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Accurate all-electron calculation on the vibrational and rotational spectra of ground states for O_2 and its ions*

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The potential energy curves, spectroscopic constants, and low-lying vibration–rotation levels of ground-state O_2 and its cation O_2^+ and anion O_2^- were calculated with the explicitly correlated multireference configuration interaction method. The zeroth-order reference wavefunction was treated with the complete active space multiconfigurational self-consistent field method, in which the active space was carefully selected, and an additional molecular orbital π_u was added into the full valence active space. The electron correlation of the 1s core in the oxygen atom was considered in the computations. The Davidson correction on molecular energy was considered to account for higher electron excitation. The relativistic effects, including the scalar relativistic effect and spin–orbit coupling, were considered in the computation of potential energy curves. These physical effects on the spectroscopic constants were examined. The low-lying levels of vibration–rotation spectra of O_2 and its ions were determined based on the computed potential energy curves. Comparisons with available experiments were made and excellent agreement was obtained for the vibrational and rotational parameters. The spectroscopic constants and vibration–rotation spectrum of O_2^-, which is sparse in experiments, were provided. Our study will shed some light on further theoretical and experimental studies on these simple but important molecular systems.

Keywords: O_2 molecule/molecular ion, explicitly correlated multireference configuration interaction, spectroscopic constant, vibration–rotation spectrum

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1. Introduction

Oxygen is one of the most important gas-phase molecules in the earth's atmosphere, and its positive and negative molecular ions are also very important to the physics and chemistry of upper atmospheric, life science, or life evolution processes.[1,2] The neutral and ionic compositions of O_2 exist in different altitudes, which manifestly plays a diverse role in the maintenance of life on earth. The potential energy curves (PECs) of molecules can be constructed by measuring the molecular spectra so as to further understand the electronic structures of molecules. Theoretical calculations of the potential energy curve, spectroscopic constants, and vibration–rotation levels of a molecular electronic state are also important to test the theory of electronic structure and to aid experimental measurements of the molecular spectrum.[3–9]

Over the past decades, the potential curve, spectroscopic constants, and vibration–rotation spectrum of the triplet ground state $X^3\Sigma_g^-$ of O_2 molecule have attracted extensive experimental and theoretical interest. For example, Cheung *et al.*[7] obtained the accurate spectroscopic constants and energy levels of the $X^3\Sigma_g^-$ state through Schumann–Runge absorption spectroscopy. Bytautas *et al.*[8,9] performed high-level *ab initio* calculations on the potential energy curves of O_2 with consideration of various physical effects, and obtained an accurate vibrational and rotational spectrum of the $X^3\Sigma_g^-$ state. For the ground state of O_2^+, the vibrational constants $\omega_e = 1917.8\pm0.7$ cm^{-1} and $\omega_e\chi_e = 16.92\pm0.02$ cm^{-1} were obtained by a high resolution threshold photoelectron spectrum experiment[10] using synchrotron radiation. More accurate information of the ground state of O_2^+ was given by the $A^2\Pi_u$–$X^2\Pi_g$ Fourier transform emission spectroscopy,[11] the results of which were $\omega_e = 1905.892\pm0.082$ cm^{-1}, $\omega_e\chi_e = 16.489\pm0.013$ cm^{-1}, $B_e = 1.689824\pm0.00091$ cm^{-1}, and $R_e = 1.116877\pm0.000030$ Å. According to these spectroscopic constants, the vibrational and rotational levels of the state were also given in the experiments.

The adiabatic electron affinity of O_2 is about 0.45 eV.[12] It is indicated that the only stable electronic state of the anion O_2^- is the ground electronic state. The characterization and understanding of the anion O_2^- are far less than those of the neutral O_2 and cation O_2^+, especially the accurate spectroscopic constants and vibrational spectrum information. Huber and Herzberg *et al.*[13] compiled and evaluated the experimental data of spectroscopic constants of the ground state of O_2^- in early studies with low-resolution spectroscopic measurements. Later, Travers[14] and Ervin[12] obtained some spectroscopic parameters of the ground state by using negative ion photoelectron spectroscopy and extreme ultraviolet photoelectron

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spectroscopy, respectively. Theoretical studies on the electronic states of O_2^- were also performed using multireference configuration interaction methods.[15]

In this paper, we focus on the ground electronic states of O_2 and its ions (O_2^+ and O_2^-). The ground state wave function was optimized by using the appropriate active space multiconfiguration self-consistent field method. The system energy was calculated through the explicitly correlated multireference configuration interaction method including the electron dynamic correlation. The potential energy curves of the ground state of the molecular systems were calculated by considering various physical correction and accurate spectroscopic constants and vibrational and rotational levels were obtained.

