3.8209	0.2209	336.7	1.36		0.09222	3.3	
Theory[32]	3.2302	0.258	316					
Theory[33]	3.3049	0.2199	347					

Mochizuki *et al.*[26] used the CASSCF method with a contracted Gaussian basis set [3s3p1d] to calculate the electronic structure of As_2. In their calculations, the model potential technique was used to replace the core atomic orbitals of the As atom. Obviously, their results are also far from the observations.[10]

Three studies[28–30] performed the CCSD(T) calculations for the ground state of As_2 molecule. Martin and Sundermann[28] in 2001 employed the CCSD(T) method with the basis sets of cc-pVTZ and cc-pVQZ quality to calculate the ground-state spectroscopic parameters. In their calculations, the relativistic correction was included and the way to consider the correction was to optimize the basis sets with large-core Stuttgart–Dresden–Bonn (SDB) relativistic pseudopotentials. The favourable results obtained by the SDB-cc-pVQZ basis set are collected in Table 4. Deyonker *et al.*[29] repeated the CCSD(T) calculations with the aug-cc-pCVnZ (n = D, T, Q, 5) and aug-cc-pwCVnZ (n = D, T, Q, 5) basis sets. Obviously, the spectroscopic parameters obtained by the aug-cc-pwCV5Z basis set are closest to the measurements among their results

obtained. Later, Al-Saidi[30] used the same method to perform the benchmark calculations on the spectroscopic properties of As_2 molecule, the relativistic correction was also included and the way to consider the correction is to employ the pseudopotential basis set, aug-cc-pV5Z-PP. Although the qualities of R_e and ω_e values[28–30] are slightly superior to the present ones compared with the experimental data, they only determined two spectroscopic parameters (R_e and ω_e). Other important spectroscopic parameters, such as B_e, $\omega_e x_e$, and α_e, were not evaluated in their work.

More sophisticated methods, such as the multireference singly and doubly excited configuration interaction (MR-CISD) approach, were employed by Mochizuki and Tanaka.[31] In their work, the CASSCF was used to prepare the MO for the MR-CISD calculations and the size-inconsistency error was considered by the Davidson modification. The basis set they used was all-electron [8s6p4d2f1g] basis set. Unfortunately, their spectroscopic parameters are inferior to the present ones compared with the experimental data.[10]

Balasubramanian[32] in 1987 made the complete active space MCSCF calculations followed by the first-order configuration interaction (FOCI) calculations on 18 electronic states. In his method, valence electrons are distributed in all possible ways among a chosen set of orbitals referred to as the internal space of orbitals. The basis set used in his work was a valence Gaussian basis set [3s3p1d]. As indicated in Table 4 they only calculated three parameters (T_e, R_e, and ω_e) for the electronic states involved here, and the results are still far from the experimental data[10] except the ω_e for the $e^3\Delta_u$ and $a^3\Sigma_u^-$ and the T_e for the $e^3\Delta_u$ electronic state compared with the present ones.

Later, Toscano and Russo[33] performed the LCGTO MP local spin density (LSD) calculations with the valence orbital basis set (311/211/1*) in several low-lying electronic states. Similar to the Ref. [32], only three parameters were evaluated in their work. From Table 4, we could still see that great differences exist between their results and the available measurements for the electronic states involved here.

According to the above discussion and comparison in Table 4, we conclude that the present spectroscopic parameters of As_2 molecule are more accurate and complete than those of previous theoretical studies. For example, for the R_e, the present results are in excellent agreement with the experimental ones. The deviations of R_e from the experimental ones[10] are only 0.84% for the $X^1\Sigma_g^+$, 0.75% for the $a^3\Sigma_u^-$ and 0.06% for the $d^3\Pi_g$ electronic states, and for the T_e, the present results are also in excellent agreement with all the experimental ones except the $d^3\Pi_g$ electronic state, and the differences between the present results and the experimental ones[10] are 0.97% for the $e^3\Delta_u$ and 0.94% for the $a^3\Sigma_u^-$ electronic state, respectively.

As to the ω_e, $\omega_e x_e$, B_e, and α_e, the present results are still in good accordance with the experimental data. Taking the ω_e and $\omega_e x_e$ for example, the deviations of present ω_e from the measurements[10] are only 7.13 cm^{-1}, 6.06 cm^{-1}, 4.67 cm^{-1}, and 5.43 cm^{-1}, and the differences in $\omega_e x_e$ between the measurements[10] and the present ones are only 0.0082 cm^{-1}, 0.0001 cm^{-1}, 0.0007 cm^{-1}, and 0.1837 cm^{-1} for the $X^1\Sigma_g^+$ $e^3\Delta_u$ $a^3\Sigma_u^-$, and $d^3\Pi_g$ electronic states respectively. According to these, one could conclude that the present spectroscopic parameters are of high quality.

As shown in Table 4, although the extrapolation results with the relativistic correction are in excellent agreement with the experimental data[10] there still exist some residual errors. For example, the deviations of the R_e from the experimental data[10] are 0.00178 nm, 0.00173 nm, and 0.00014 nm for the $X^1\Sigma_g^+$, $a^3\Sigma_u^-$, and $d^3\Pi_g$ electronic states, and the deviations of the ω_e from the experimental data[10] are 7.13 cm^{-1}, 6.06 cm^{-1}, 4.67 cm^{-1}, and 5.43 cm^{-1} for the $X^1\Sigma_g^+$, $e^3\Delta_u$, $a^3\Sigma_u^-$, and $d^3\Pi_g$ electronic states, respectively. We think that the most important contribution to the residual errors might be from the extrapolation approach

As is well known, total energy consists of reference energy and correlation energy. Strictly speaking, the reference and correlation energy should be extrapolated separately because they have different convergence behaviors.[40] In the present paper, we try to employ the same exponent in both cases and extrapolate the total energy to the CBS limit since there is no well-founded way to evaluate the separate exponents for reference- and electron-correlation energy. We think that the same exponent in both cases might be the most important contribution to the residual errors.

