International Journal of Chemistry, Mathematics and Physics (IJCMP)
[Vol-9, Issue-2, Apr-Jun, 2025]
https://dx.doi.org/10.22161/ijcmp.9.2.4
ISSN: 2456-866X

Potential energy curves, spectroscopic parameters, vibrational levels and molecular constants for 37 low-lying electronic states of He_2

Michel Douglas Epée Epée[1], Roland Kevin Douthio Mbayang[2]

[1]Department of Physics, Faculty of Science, University of Douala, P. O. Box: 24157, Douala, Cameroon
[2]Postgraduate Training Unit for Mathematics, Applied Computer Science and Pure Physics, University of Douala, Douala, Cameroon
Corresponding author: epeemichel23@yahoo.fr

Received: 20 May 2025; Received in revised form: 18 Jun 2025; Accepted: 22 Jun 2025; Available online: 26 Jun 2025

***Abstract*— *A manifold of singlet and triplet electronic states of He_2 is characterized theoretically using the R-matrix method. Potential energy curves have been calculated for ${}^1\Sigma_u^+$, ${}^1\Sigma_g^+$, ${}^1\Pi_u$, ${}^1\Pi_g$, ${}^3\Sigma_u^+$, ${}^3\Sigma_g^+$, ${}^3\Pi_u$, ${}^3\Pi_g$ electronic states. These potential curves are then fitted to analytical potential energy functions (APEFs) using the Murrell-Sorbie potential function. The spectroscopic parameters, such as D_e, ω_e, $\omega_e x_e$, B_e, α_e are determined using the obtained APEFs, and compared with theoretical and experimental data available. A whole set of vibrational level $G(v)$ and inertial rotation constant B_v predicted for these electronic states by solving the ro-vibrational Schrödinger equation of nuclear motion using Numerov's method completes these characterization.*

***Keywords*— Spectroscopic parameters, molecular constant, vibrational level.**

I. INTRODUCTION

The properties of rare gases are of considerable interest for the development of modelling and as standard values for experiments. The interatomic potential is of fundamental importance for understanding the dynamic and static properties of gases, liquids, and solids. With only four electrons, He_2 belong to the limited class of molecular system for which highly accurate ab-initio quantum mechanical calculations are feasible. The potential energy curve of the ground state of He_2 is purely repulsive, exhibiting a very shallow van-der-walls Minimum of 9.1 10^{-3} eV at 2.97 Å [1, 2]. The low-lying excited states of the helium dimer He_2 are more or less strongly covalently bound [3, 4]. The occurrence of highly excited bound states above a repulsive ground states suggests several important applications. Since these molecular excited states are generated in rare gas discharges, one can use the continuum emissions from these states as light sources in the vacuum ultraviolet [5, 6]. The existence of humps on nearly all potential curves of bound excited states of He_2 has caused a great amount of theoretical studies, both in qualitative and quantitative way. More than 60 electronic states are known for He_2 mainly through the extensive classical grating measurements of Ginter et al [7]. The low-lying electronic states of He_2 have been the subject of theoretical and experimental studies [8, 9] but have not been treated a whole; with the exception of some states which have been studied in context of particular problems such as the excited triplet states which are important in the study of penning ionization while the lowest triplet states are of interest in spectroscopy and scattering studies and as potential means of energy storage [10]. The first calculation of potential energy curves of the excited states for He_2 has been reported by Buckingham and Dalgarno[11]. Subsequently, many calculation of the low-lying electronic states were performed. The lowest ${}^1\Sigma_u^+$, ${}^3\Sigma_g^+$ and the first excited ${}^1\Sigma_g^+$ states of He_2 were computed by Browne [12]. The lowest singlet $A\,{}^1\Sigma_u^+$ excited state was calculated by Mukamel and kadldor [13] and Komasa [14]. The diabatic and adiabatic potential energy curve for the $^3\Sigma_u^+$, $^3\Sigma_g^+$, $^3\Pi_u$, $^3\Pi_g$, $^3\Delta_u$, $^3\Delta_g$ was obtained by Cohen[8]. Sunil et al. [15] used the Unitary Group multiconfiguration self-consistent field (MCSCF) procedure to calculate the potential energy curves of $C\ ^1\Sigma_g^+$, $c\ ^3\Sigma_g^+$, $A\ ^1\Sigma_u^+$, $a\ ^3\Sigma_u^+$. They also produced spectroscopic constants and vibrational energy levels and their spacing from these curves. The potential energy curves, vibrational levels and their spacing for the $A\ ^1\Sigma_u^+$ and $C\ ^1\Sigma_g^+$ states have been obtained by Jordan [16] by combining scattering, spectroscopy and ab- initio theory. The properties for $A\ ^1\Sigma_u^+$, $C\ ^1\Sigma_g^+$, $B\ ^1\Pi_g$, $a\ ^3\Sigma_g^+$, $^3\Pi_u$, $b\ ^3\Pi_g$ excited states of He$_2$ have also been calculated by Yarkony [4]. As can be seen in the literature, these studies mainly concentrated on the properties of $A\ ^1\Sigma_u^+$, $C\ ^1\Sigma_g^+$, $B\ ^1\Pi_g$, $a\ ^3\Sigma_g^+$, $^3\Pi_u$, $b\ ^3\Pi_g$, excited states. The properties of more electronic singlet and triplet excited states still remain unknown.

The present work is devoted to an accurate description of the 18 singlet and 19 triplet excited electronic states of He$_2$. The potential energy curve , the spectroscopic constants R_e, T_e, D_e, ω_e, $\omega_e x_e$, B_e, α_e of the corresponding $^1\Sigma_u^+$, $^1\Sigma_g^+$, $^1\Pi_u$, $^1\Pi_g$, $^3\Sigma_u^+$, $^3\Sigma_g^+$, $^3\Pi_u$, $^3\Pi_g$ electronic states have been investigated along their vibrational levels and the inertial rotation constant B_v.

II. COMPUTATIONAL DETAILS

In this work, we use the R-Matrix method [17] as implemented in the UKRMol codes [18]. The basis set employed is the cc-pVTZ Gaussian basis set for He$_2$ molecule. This set includes polarization functions. The molecule is treated in a reduced D_{2h} symmetry in which there are eight symmetries A$_g$, A$_u$, B$_{1g}$, B$_{1u}$, B$_{2g}$, B$_{3g}$, B$_{2u}$, B$_{3u}$. An initial set of molecular orbital was obtained by performing Self-Consistent Field (SCF) calculations for the $X\ ^1\Sigma_g^+$ state of He$_2$, although in practice the choice of orbitals is not important in a full configuration interaction (FCI) calculation. In the close coupling expansion of the trial wave function of the He$_2$ system, we include the ground state $X\ ^1\Sigma_g^+$ and the eight lowest excited state $A\ ^1\Sigma_u^+$ $B\ ^1\Pi_g$, $C\ ^1\Sigma_g^+$ and $F\ ^1\Pi_u$, $a\ ^3\Sigma_u^+$, $b\ ^3\Pi_g$, $c\ ^3\Sigma_g^+$, $f\ ^3\Pi_u$. Each state was represented by an FCI wave function. In our CI model we have the occupied orbitals which are augmented by the virtual molecular orbital up 11a$_g$, 5b$_{2u}$, 5b$_{3u}$, 2b$_{1g}$, 11b$_{1u}$, 5b$_{2g}$, 5b$_{3g}$, 2a$_u$. To obtain potential energy curves, Our FCI calculations were performed for several bondlengths.

The potential curves obtained are then fitted to analytical potential energy functions (APEFs) using the Murrell-Sorbie potential function [19]. The general expression of the Murrell potential function is:

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

where $\rho = R - R_e$, R is the inter-nuclear distance of diatomic molecule, R_e is it equilibrium inter-nuclear distance and is regarded as a fixed parameter in the fitting process. The parameters D_e and $a_i\,(i = 1,2,3\ldots..n)$ are determined by fitting. The quadratic, cubic, and quartic force constants $f_n\ (f_n = \frac{d^nV}{dR^n},\ n = 2, 3$ and $4)$ could be derived from function at the equilibrium position as followed

$$f_2 = D_e(a_1^2 - 2a_2) \qquad (2)$$

$$f_3 = -6D_e(a_3 - a_1a_2 + \tfrac{1}{3}a_1^3) \qquad (3)$$

$$f_4 = D_e(3a_1^4 - 12a_1^2a_2 + 24a_1a_3) \qquad (4)$$

The expression relating the spectroscopic constants with the force constants f_2, f_3 and f_4 for diatomic molecules may be found as

$$B_e = \frac{h}{8\pi c\mu R_e^2} \qquad (5)$$

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2 mc^2}} \qquad (6)$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(\frac{f_3R_e}{3f_2} + 1\right) \qquad (7)$$

$$\omega_e x_e = \frac{B_e}{8}\left[-\frac{f_4R_e^2}{f_2} + 15\left(1 + \frac{\omega_e\alpha_e}{6B_e^2}\right)^2\right] \qquad (8)$$

Based on the relationship equations among spectroscopic parameters and force constants (6)-(8), the spectroscopic data of diatomic molecule can be calculated. Using the potential energy curves obtained at the MRCI/ cc-pV5Z level of theory, the radial Schrödinger equation of nuclear motion is numerically solved using the Numerov method [20] to get the vibrational states when $J = 0$. The complete vibrational levels $\mathrm{G(v)}$, inertial rotation constant $\mathrm{B_v}$ are calculated.

III. RESULTS AND DISCUSSION

The potential energy curves of 37 electronic states of He$_2$ have been investigate, namely four $^1\Sigma_u^+$, five $^1\Pi_u$, four $^1\Sigma_g^+$, five $^1\Pi_g$ for singlet states and five $^3\Sigma_u^+$, five $^3\Pi_u$, four $^3\Sigma_g^+$ and five $^3\Pi_g$ for triplet states. To obtain the potential energy curves for the low-lying electronic states of

He$_2$ our calculation were repeated for 130 bondlengths in the range $R = 1.0$ to 13.0 a.u. Figure 1 and 2 display, respectively, singlet $^1\Sigma_u^+$, $^1\Pi_u$, $^1\Sigma_g^+$, $^1\Pi_g$ and triplet $^3\Sigma_u^+$, $^3\Pi_u$, $^3\Sigma_g^+$, $^3\Pi_g$ electronic states as function of internuclear distance. From Figures 1 and 2, one can see the existence of humps at about 2-3 Å on nearly all the potential energy curves of the excited states computed in the present work . It is seen in these figure that the general profile of singlet $A\ ^1\Sigma_u^+$, $C\ ^1\Sigma_g^+$, $B\ ^1\Pi_g$ and triplet $a\ ^3\Sigma_u^+$, $c\ ^3\Sigma_g^+$, $b\ ^3\Pi_g$ potential curves is similar to the ones described by Sunil et al [15] and Yarkony[4] and are in satisfactory agreement. The spectroscopic parameters such as the equilibrium distance R_e , the dissociation energy D_e, The adiabatic excitation energies T_e, the vibrational harmonic constant ω_e, the anharmonic frequencies $\omega_e x_e$, the rotational constant B_e for the 37 electronic states obtained in this work are presented in Table 1 for $^1\Sigma_u^+$ and $^1\Pi_u$, Table 2 for $^1\Sigma_g^+$and $^1\Pi_g$, Table 3 for $^3\Sigma_u^+$and $^3\Pi_u$, and Table 4 for $^3\Sigma_g^+$ and $^3\Pi_g$ along with the experimental and theoretical results available.

The lowest excited singlet states of He$_2$ are $A\ ^1\Sigma_u^+$ $B\ ^1\Pi_g$, $C\ ^1\Sigma_g^+$ and $F\ ^1\Pi_u$.

For the $A\ ^1\Sigma_u^+$ state, the R$_e$ value obtained in this work is 1.0419 Å that compares favorably with the 1.0404 Å and 1.0406 Å experimental results of Huber and Herzberg [9] and Focsa [22]. The theoretical R$_e$ obtained by Wasilewki et al. [23], Sunil et al [15] and Yarkony [4] are slightly higher than the experimental results and our calculation. In the case of the spectroscopic constants (ω_e, $\omega_e x_e$, α_e , B_e), our results (1838.45 cm^{-1} , 33.39 cm^{-1}, 7.7024 cm^{-1}, 0,2227 cm^{-1}) are reasonably in good agreement with the theoretical results of Wasilewki et al. [23] and Sunil et al [15] and the experimental results of Huber and Herzberg[9], and Focsa[22] as shown in Table 1.

The $B\ ^1\Pi_g$ electronic state, with a dissociation energy of 20271.92 cm^{-1}, is located at 150351 cm^{-1} (T$_e$) above the $X\ ^1\Sigma_g^+$ state. Our results for $\omega_e =$ $1752.974\ cm^{-1}$, $\omega_e x_e$ =36.7169 cm^{-1}, B_e =7.37848 cm^{-1} α_e=0.2337 cm^{-1} are in good agreement with those obtained by Huber and Herzberg [9] (1.0667 cm^{-1}, 1765.76 cm^{-1}, 7.4030 cm^{-1} , 0.2160 cm^{-1}) respectively.

The C $^1\Sigma_g^+$ state equilibrium inter-nuclear distance R$_e$, dissociation energy D$_e$, vibrational harmonic constant, anharmonic frequencies ω_e and rotational constant B_e computed to be respectively 1.0930 Å, 1654.643 cm^{-1}, 43.0382 cm^{-1} and 7.0286 cm^{-1} are in reasonably good agreement with the theoretical MCSCF calculations of Sunil et al.[15] and the experimental data of Huber and Herzberg [9](see Table 2).

The F $^1\Pi_u$ state located at 165971 cm^{-1} above $X\ ^1\Sigma_g^+$ state with a dissociation energy of 4862.95 cm^{-1} , the equilibrium inter-nuclear distance R$_e$ = 1.0822 Å, $\omega_e =$ 1681.95 cm^{-1} compares well with the experimental results of Huber and Herzberg [9].

The lowest triplet electronic states are $a\ ^3\Sigma_u^+$, $b\ ^3\Pi_g$, $c\ ^3\Sigma_g^+$, $f\ ^3\Pi_u$. The lowest-lying electronic state of He$_2$ is the $a\ ^3\Sigma_u^+$, $T_e = 144\,192\ cm^{-1}$, $R_e = 1.0459$ Å, $\omega_e = 1781.862\ cm^{-1}$, $\omega_e x_e = 42.3944\ cm^{-1}$ and $B_e =$ $7.6981\ cm^{-1}$. Beside the $a\ ^3\Sigma_u^+$ state, there is another excited state that correlates with the first dissociation channel He(1s^2 ^{1}S)+He(2s ^{3}S): the $c\ ^3\Sigma_g^+$ state $T_e =$ $155\,183\ cm^{-1}$, $R_e = 1.0974$ Å, $\omega_e = 1570.776\ cm^{-1}$, $\omega_e x_e = 55.46\ cm^{-1}$ and $B_e = 6.9990\ cm^{-1}$. The $b\ ^3\Pi_g$ state, $T_e = 149\,171\ cm^{-1}$, $R_e = 1.0640$ Å , $\omega_e =$ $1769.593\ cm^{-1}$, $\omega_e x_e = 40.4618\ cm^{-1}$ and $B_e =$ $7.4389\ cm^{-1}$ dissociating in the same channel He(1s^2 ^{1}S)+He(2p ^{3}S) with $f\ ^3\Pi_u$ is the second lowest triplet excited state. From Table 3 and 4, it is not difficult to find that our calculated bond lengths are in good agreement with the experimental values of Huber and Herzberg [9]. The dissociation energy for $a\ ^3\Sigma_u^+$ and $c\ ^3\Sigma_g^+$ are 150-650 cm^{-1} closer to theoretical and experimental values available. For ω_e and B_e the agreement between our results, the theoretical data computed by Sunil et al [15] and experimental values of Huber and Herzberg [9], and Focsa [22] is reasonably good. Our results for $\omega_e x_e$ shows a slight gap in comparison with other theory and experiments.

For the other singlet $^1\Sigma_u^+$, $^1\Pi_u$, $^1\Sigma_g^+$, $^1\Pi_g$ and triplet $^3\Sigma_u^+$, $^3\Pi_g$, $^3\Sigma_g^+$, $^3\Pi_u$ electronic states, From Table 1-4 the comparisons of our calculated data with the experimental values of Huber and Herzberg [9], one can find that an excellent agreement is obtained for the values of the equilibrium interatomic separation R$_e$ with the relative difference $0.061\ \% < \frac{\Delta R_e}{R_e} < 1.54\%$ and a very good agreement for the values of B$_e$ with the relative difference $1.01.10^{-5}\ \% < \frac{\Delta B_e}{B_e} < 1.6\%$. The values of ω_e are in good accordance with the experimental data. A slight deviation can be observed between our results for $\omega_e x_e$ and the experiment.