3.2. Vibrational manifolds

Using the PECs obtained by the MRCI/Q5-ex+DK calculations, we determine the vibrational level $G(\upsilon)$, inertial rotation constant B_υ and centrifugal distortion constant D_υ for the $X^1\Sigma_g^+$, $e^3\Delta_u$, $a^3\Sigma_u^-$, and $d^3\Pi_g$ electronic states with the aid of module VIBROT in the MOLCAS 7.4 program package.[40] As mentioned above, the present T_e of $d^3\Pi_g$ electronic state is far from the experimental data. To further identify the creditability of the present results, we list the molecular constants of the first 40 vibrational states for the $d^3\Pi_g$ electronic state in Table 5 for comparison with the available measurements.

Only one study[10] reported on the inertial rotation constant for the $d^3\Pi_g$ electronic states of As_2 molecule. For convenient comparison with the present results, we also list these data in Table 5. Excellent agreement could be found between the RKR data and the present ones. For example, the differences in B_υ between the present results and the experimental ones[10] are only 0.15%, 0.20%, and 0.30% for $\upsilon = 0$, 1, and 3, respectively. As a result, these comparisons show that the B_υ results in Table 5 are accurate, though no experimental values for the higher vibrational states can be presented for comparison with them.

Table 5. Comparisons of molecular constants between our results and the RKR data for the $As_2(d^3\Pi_g)$ when $J = 0$.

υ	$G(\upsilon)$/cm^{-1}	10^1B_υ/cm^{-1}		10^8D_υ/cm^{-1}	υ	$G(\upsilon)$/cm^{-1}	10^1B_υ/cm^{-1}	10^8D_υ/cm^{-1}
	This work	This work	Exp.[10]	This work		This work	This work	This work
0	170.79	0.919113	0.9205	7.88061	20	6447.59	0.842947	2.99491
1	510.57	0.915349	0.9172	2.68692	21	6729.32	0.839136	3.01762
2	847.92	0.911591	0.9139	2.69765	22	7007.63	0.835332	3.04390
3	1182.78	0.907823	0.9106	2.71003	23	7282.48	0.831531	3.07311
4	1515.10	0.904041		2.72243	24	7553.80	0.827730	3.10434
5	1844.85	0.900252		2.73600	25	7821.56	0.823932	3.13092
6	2171.96	0.896454		2.74828	26	8085.71	0.820142	3.16823
7	2496.39	0.892646		2.76305	27	8346.19	0.816366	3.19960
8	2818.09	0.888834		2.77704	28	8602.96	0.812609	3.23269
9	3137.00	0.885018		2.79127	29	8855.97	0.808871	3.26926
10	3453.09	0.881199		2.80428	30	9105.16	0.805150	3.30991
11	3766.31	0.877380		2.81946	31	9350.50	0.801446	3.35466
12	4076.59	0.873562		2.83565	32	9591.92	0.797761	3.40095
13	4383.90	0.869740		2.85308	33	9829.39	0.794095	3.20716
14	4688.18	0.865916		2.87137	34	10062.84	0.790468	3.50249
15	4989.39	0.862089		2.89047	35	10292.24	0.786874	3.55477
16	5287.47	0.858259		2.91033	36	10517.54	0.783318	3.61265
17	5582.39	0.854427		2.94427	37	10738.68	0.779808	3.68140
18	5874.07	0.850595		2.95187	38	10955.61	0.776386	6.54204
19	6162.49	0.846768		3.02157	39	11168.30	0.772935	3.83095

Unfortunately, no experiments can be found in the literature about the $G(\upsilon)$ and D_υ of this excited electronic state. Thus, we cannot make any direct comparison between them. But according to the excellent agreement between the present results and the available measurements, we have reasons to believe that the results collected in Table 5 are reliable and accurate.

4. Conclusions

In this paper, the PECs of $X^1\Sigma_g^+$, $e^3\Delta_u$, $a^3\Sigma_u^-$, and $d^3\Pi_g$ electronic states of As_2 molecule have been studied using the MRCI theory in combination with the correlation-consistent AV5Z basis set in the valence range. The effect of the relativistic correction on spectroscopic parameters is taken into consideration. The way to consider the relativistic corrections is to use the second-order Douglas–Kroll Hamiltonian approximation. All these corrections are carried out at the level of cc-pV5Z basis set. These PECs are extrapolated to the CBS limit by the two-point total-energy extrapolation formula. The spectroscopic parameters are determined using these PECs. The results obtained by the MRCI/Q5-ex+DK calculations are compared with the experimental data and other theoretical ones. Excellent agreement is found between the present spectroscopic results and the experimental data. With the PECs determined by the MRCI/Q5-ex+DK calculations, we compute the first 40 vibrational states of these four electronic states. The vibrational levels, inertial rotation and centrifugal distortion constants are reported for the first 40 vibrational states for the $d^3\Pi_g$ electronic state when $J = 0$, which are in excellent agreement with the available measurements. The present results show that the two-point extrapolation for total-energy extrapolation used here could improve the quality of spectroscopic parameters and molecular constants.

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