Vibrational energy level for singlet $^1\Sigma_u^+$, $^1\Pi_u$, $^1\Sigma_g^+$, $^1\Pi_g$ and triplet $^3\Sigma_u^+$, $^3\Pi_u$, $^3\Sigma_g^+$, $^3\Pi_g$ electronic states was calculated by solving the radial Schrödinger

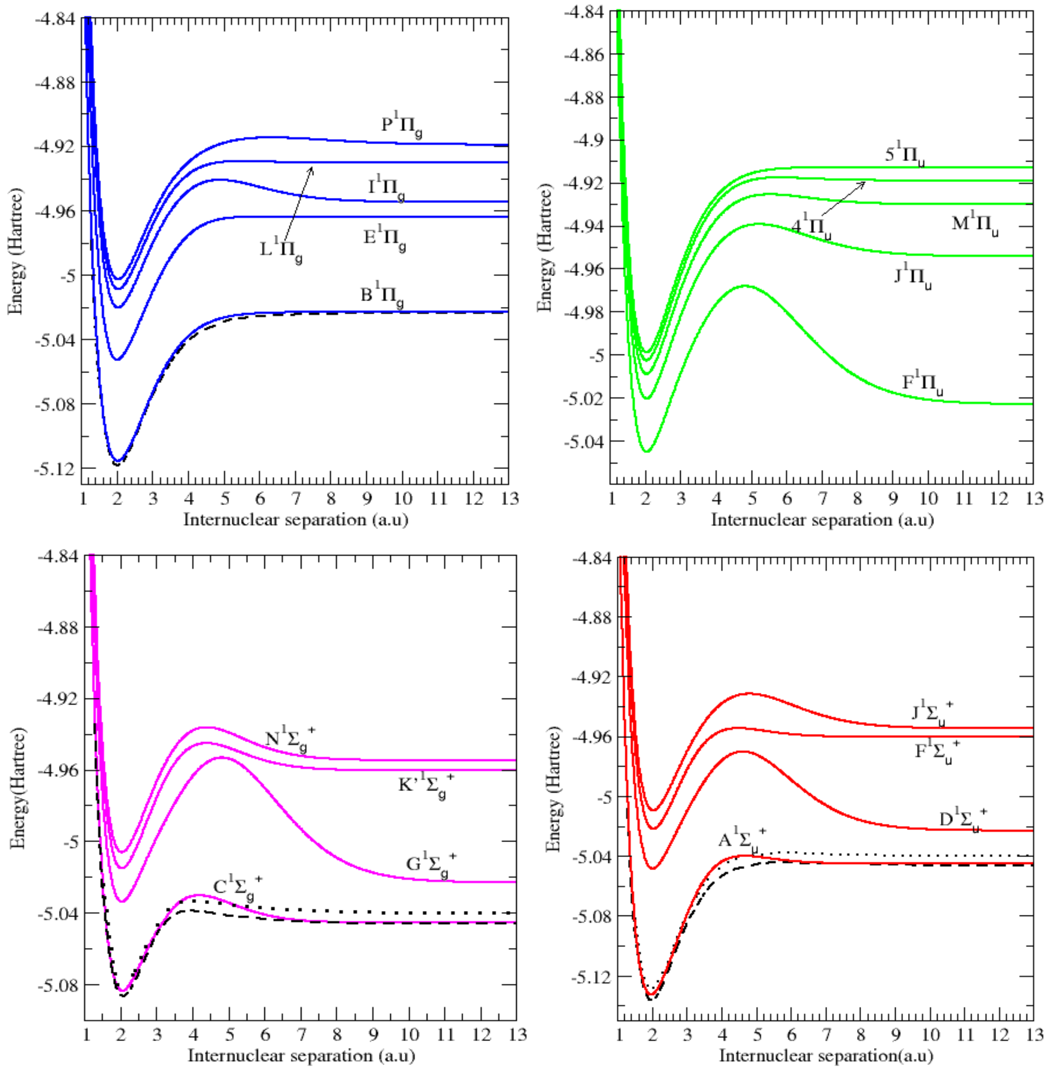

Fig.1: Potential energy curves of the lowest-lying singlet states of the molecule He_2 molecule. The symmetry of each electronic states is indicated in the panel. Present calculation: continuous curves. Black dash and dotted curves in the $^1\Sigma_u^+$, $^1\Sigma_g^+$ and $^1\Pi_g$ figures; Yarkony [4] and Sunil et al. [15]

equation numerically. We have obtained the maximum vibrational levels to be: 25 for $A\ ^1\Sigma_u^+$, 22 for $D\ ^1\Sigma_u^+$, 17 for $F\ ^1\Sigma_u^+$, 21 for $J\ ^1\Sigma_u^+$; 21 for $B\ ^1\Pi_g$, 22 for $E\ ^1\Pi_g$, 20 for $I\ ^1\Pi_g$ and 21 for $L\ ^1\Pi_g$; 19 for $F\ ^1\Pi_u$, 20 for $J\ ^1\Pi_u$, 21 for $M\ ^1\Pi_u$ and 23 for $Q\ ^1\Pi_u$; 16 for $C\ ^1\Sigma_g^+$, 17 for 2 $^1\Sigma_g^+$, 19 for $G\ ^1\Sigma_g^+$ and 20 for $K'\ ^1\Sigma_g^+$; 27 for $a\ ^3\Sigma_u^+$, 19 for $d\ ^3\Sigma_u^+$, 20 for $h\ ^3\Sigma_u^+$, 21 for $k\ ^3\Sigma_u^+$, 22 for $o\ ^3\Sigma_u^+$; 23 for $b\ ^3\Pi_g$, 22 for $e\ ^3\Pi_g$, $i\ ^3\Pi_g$, $l\ ^3\Pi_g$, 20 for $p\ ^3\Pi_g$; 17 for $c\ ^3\Sigma_g^+$, 22 for $g\ ^3\Sigma_g^+$, 21 for $k'\ ^3\Sigma_g^+$, $n\ ^3\Sigma_g^+$; 19 for $f\ ^3\Pi_u$, 22 for $j\ ^3\Pi_u$, 21 for m $^3\Pi_u$, 22 for $q\ ^3\Pi_u$.

The vibrational levels spacing $G(v+1) - G(v)$ between the adjacent vibrational states for the 37 electronic states have been calculated. The first six ($v = 0 - 5$) are collected in Table 5 for singlet states $^1\Sigma_u^+$, $^1\Pi_u$, $^1\Sigma_g^+$, $^1\Pi_g$ and Table 6 for triplet $^3\Sigma_u^+$, $^3\Pi_u$, $^3\Sigma_g^+$, $^3\Pi_g$ states; the remaining ones are available upon request. For the lowest singlet $A\ ^1\Sigma_u^+$ $B\ ^1\Pi_g$, $C\ ^1\Sigma_g^+$ and $F\ ^1\Pi_u$ states and triplet $^3\Sigma_u^+$, $b\ ^3\Pi_g$, $c\ ^3\Sigma_g^+$, $f\ ^3\Pi_u$ states, as can be seen from Tables 5 and 6, the present results are in excellent agreement with the experimental data of Brown [25], the MCSCF calculation of Sunil et al.[14], the MCSCF/CI calculation of Yarkony[4] and the CI results of Jordan[16] with the deviations less than 0.18%, 0.048%, 0.45%, 0.38%, 0.06% and 0.28% when $v = 0, 1, 2, 3, 4, 5$ respectively. The present data of B_v are reported in Tables 7 and 8 respectively for the singlet $A\ ^1\Sigma_u^+$ $B\ ^1\Pi_g$, $C\ ^1\Sigma_g^+$

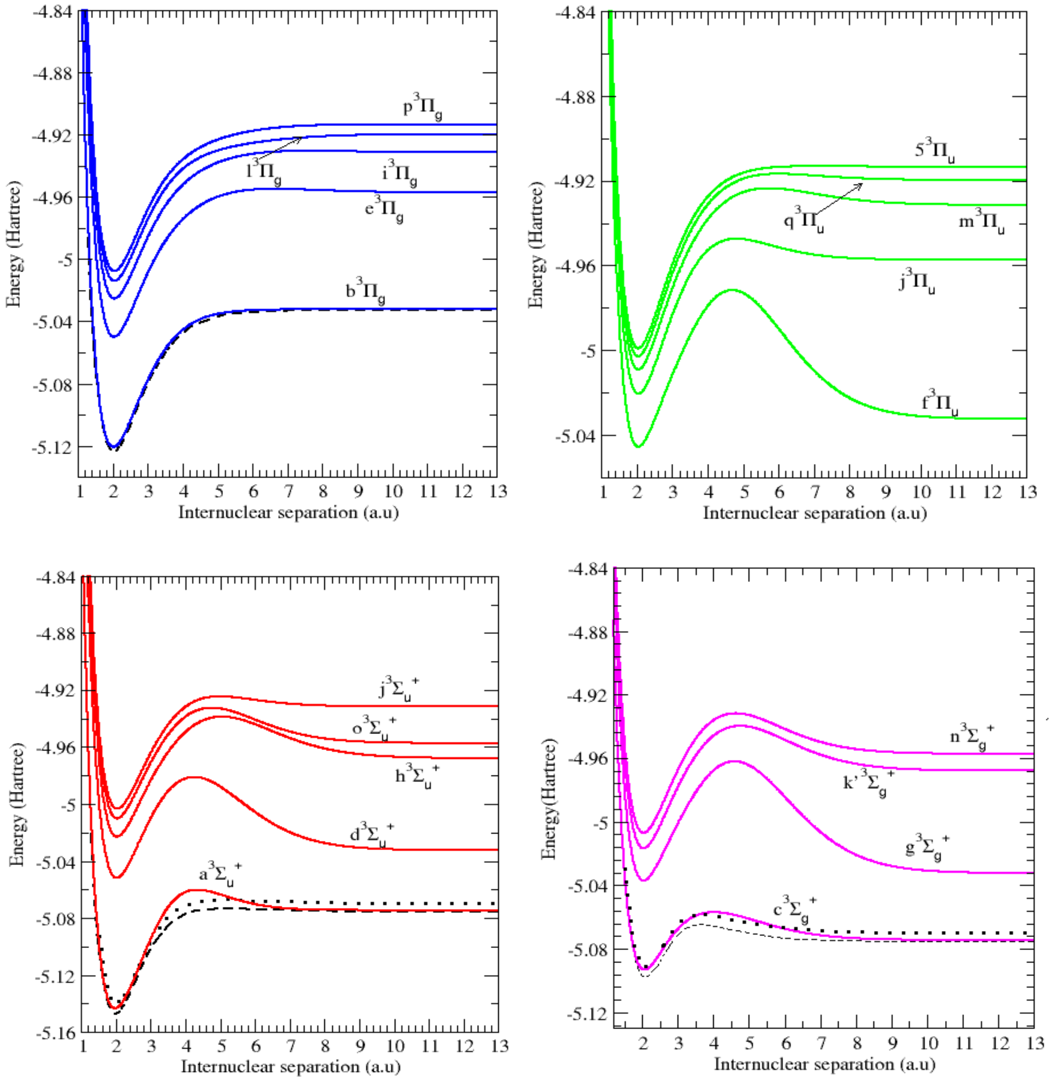

Fig.2: Potential energy curves of the lowest-lying singlet states of the molecule He₂ molecule. The symmetry of each electronic states is indicated in the panel. Present calculation: continuous curves. Black dash and dotted curves in the $^3\Sigma_u^+$, $^3\Sigma_g^+$ and $^3\Pi_g$ figures; Yarkony [4] and Sunil et al.[15]

and $F\ ^1\Pi_u$ states and triplet $^3\Sigma_u^+$, $b\ ^3\Pi_g$, $c\ ^3\Sigma_g^+$, $f\ ^3\Pi_u$ state. For convenient comparison with the present results for $A\ ^1\Sigma_u^+$, $C\ ^1\Sigma_g^+$, $a\ ^3\Sigma_u^+$, $b\ ^3\Pi_g$ and $c\ ^3\Sigma_g^+$ electronic states , we also tabulate in Tables 7 and 8 the values from theories and experiments for these states. From Tables 7-8, it is not difficult to find the excellent agreement between the present results, theoretical values of Yarkony[4], Sunil et al.[14], Jordan[16] and experimental data of Brown and Ginter [25] and Focsa et al. [22] with the errors $0.058\ cm^{-1}$, $0.012\ cm^{-1}$, $0.023\ cm^{-1}$, $0.072\ cm^{-1}$, $0.041\ cm^{-1}$ and $0.029\ cm^{-1}$ for $v = 0, 1, 2, 3, 4, 5$ respectively.

Unfortunately, no theoretical results, no experiments can be found in the literature about $G(v)$ and B_v for other excited states of He₂ than the singlet $A\ ^1\Sigma_u^+$ $B\ ^1\Pi_g$, $C\ ^1\Sigma_g^+$ and $F\ ^1\Pi_u$ states and triplet $a\ ^3\Sigma_u^+$, $b\ ^3\Pi_g$, $c\ ^3\Sigma_g^+$, $f\ ^3\Pi_u$. We cannot make any direct comparison. According to the excellent agreement between the present spectroscopic parameters, vibrational levels spacing, the inertial rotation constant B_v and the available theoretical and experimental results, we have reasons to believe that the results presented in Tables 1-8 4 are accurate and must be reliable.

IV. CONCLUSION

In the present work, the study for the 37 low-lying singlet $^1\Sigma_u^+$, $^1\Pi_u$, $^1\Sigma_g^+$, $^1\Pi_g$ and triplet $^3\Sigma_u^+$,

Table 1 : Spectroscopic constants of He_2 *singlet* $^1\Sigma_u^+$, $^1\Pi_u$ *electronic states*

State	R_e(Å)	$D_e(cm^{-1})$	$T_e(cm^{-1})$	$\omega_e(cm^{-1})$	$\omega_e x_e(cm^{-1})$	$B_e(cm^{-1})$	$\alpha_e(cm^{-1})$
$2s\sigma\ A\ ^1\Sigma_u^+$							
This work	1.0419	19185.8442	146 545	1838.45	33.39	7.7024	0.2227
CEPA[a]	1.0457	19324.0742		1846.33	33.78		
MCSCF[b]	1.0457	19453.4843		1848.10	34.20	7.7030	0.2155
MCSCF/CI[c]	1.0440	19804	146 120	1860.30			
ECG[d]		19996	146 390	1863.10			
Experiment[e]	1.0406		146 365	1861.33	35.28	7.7789	0.2166
Experiment[f]	1.0404			1861.30	35.20	7.7814	0.2197
$3s\sigma\ D\ ^1\Sigma_u^+$							
This work	1.0671	5607.1225	165 002	1712.55	35.86	7.3905	0.2811
Experiment[e]	1.0694		165 085	1746.43	35.54	7.3650	0.2180
$3d\sigma\ F\ ^1\Sigma_u^+$							
This work	1.0797	4966.1907	165 643	1718.18	42.49	7.2616	0.2479
Experiment[e]	1.0894		165 813	1564.25	40.00	7.0980	0.2460
$4s\sigma\ H\ ^1\Sigma_u^+$							
This work	1.0789	13488.2263	170 850	16691.12	42.72	7.2358	0.2216
Experiment[e]	1.0770		171 951			7.2600	0.2300
$4d\sigma\ J\ ^1\Sigma_u^+$							
This work	1.0790	1323.1801	172 222	1707.89	34.79	7.1980	0.2178
$5s\sigma\ ^1\Sigma_u^+$							
This work	1.0774	12026.4901	173 548	1708.16	41.05	7.2553	0.2357
$5d\sigma\ M\ ^1\Sigma_u^+$							
This work	1.0797	10656.204	173 667	1712.75	35.81	7.2221	0.2229
Experiment	1.0910		174 748				
$^1\Pi_u$							
$3d\pi\ F\ ^1\Pi_u$							
This work	1.0822	4862.95	165 745	1681.95	48.77	7.1920	0.2498
Experiment[d]	1.0849	5162.4133	165 971	1670.57	40.03	7.1560	0.2350
$4d\pi\ J\ ^1\Pi_u$							
This work	1.0817	14502.17	171 181	1691.52	40.32	7.1974	0.2325
Experiment[d]	1.0908		172 290			7.080	
$5d\pi\ M\ ^1\Pi_u$							
This work	1.0805	17261.05	173 706	1702.67	37.8620	7.2144	0.2299
Experiment[d]	1.0910		174 788			7.0700	
$6d\pi\ ^1\Pi_u$							
This work	1.0806	18349.05	175 065	1698.76	34.4075	7.2131	0.2283
$7d\pi\ ^1\Pi_u$							
This work	1.0807	18866.41	175 882	1703.47	29.9749	7.2116	0.2215

[a] CEPA calculations of Wasilewsli et al [23]
[b] MCSCF calculations of Sunil et al [15]
[c] MCSCF/CI calculation of yarkony [4]
[d] ECG calculation of Komasa [14]
[e] Experiment from Huber and Herzberg [9]
[f] Experiment from Focsa et al. [22]

$^3\Pi_u$, $^3\Sigma_g^+$, $^3\Pi_g$ electronic states of He_2 molecule has been performed using the UK R-Matrix molecular codes. The potential energy curves and the spectroscopic constant have been determined for the lowest-lying states. The comparison of our results, for different states, with theoretical data and experiment shows an excellent agreement. For excited states other than $A\ ^1\Sigma_u^+$ $B\ ^1\Pi_g$, $C\ ^1\Sigma_g^+$, $C\ ^1\Sigma_g^+$, $F\ ^1\Pi_u$, $^3\Sigma_u^+$, $b\ ^3\Pi_g$, $c\ ^3\Sigma_g^+$, $f\ ^3\Pi_u$, Vibrational states have been predicted for the first time. For each vibrational state, the vibrational levels

Table 2 : Spectroscopic constants of singlet $^1\Sigma_g^+$, $^1\Pi_g$ electronic states

State	R_e(Å)	$D_e(cm^{-1})$	$T_e(cm^{-1})$	$\omega_e(cm^{-1})$	$\omega_e x_e(cm^{-1})$	$B_e(cm^{-1})$	$\alpha_e(cm^{-1})$
$^1\Sigma_g^+$							
$2p\sigma\ C\ ^1\Sigma_g^+$							
This work	1.0930	8680.967	157 669	1654.643	43.0382	7.0286	0.2489
CEPA[a]	1.0970	8380.178		1652.43	28.74		
MCSCF[b]	1.0953	8729.935		1652.90	40.40	7.0202	0.2300
MCSCF/CI[c]	1.0960	8819	157 108	1655.60			
Experiment[e]	1.0917	8862842	157 415	1653.43	41.04	7.0520	0.2150
Experiment[f]	1.0915			1571.809		7.07067	0.2470
$3p\sigma\ ^1\Sigma_g^+$							
This work	1.0811	2375.710		1694.27	49.3427	7.2061	0.2590
$4p\sigma\ G\ ^1\Sigma_g^+$							
This work	1.0808	12019.30	168 233	1697.35	47.3762	7.2088	0.2260
$5p\sigma\ K'\ ^1\Sigma_g^+$							
This work	1.0798	11277.42	172 319	1705.64	46.7682	7.2236	0.2291
$^1\Pi_g$							
$2p\pi\ B\ ^1\Pi_g$							
This work	1.0686	20271.92	150 351	1752.974	36.7169	7.37848	0.2337
CEPA	1.0726	20355.86		1744.76	32.59		
MCSCF/CI	1.0710	20925	150 012	1764.3			
Experiment[e]	1.0667	21219.76	149 914	1765.76	34.39	7.4030	0.2160
Experiment[f]	1.0672			1766.151	34.586	7.3955	0.2156
$3p\pi\ E\ ^1\Pi_g$							
This work	1.0791	14392.23	165 791	1705.918	32.1155	7.2329	0.2270
Experiment[e]	1.0764		165 911	1721.19	34.76	7.2705	0.2156
$4p\pi\ I\ ^1\Pi_g$							
This work	1.0804	17227.48	171 186	1699.204	33.2736	7.2151	0.2224
Experiment[e]	1.078		172 266			7.242	0.223
$5p\pi\ L\ ^1\Pi_g$							
This work	1.0791		173 692	1705			
Experiment[e]	1.079		174 794			7.23	0.222
$6p\pi\ P\ ^1\Pi_g$							
This work	1.0808	18364.31	175 027	1709.67	35.4396	7.2096	0.2140
Experiment[e]	1.080		176 160			7.23	0.222

[a] CEPA calculations of Wasilewsli et al. [23]

[b] MCSCF calculations of Sunil et al. [15]

[c] MCSCF/CI calculation of yarkony [4]

[d] ECG calculation of Komasa [14]

[e] Experiment from Huber and Herzberg [9]

[f] Experiment from Focsa et al. [22]

and the inertial rotation constants are determined. As a whole, comparison of our potential energy curves, spectroscopic constants, vibrational levels and inertial rotation constants with the available experiments and theories shows that the present results are both accurate and reliable. The new excited electronic states may provide a reliable theoretical basis and information for the experimental spectral properties related to the electronic structure for He_2 molecule and the potential curves will be a useful guide for the experimentalist to properly assign the transitions resulting from the highly dense set of excited states.

Table 3 : Spectroscopic constants of He₂ triplet $^3\Sigma_u^+$, $^3\Pi_u$ *electronic states*

State	$R_e(\text{Å})$	$D_e(cm^{-1})$	$T_e(cm^{-1})$	$\omega_e(cm^{-1})$	$\omega_e x_e(cm^{-1})$	$B_e(cm^{-1})$	$\alpha_e(cm^{-1})$
$^3\Sigma_u^+$							
$2s\sigma\ a\ ^3\Sigma_u^+$							
This work	1.0459	15151.723	144 192	1787.862	42.3944	7.6981	0.2467
CEPA[a]	1.0483	15057.039		1816.00	34.50		
MCSCF[b]	1.0504	15312.362		1794.50	36.40	7.6342	0.2291
MCSCF/CI[c]	1.0500	15751	143 907	1808.2	38.89		
Experiment[e]	1.0457	15805.519	144 048	1808.56	38.21	7.7036	0.228
Experiment[f]	1.0454			1808.50	37.812	7.7076	0.2340
$3s\sigma\ d\ ^3\Sigma_u^+$							
This work	1.0705	12822.321	164 278	1744.252	34.9554	7.3498	0.2206
Experiment[e]	1.0712		164 479	1728.01	36.13	7.3412	0.2244
$3d\sigma\ f\ ^3\Sigma_u^+$							
This work	1.0749			1713.78	37.6847		
Experiment[e]	1.0914		165 685	1635.77	44.41	7.071	0.246
$4s\sigma\ h\ ^3\Sigma_u^+$							
This work	1.0754	4282.231	170 628	1720.027	38.7203	7.2828	0.2347
Experiment[e]	1.077		180884	1637.9		7.264	0.23
$4d\sigma\ j\ ^3\Sigma_u^+$							
This work	1.0846		170 628				
Experiment[e]			171323				
$5s\sigma\ k\ ^3\Sigma_u^+$							
This work	1.0766	11611.005	173 427	1716.256	38.8348	7.2670	0.2370
Experiment[e]	1.079		173698	1635.3		7.232	0.23
$5d\sigma\ m\ ^3\Sigma_u^+$							
This work	1.0815						
Experiment[e]	1.091		173730				
$^3\Pi_u$							
$3d\pi\ f\ ^3\Pi_u$							
This work	1.0891	2886.745	165 674	1656.729	46.3226	7.1948	0.2482
Experiment[e]	1.0865		165 877	1661.48	44.79	7.136	0.235
$4d\pi\ j\ ^3\Pi_u$							
This work	1.0849	13840.001	171 198	1654.725		7.1557	0.2361
Experiment[e]	1.0827		171 402	1680.94	40.81	7.1860	0.2296
$5d\pi\ m\ ^3\Pi_u$							
This work	1.0818	17017.051	173 674	1692.115		7.1972	0.2287
Experiment[e]	1.091		174 778			7.07	
$6d\pi\ q\ ^3\Pi_u$							
This work	1.0809	18226.804	175 047	1701.809		7.2074	0.2241
Experiment[e]	1.0898		176 169			7.092	
$7d\pi\ ^3\Pi_u$							
This work	1.0804	18818.942	175 848	1709.569		7.2146	0.2196

[a] CEPA calculations of Wasilewsli et al. [23]

[b] MCSCF calculations of Sunil et al. [15]

[c] MCSCF/CI calculation of yarkony [4]

[d] ECG calculation of Komasa [14]

[e] Experiment from Huber and Herzberg [9]

[f] Experiment from Focsa et al. [22]

Table 4 : Spectroscopic constants of He₂ triplet ${}^3\Sigma_g^+$, ${}^3\Pi_g$ *electronic states*

State	R_e(Å)	$D_e(cm^{-1})$	$T_e(cm^{-1})$	$\omega_e(cm^{-1})$	$\omega_e x_e(cm^{-1})$	$B_e(cm^{-1})$	$\alpha_e(cm^{-1})$
${}^3\Sigma_g^+$							
$2p\sigma\ \ c\ {}^3\Sigma_g^+$							
This work	1.0974	4158.907	155 183	1570.776	55.46	6.9990	0.3061
CEPA[a]	1.0980	4015.210		1644.85	35.04		
MCSCF[b]	1.1004	4606.30		1582.60	52.50	6.9322	0.2560
MCSCF/CI[c]	1.1030	4858	154 703	1589.5			
Experiment[d]	1.0977	4802.16	155 053	1583.85	52.74	7.0048	0.3105
Experiment[e]				1588.34	54.16	6.9900	0.2638
$3p\sigma\ \ {}^3\Sigma_g^+$							
This work	1.0825	1064.052		1676.084	55.53	7.1877	0.2616
Experiment[d]							
$4p\sigma\ g\ {}^3\Sigma_g^+$							
This work	1.0814	10738.52		1694.519	44.24	7.2016	0.2378
Experiment[d]	1.0801			1589.92	41	7.2207	0.2478
$5p\sigma\ k'\ {}^3\Sigma_g^+$							
This work	1.0811	10924.47		1700.933	44.16	7.2067	0.2234
Experiment[d]	1.0684			1686.90	38.10	7.379	0.349
${}^3\Pi_g$							
$2p\pi\ \ b\ {}^3\Pi_g$							
This work	1.0640	19403.571	149 171	1769.593	40.4618	7.4389	0.2508
CEPA[a]	1.0689	19341.562		1756	33.22		
MCSCF/CI[c]	1.0681	19947	148 943				
Experiment[d]	1.0635	20250.93	148 835	1769.07	35.02	7.4473	0.2196
Experiment[e]	1.0645				35.249	7.4334	0.2191
$3p\pi\ e\ {}^3\Pi_g$							
This work	1.0758	20343.64	164 695	1732.021	35.0069	7.2776	0.2162
Experiment[d]	1.0754		165 598	1721.22	34.970	7.2838	0.2215
$4p\pi\ i\ {}^3\Pi_g$							
This work	1.0807	20626.07	170 065	1703.236	34.5463	7.2114	0.2163
Experiment[d]	1.0785		171 290	1637.94	35.25	7.242	0.223
$5p\pi\ l\ \ {}^3\Pi_g$							
This work	1.0817	20721.44	172 553	1701.272	33.8314	7.1979	0.2128
Experiment[d]	1.0797		173 884	1633.96	35.25	7.226	0.222
$6p\pi\ \ q\ {}^3\Pi_g$							
This work	1.0811	20729.43	173 937	1705.911	31.3335	7.2058	0.2115
Experiment[d]	1.0801		175 281	1701.18	35.35	7.220	0.224

[a] CEPA calculations of Wasilewsli et al. [23]

[b] MCSCF calculations of Sunil et al. [15]

[c] MCSCF/CI calculation of yarkony [4]

[d] Experiment from Huber and Herzberg [9]

[e] Experiment from Focsa et al. [22]

Table 5 : Vibrational energy levels spacing $E_{v+1} - E_v$ (cm^{-1}) for $^1\Sigma_u^+$, $^1\Pi_g$, $^1\Sigma_g^+$ and $^1\Pi_u$ singlet States of He₂

State	v	0	1	2	3	4	5
$2s\sigma\ A\ ^1\Sigma_u^+$	This work	1788.2443	1718.0851	1657.9791	1597.9264	1507.9269	1427.9807
	MCSCF[a]	1779.20	1708.85	1637.75	1566.17	1492.43	1417.30
	MCSCF/CI[b]	1789.76	1719.25	1648.46	1577.17	1503.93	1429.25
	ECG[c]	1791.56	1720.38	1648.05	1575.23	1501.73	1426.82
	Experiment[f]	1790.76	1719.69	1647.98	1575..40	1501.90	
$3s\sigma\ D\ ^1\Sigma_u^+$	This work	1620.0748	1529.4481	1440.7501	1353.9809	1269.1405	1186.2289
$3d\sigma\ F\ ^1\Sigma_u^+$	This work	1633.8730	1550.7592	1468.8867	1388.2556	1308.8658	1230.7173
$4s\sigma\ H\ ^1\Sigma_u^+$	This work	1624.3542	1553.9856	1479.8557	1401.9646	1320.3123	1234.8988
$4d\sigma\ J\ ^1\Sigma_u^+$	This work	1637.6142	1566.1002	1493.2963	1419.2026	1343.8191	1267.1456
$5s\sigma\ ^1\Sigma_u^+$	This work	1632.0840	1555.6589	1478.8686	1401.7133	1324.1929	1246.3074
$5d\sigma\ M\ ^1\Sigma_u^+$	This work	1640.6387	1567.6437	1493.7295	1418.8960	1343.1433	1266.4773
$^1\Pi_g$							
$2p\pi\ B\ ^1\Pi_g$	This work	1640.2003	1677.8059	1514.3799	1449.9221	1384.4325	1317.9112
$3p\pi\ E\ ^1\Pi_g$	This work	1659.7599	1587.8686	1514.8809	1440.7968	1365.6162	1289.3392
$4p\pi\ I\ ^1\Pi_g$	This work	1634.9500	1566.0122	1496.3942	1426.0959	1355.1173	1283.4585
$4f\pi\ ^1\Pi_g$	This work	1632.8916	1563.1812	1492.3829	1420.4965	1347.5222	1273.4598
$5p\pi\ L\ ^1\Pi_g$	This work	1630.3919	1560.4173	1489.2295	1416.8287	1343.2148	1268.3878
$5f\pi\ ^1\Pi_g$	This work	1636.8370	1565.9909	1494.0392	1420.9818	1346.8188	1271.5501
$6p\pi\ P\ ^1\Pi_g$	This work	1641.2428	1571.8551	1501.4703	1430.0884	1357.7094	1284.3334
$6f\pi\ ^1\Pi_g$	This work	1635.0122	1566.2296	1496.4363	1425.6324	1353.8178	1280.9925
$^1\Sigma_g^+$							
$2p\sigma\ C\ ^1\Sigma_g^+$	This work	1579.1033	1494.1395	1404.7647	1305.9818	1198.7898	1070.1888
	MCSCF[a]	1572.60	1491.13	1405.44	1311.47	1206.55	1081.32
	VBPA[d]	1573.11	1488.02	1400.14	1307.73	1203.24	1070.4
	Experiment[f]	1571.82	1489.26	1402.11	1308.17	1202.33	
$3p\sigma\ ^1\Sigma_g^+$	This work	1603.2510	1511.4271	1418.7640	1325.2617	1230.9203	1135.2617
$4p\sigma\ ^1\Sigma_g^+$	This work	1627.9266	1556.6480	1483.4340	1408.2845	1331.1997	1252.1795
$4f\sigma\ C\ ^1\Sigma_g^+$	This work	1639.9846	1566.8975	1492.5799	1416.7319	1339.6535	1261.2446
$5p\sigma\ C\ ^1\Sigma_g^+$	This work	1632.6517	1558.4528	1482.9929	1406.2721	1328.2904	1249.0477
$5f\sigma\ C\ ^1\Sigma_g^+$	This work	1636.2473	1562.3533	1487.5834	1411.9375	1335.4156	1258.0177
$^1\Pi_u$							
$3d\pi\ F\ ^1\Pi_u$	This work	1598.2935	1514.1571	1429.5253	1344.3982	1258.7758	1172.6581
	CI[e]	1604	1516	1334			
$4d\pi\ J\ ^1\Pi_u$	This work	1616.1537	1540.2523	1463.7894	1386.7650	1309.1791	1231.0317
$5d\pi\ M\ ^1\Pi_u$	This work	1627.7894	1552.6459	1476.8672	1400.5718	1323.7596	1246.4307
$6d\pi\ ^1\Pi_u$	This work	1627.0210	1555.1979	1483.2895	1411.2958	1339.2169	1267.0527
$7d\pi\ ^1\Pi_u$	This work	1633.2980	1562.0982	1489.8304	1416.4947	1342.0912	1266.6197

[a] MCSCF calculations of Sunil et al [15]

[b] MCSCF/CI calculation of yarkony[4]

[c] ECG calculation of Komasa [14]

[d] Valence Bond pseudopotential approcach (VBPA) of Jordan [16]

[e] CI Method of Chabalowski [24]

[f] Experiment of Brown et Ginter[26]

Table 6 : Vibrational energy levels spacing $E_{v+1} - E_v$ (cm^{-1}) for $^3\Sigma_u^+$, $^3\Pi_g$, $^3\Sigma_g^+$ and $^3\Pi_u$ Triplet States of He2

State	v	**0**	**1**	**2**	**3**	**4**	**5**
$2s\sigma\ a\ ^3\Sigma_u^+$	This work	1714.1754	1650.6992	1589.6591	1531.0552	1474.8874	1421.1559
	MCSCF[a]	1720.38	1643.05	1563.88	1482.53	1397.10	1308.21
	MCSCF/CI[b]	1731.05	1653.95	1576.24	1496.09	1409.44	1321.50
	CI[c]	1736	1655	1577	1506	1412	1312
	Experiment[d]	1732.14	1654.31	1574.31	1492.76	1408.11	
$3s\sigma\ d\ ^3\Sigma_u^+$	This work	1673.2273	1600.2297	1525.1740	1448.0604	1368.8889	1287.6594
$3d\sigma\ f\ ^3\Sigma_u^+$	This work	1584.7543	1528.9654	1500.8587	1500.4343		
$4s\sigma\ h\ ^3\Sigma_u^+$	This work	1642.3289	15841737	1485.5422	1406.4343	1326.8501	1246.7896
$4d\sigma\ j\ ^3\Sigma_u^+$	This work	1605.1672	2537.6206	1470.5430	1403.9345	1337.7949	1272.1243
$5s\sigma\ k\ ^3\Sigma_u^+$	This work	1638.3830	1560.1509	1481.5437	1402.5616	1323.2043	1243.4721
$5d\sigma\ m\ ^3\Sigma_u^+$	This work	1629.2474	1557.1552	1484.3147	1410.7258	1336.3887	1261.3032
$6s\sigma\ o\ ^3\Sigma_u^+$	This work	1630.3698	1557.1924	1483.7196	1409.9512	1335.8874	1261.5281
$6d\sigma\ d\ ^3\Sigma_u^+$	This work	1626.1563	1562.3987	1494.6169	1422.8108	1346.9805	1267.1260
$^3\Pi_g$							
$2p\pi\ b\ ^3\Pi_g$	This work	1682.7091	1596.7356	1511.7126	1427.6401	1344.518	1262.3468
	MCSCF/CI[b]	1696.50	1625.17	1550.60	1478.25	1410.12	1334
	CI[c]	1697	1629	1558	1485	1416	1342
	Experiment[d]	1698.87	1628.25	1557.62			
$3p\pi\ e\ ^3\Pi_g$	This work	1662.1265	1591.4575	1519.9808	1447.6964	1374.6043	1300.7046
$4p\pi\ i\ ^3\Pi_g$	This work	1634.9500	1566.0122	1496.3942	1426.0959	1355.1173	1283.4585
$4f\pi\ ^3\Pi_g$	This work	1634.8957	1568.3629	1500.9208	1432.5693	1363.3083	1293.1380
$5p\pi\ l\ ^3\Pi_g$	This work	1634.4627	1566.7118	1497.9783	1428.2623	1357.5637	1285.8826
$5f\pi\ ^3\Pi_g$	This work	1641.5362	1569.5846	1496.7210	1422.9454	1348.2578	1272.6582
$6p\pi\ p\ ^3\Pi_g$	This work	1638.9041	1570.2252	1499.8019	1427.6341	1353.7218	1278.0651
$^3\Sigma_g^+$							
$2p\sigma\ c\ ^3\Sigma_g^+$	This work	1477.7705	1367.983	1240.5562	1096.0440	934.2619	785.2097
	MCSCF[a]	1479.39	1371.63	1247.23	1093.80	872.54	
	Experiment[d]	1480.02	1371.72	1247.56	1095.84	882.30	
$3p\sigma\ ^3\Sigma_g^+$	This work	1590.3228	1505.4479	1421.4982	1338.4736	1256.3742	1175.2000
$4p\sigma\ g\ ^3\Sigma_g^+$	This work	1620.4046	1545.8592	1470.8643	1395.4199	1319.5261	1243.1827
$4f\sigma\ ^3\Sigma_g^+$	This work	1638.2468	1562.4306	1486.3166	1409.9047	1333.1949	1256.1873
$5p\sigma\ k'\ ^3\Sigma_g^+$	This work	1630.3905	1558.9147	1486.4653	1413.0425	1338.6462	1262.2763
$5f\sigma\ ^3\Sigma_g^+$	This work	1639.9878	1565.7257	1490.5378	1414.4240	1337.3845	1259.4191
$^3\Pi_u$							
$3d\pi\ f\ ^3\Pi_u$	This work	1559.9702	1464.5234	1370.4452	1277.7355	1186.3944	1096.4219
$4d\pi\ j\ ^3\Pi_u$	This work	1583.7719	1512.5752	1441.1247	1369.4203	1297.4620	1225.2499
$5d\pi\ m\ ^3\Pi_u$	This work	1618.3158	1543.9267	1468.9215	1393.3004	1317.0633	1240.2103
$6d\pi\ q\ ^3\Pi_u$	This work	1629.9540	1558.1398	1486.3683	1414.6395	1342.9324	1271.3099
$7d\pi\ ^3\Pi_u$	This work	1638.4887	15566.2396	1492.7709	1418.0824	1342.1744	1265.0467

[a] MCSCF calculations of Sunil et al [15]

[b] MCSCF/CI calculation of yarkony[4]

[c] CI Method of Chabalowski [24]

[d] Experiment of Brown et Ginter[26],

Table 7 : Rotational constant B_v (cm^{-1}) *for* ${}^1\Sigma_u^+$, ${}^1\Pi_g$, ${}^1\Sigma_g^+$ *and* ${}^1\Pi_u$ *singlet States of* He_2

State	v	**0**	**1**	**2**	**3**	**4**	**5**
$2s\sigma\ A\ {}^1\Sigma_u^+$	This work	7.64806	7.43851	7.24214	7.05895	6.78895	6.53212
	ECG[a]	7.67010	7.44750	7.2128	6.9857	6.7505	6.5096
	VBPA[b]	7.66800	7.44420	7.2174	6.9876	6.753	6.510
	Experiment[c]	7.70600	7.44670	7.2194	6.9870	6.748	6.503
	Experiment[d]	7.67101	7.44692				
$3s\sigma\ D\ {}^1\Sigma_u^+$	This work	7.25567	6.97204	6.68584	6.39706	6.10571	5.81179
$3d\sigma\ F\ {}^1\Sigma_u^+$	This work	7.13717	6.88501	6.62862	6.35799	6.10313	5.83402
$4s\sigma\ H\ {}^1\Sigma_u^+$	This work	7.12522	6.90513	6.68654	6.46945	6.25346	6.03976
$4d\sigma\ J\ {}^1\Sigma_u^+$	This work	7.08861	6.86699	6.64156	6.41232	6.17927	5.94241
$5s\sigma\ {}^1\Sigma_u^+$	This work	7.13709	6.89545	6.65699	6.41263	6.16539	5.91526
$5d\sigma\ M\ {}^1\Sigma_u^+$	This work	7.11024	6.88379	6.65378	6.42023	6.18312	5.94246
${}^1\Pi_g$							
$2p\pi\ B\ {}^1\Pi_g$	This work	7.19654	6.986111	6.77652	6.56775	6.35982	6.15273
$3p\pi\ E\ {}^1\Pi_g$	This work	7.16980	6.94564	6.71769	6.48594	6.25040	6.01106
$4p\pi\ I\ {}^1\Pi_g$	This work	7.11919	6.89042	6.65987	6.42754	6.19344	5.95755
$4f\pi\ {}^1\Pi_g$	This work	7.10497	6.88256	6.65964	6.43623	6.21231	5.98789
$5p\pi\ L\ {}^1\Pi_g$	This work	7.10413	6.88391	6.66587	6.45001	6.23633	6.02484
$5f\pi\ {}^1\Pi_g$	This work	7.10794	6.88610	6.66283	6.43813	6.21200	5.98443
$6p\pi\ P\ {}^1\Pi_g$	This work	7.10216	6.88431	6.66257	6.43695	6.20744	5.97405
$6f\pi\ {}^1\Pi_g$	This work	7.09528	6.87739	6.65680	6.43350	6.20749	5.97877
${}^1\Sigma_g^+$							
$2p\sigma\ C\ {}^1\Sigma_g^+$	This work	6.97163	6.71222	6.43761	6.14780	5.84280	5.52259
	VBPA[b]	6.9463	6.6967	6.4364	6.1632	5.8690	5.5240
	Experiment[e]	6.9450	6.7000	6.4410	6.1670	5.8670	5.5300
$3p\sigma\ 2\ {}^1\Sigma_g^+$	This work	7.07548	6.80743	6.53032	6.24414	5.94888	5.62456
$4p\sigma\ G\ {}^1\Sigma_g^+$	This work	7.09580	6.86991	6.64415	6.41850	6.19297	5.96756
$4f\sigma\ {}^1\Sigma_g^+$	This work	7.11355	6.88806	6.65772	6.42253	6.18248	5.93759
$5p\sigma\ K'\ {}^1\Sigma_g^+$	This work	7.10877	6.87735	6.64363	6.40763	6.16934	5.92877
$5f\sigma\ {}^1\Sigma_g^+$	This work	7.11878	6.88729	6.65355	6.41758	6.17938	5.93894
${}^1\Pi_u$							
$3d\pi\ F\ {}^1\Pi_u$	This work	7.06636	6.81065	6.54907	6.28160	6.00826	5.72904
$4d\pi\ J\ {}^1\Pi_u$	This work	7.08064	6.84441	6.60442	6.36069	6.11321	5.86199
$5d\pi\ M\ {}^1\Pi_u$	This work	7.09908	6.86620	6.63041	6.39171	6.15009	5.90556
$6d\pi\ {}^1\Pi_u$	This work	7.09900	6.87128	6.64414	6.41760	6.19165	5.96629
$7d\pi\ {}^1\Pi_u$	This work	7.10096	6.88043	6.66092	6.44242	6.22493	6.00846

[a] ECG calculation of Komasa [14]

[b] Valence Bond pseudopotential approcach (VBPA) of Jordan [16]

[c] Experiment of Brown et Ginter[26]

[d] Experiment from Focsa et al. [22]

[e] Experiment from Ginter [25]

Table 8 : Rotational constant B_v (cm^{-1}) for $^3\Sigma_u^+$, $^3\Pi_g$, $^3\Sigma_g^+$ and $^3\Pi_u$ triplet States of He₂

State	v	**0**	**1**	**2**	**3**	**4**	**5**
$2s\sigma\ a\ ^3\Sigma_u^+$	This work	7.57637	7.34312	7.12337	6.91710	6.72433	6.54506
	Experiment[a]	7.58914	7.34874	7.10175			
$3s\sigma\ d\ ^3\Sigma_u^+$	This work	7.23884	7.01339	6.78313	6.54806	6.30819	6.06352
$3d\sigma\ f\ ^3\Sigma_u^+$	This work	7.12114	6.82764	6.59118	6.41176	6.28938	6.22404
$4s\sigma\ h\ ^3\Sigma_u^+$	This work	7.16484	6.92540	6.68124	6.43235	6.17875	5.92042
$4d\sigma\ j\ ^3\Sigma_u^+$	This work	7.04669	6.82075	6.59602	6.37250	6.15019	5.92910
$5s\sigma\ k\ ^3\Sigma_u^+$	This work	7.14804	6.90736	6.66298	6.41489	6.16311	5.90763
$5d\sigma\ m\ ^3\Sigma_u^+$	This work	7.08884	6.86226	6.63254	6.39970	6.16372	5.92462
$6s\sigma\ o\ ^3\Sigma_u^+$	This work	7.12082	6.88906	6.65652	6.42320	6.18909	5.95420
$6d\sigma\ d\ ^3\Sigma_u^+$	This work	7.06020	6.85960	6.65572	6.44856	6.23813	6.02443
$^3\Pi_g$							
$2p\pi\ b\ ^3\Pi_g$	This work	7.31282	7.05678	6.79555	6.52913	6.25753	5.98073
	Experiment[a]	7.32343	7.10061				
$3p\pi\ e\ ^3\Pi_g$	This work	7.16903	6.94914	6.72558	6.49835	6.26745	6.03287
$4p\pi\ i\ ^3\Pi_g$	This work	7.10281	6.88334	6.66077	6.43511	6.20635	5.97451
$4f\pi\ ^3\Pi_g$	This work	7.09250	6.87799	6.66103	6.44163	6.21977	5.99546
$5p\pi\ l\ ^3\Pi_g$	This work	7.09112	6.87523	6.65629	6.43430	6.20925	5.98116
$5f\pi\ ^3\Pi_g$	This work	7.11389	6.89183	6.66766	6.44137	6.21296	5.98244
$6p\pi\ p\ ^3\Pi_g$	This work	7.09974	6.88553	6.66856	6.44883	6.22634	6.00110
$6f\pi\ ^3\Pi_g$	This work	7.07616	6.78037	6.47305	6.15420	5.82381	5.12845
$^3\Sigma_g^+$							
$2p\sigma\ c\ ^3\Sigma_g^+$	This work	6.84315	6.51479	6.16414	5.79121	5.39600	4.97850
	Experiment[a]	6.85395	6.55682	6.22636			
$3p\sigma\ 2\ ^3\Sigma_g^+$	This work	7.05653	6.79180	6.52393	6.25293	5.97878	5.70150
$4p\sigma\ g\ ^3\Sigma_g^+$	This work	7.08536	6.85084	6.61357	6.37355	6.13079	5.88527
$4f\sigma\ ^3\Sigma_g^+$	This work	7.12159	6.88490	6.64707	6.40809	6.16798	5.92672
$5p\sigma\ k'\ ^3\Sigma_g^+$	This work	7.094472	6.86879	6.64031	6.40928	6.17572	5.93960
$5f\sigma\ ^3\Sigma_g^+$	This work	7.11295	6.88359	6.65055	6.41381	6.17339	5.92928
$^3\Pi_u$							
$3d\pi\ f\ ^3\Pi_u$	This work	7.05120	6.75975	6.46272	6.16011	5.85191	5.53813
$4d\pi\ j\ ^3\Pi_u$	This work	7.03778	6.80277	6.56892	6.33621	6.10465	5.87425
$5d\pi\ m\ ^3\Pi_u$	This work	7.08244	6.84993	6.61370	6.37372	6.13001	5.88257
$6d\pi\ q\ ^3\Pi_u$	This work	7.09602	6.86846	6.63745	6.40298	6.16506	5.92368
$7d\pi\ ^3\Pi_u$	This work	7.10442	6.88154	6.65545	6.42613	6.19358	5.71882

[a] Experiment of Focsa et al. [22]

REFERENCES

[1] A. I. J. Burgmans, J. M. Farrar, and Y. T. Lee, *J. Chem. Phys*., Vol. 64, pp. 1345, 1976.

[2] P. G. Burton, *J. Chem. Phys*., Vol. 70, pp. 3112, 1979.

[3] K. Huber and G. Herzberg, in Molecular Spectra, Molecular structur*e,* Vol. 4. Constants of diatomic Molecules, Van Nostrand Reinhold, New York, 1979.

[4] D. R. Yarkony " On the quenching of helium 2 ^{2}S: Potential energy curves for, and nonadiabatic, relativistic, and radiative coupling between, the a $^3\Sigma_u^+$, A $^1\Sigma_u^+$, *B* $^3\Pi_g$,

$b\ {}^1\Pi_g$, c ${}^3\Sigma_g^+$ and C ${}^1\Sigma_g^+$ states of He_2. J. Chem. Phys., Vol. 90(12), pp. 7164-7175, 1989.

[5] R. E. Huffmann, Y. Tanaka and J. C. Larrabee, *J. Opt. Soc. Am*. Vol. 52, pp. 851, 1962.

[6] R. E. Huffmann, Y. Tanaka and J. C. Larrabee, *Appl. Opt.*, Vol. 2, pp. 617, 1963.

[7] D. S. Ginter, M. L. Ginter and C. M. Brown, J. *Chem. Phys.* Vol. 81, pp. 6013-6025, 1984

[8] J. S. Cohen, “Diabatic-states representation for He*(n ≥3)+ He collisions”, Phys. Rev. A, Vol. 13, pp. 86-98, 1976.

[9] K. P. Huber and G. Herzberg, “Constants of Diatomic molecules”, in Molecular spectra and Molecular structure, Vol.4, New York/ Van Nostrand-Reinhold, 1979.

[10] D. D. Konowalow and B. H. Lengsfield III, “The electronic and vibrational energies of two doublewelled ${}^3\Sigma_u^+$ states of He_2”, *J. Chem. Phys*., Vol. 87, pp. 4000-4007, 1987

[11] R. A. Buckingham and A. Dalgarno, *Proc. R. Soc. London*, Vol. A213, 327, pp. 506, 1952.

[12] J. C. Browne, “Some excited states of helium molecules I, the lowest ${}^1\Sigma_u^+$ and ${}^3\Sigma_g^+$ states and the first excited ${}^1\Sigma_g^+$ states”, J. Chem. Phys., Vol. 42, pp. 2826-2829, 1965.

[13] S. Mukamel and U. Kaldor, “Potential of the A ${}^1\Sigma_u^+$ state of He_2”, *Mol. Phys*. Vol. 22, pp. 1107-1117, 1971.

[14] J. Komasa, “Theoretical study of A ${}^1\Sigma_u^+$ state of helium dimer”, *Mol. Phys*. Vol. 104, pp.2193-2202, 2006.

[15] K. K. Sunil, J. Lin, H. Siddiqui, P. E. Siska, K. D. Jordan and R. Shepard, “Theoretical investigation of the a ${}^3\Sigma_u^+$, A ${}^1\Sigma_u^+$, c ${}^3\Sigma_g^+$ and C ${}^1\Sigma_g^+$ potential energy curve of He_2 and of He(2^1S, 2^3S)+ He scattering”, *J. Chem. Phys.*, Vol. 78, pp. 6190-6202, 1983.

[16] R. M. Jordan and P. E. Siska, “Potential energy curves for the A ${}^1\Sigma_u^+$ and C ${}^1\Sigma_g^+$ states of He2 obtained by combining scattering, spectroscopy and *ab initio* theory”, J. Chem. Phys., Vol. 80, pp.5027-5035, 1984.

[17] J. Tenysson, Phys. Rep. Vol. 491, pp. 29-76, 2010.

[18] J. M. Carr, P. G. Galiatsatos, J. D. Gorfinkiel, A. G. Harvey M. A. Lysaght, D. Madden, Z. Masin, M. Plummer and J. Tennyson, Eur. J. Phys. D, Vol. 66, pp. 58, 2012.

[19] J. N. Murrell, S. Carter, S. C. Farantos, P. Huxley,J. C. Varandas,”Molecular Potential Energy Function” Wiley: Chichester, 1984.

[20] B. Numerov, Publ. Obs Central Astrophys. Russ, Vol. 2, pp. 188, 1933.

[21] C. Focsa, P. F. Bernath and R. Colin, “The Low-Lying States of He_2”, *J. Mol. Spectroscopy*, Vol.191, pp.209-214, 1998.

[22] J. Wasilewski, V. Staemmler and R. Jaquet, “CAPA Calculations on Open-Shell Molecules. III. Potential Curves for the six lowest excited states of He2 in the vicinity of their equilibrium distance.” Theoret. Chem. Acta., Vol. 59, pp. 517-526, 1981.

[23] C. F. Chabalowski, J. O. Jensen, D. R. Yarkony and B. H. Lengsfield, “Theoretical study of the radiative life time for the spin forbidden transition a ${}^3\Sigma_u^+ \rightarrow$ X ${}^1\Sigma_g^+$ in He_2.”, *J. Chem. Phys.,* Vol. 90, pp. 2504-2512, 1989.

[24] M. L. Ginter, J. Chem. Phys., Vol. 42, pp. 561, 1965.

[25] G. M. Brown and M. L. Ginter, J. Mol. Spectrosc. , Vol. 40, pp. 302, 1971.