2. Methods and computational details

In this work, the explicitly correlated multireference configuration interaction (MRCI-F12) method[16] implemented in Molpro package[17] was carried out to study the electronic structure computation. Firstly, the Hartree–Fock (HF) self-consistent field method was used to construct the starting single configurational molecular orbital wavefunctions. The wave function of a single electronic ground state was further optimized using complete active space multiconfigurational self-consistent field (CASMCSCF), and finally the total energy including the electron dynamic correlation energy of the molecular system was estimated with the MRCI-F12 method. In the calculation of CASMCSCF, two active spaces were used to test computational results, one is full valence active space including all 2s2p electrons and the corresponding valence molecular orbital, which is denoted as CAS-I; the other consists of valence and an extra π_u molecular orbital, denoted as CAS-II. The CAS-I is comprised of the $2s\sigma_g$, $2p\sigma_g$, $2s\sigma_u$, $2p\sigma_u$, $2p\pi_g$, and $2p\pi_u$ molecular orbitals, totally, $2a_g+1b_{2u}+1b_{3u}+2a_u$ orbitals in D_{2h} symmetry are included. And in the CAS-II, an additional molecular orbital corresponding to $3p\pi_u$ is added, that is, $2a_g+2b_{2u}+2b_{3u}+2a_u$ orbitals in D_{2h} symmetry are included. In the calculation with MRCI-F12, the correlations of all electrons in the molecular system were considered. The correlation effect of 1s orbital was also taken into account in this work. Davidson correction (+Q) was considered in computation to overcome the size-consistency problem. The correlation consistent basis sets cc-pCVXZ-F12 ($X = \mathrm{T}(3), \mathrm{Q}(4)$)[18] including core–valence (CV) and core–core correlation effect were used in the calculations. The scalar relativistic (SR) correction effect was evaluated with MRCI method and uncontracted aug-cc-pVQZ basis set by using second order Douglas–Kroll–Hess (DKH) Hamiltonian.[19–21] The spin–orbit coupling (SOC) was calculated at the CASMCSCF/aug-cc-pVQZ level with state-interacting technique.[22]

In total 145 single energy points were calculated in the range of internuclear $R = 0.8$–200 Å, and the potential energy curve $V(R)$ of the system was obtained. The eigenvalues $E_{v,J}$ were then obtained by solving the one-dimensional radial Schrödinger equation listed as follows:

$$-\frac{\hbar}{2\mu}\frac{\mathrm{d}^2\Psi_{v,J}(R)}{\mathrm{d}R^2}+V_{v,J}(R)\Psi_{v,J}(R)=E_{v,J}\Psi_{v,J}(R), \quad (1)$$

where μ represents the reduced mass of the system, v represents the vibrational quantum number, and J is the rotational quantum number. The rotational sublevels of a given vibrational level can be expressed as

$$E_{v,J}=G(v)+B_v[J(J+1)]-D_v[J(J+1)]^2+\cdots, \quad (2)$$

where $G(v)$ is the pure vibrational term, and B_v and D_v are the first two terms of the centrifugal distortion constants. The Level program[23] was used to solve the radial Eq. (1).

3. Result and discussion

3.1. Spectroscopic constants

In Table 1, taking O_2^+ as an example, we show various physical effects on some spectroscopic constants. The results are compared with the available experimental values. Our previous study[24] indicates that the CV electron correlation on the spectroscopic constants is important, thus the CV effect is directly included in the computation by using the corresponding CV basis sets and singly, doubly electron excitation of 1s core in MRCI-F12 calculations. First of all, we discuss the influence of zero-order reference wave functions with different active spaces on the computational results of MRCI-F12. The results of CAS-II calculations are marked with MRCI-F12(Π_u) in Table 1. The contribution of additional π_u orbital in active space is estimated and denoted as $\Delta(\Pi_u)$ in Table 1. When the Davidson's correction is not included, the additional π_u orbital of the active space improves the equilibrium internuclear distance R_e and harmonic vibrational constant ω_e by 0.0014 Å and ~ 9 cm^{-1}, respectively. Little change in the anharmonic vibrational constant $\omega_e\chi_e$ is observed, and the rotational constant B_e is slightly improved. It can be seen that the configuration generated by the additional π_u molecular orbital through electronic excitation is necessary for accurate determination of spectroscopic constants. When considering the Davidson correction, the computed R_e and ω_e are improved by 0.0004 Å and ~ 3 cm^{-1}, respectively, which indicates that both Davidson correction and the additional orbital in active space improve the accuracy of computed spectroscopy. The account of Davidson correction involves the contribution of excitation of three and four electrons to the energy, and the π_u orbital in active space increases the electron configurations of zero-order reference wavefunction and further improves the correlation energy calculation. The fact that the contribution of additional π_u orbitals improves the potential energy and

electronic transition properties has also been indicated in previous computational studies.[25,26] The correction of relativistic effect is also considered. The corrections of scalar relativistic effects on R_e and ω_e are 0.0001 Å and ~ 3 cm^{-1}, respectively. The SOC only slightly modifies the potential energy curve since it does not have much effect on ω_e and $\omega_e\chi_e$. After comprehensive consideration of all of the above effects, our best estimated value of R_e coincides with the experimental value to five significant digits, with an error less than 0.0001 Å ($< 0.1\%$), 1 cm^{-1} (0.5‰), 0.2 cm^{-1}, and 0.0004 cm^{-1} for R_e, ω_e, $\omega_e\chi_e$, and B_e, respectively.

The spectroscopic constants of neutral and anion molecular systems are given in Table 2 and compared with the available experimental values. For the spectroscopic constants of O_2, by comparing with accurate experimental values,[7] it is found that the accuracy of the current calculated results for O_2 is very close to that of O_2^+, with the error being only 0.0001 Å and ~ 0.1 cm^{-1} for R_e and ω_e, respectively. For the negative ion O_2^-, the present best estimated result is in good agreement with the earlier compiled experimental value,[13] while it differs from the other two experimental values by 0.0021 Å[12] and 0.0031 Å[14] for R_e. The experimental measurement error of ω_e of O_2^- is relatively large (20 cm^{-1} and 50 cm^{-1}), which is mainly limited by the number of the observed vibrational energy levels. The error bar of early complied ω_e value is not determined; our present result differs from the complied value by ~ 26 cm^{-1}, and is close to the lower limit of early experimental value with negative ion photoelectron spectrum, but differs from the ultraviolet photoelectron spectrum experimental value by ~ 8 cm^{-1}. Our calculated spectroscopic constants of O_2^- are in reasonable agreement with recent experiment,[14] and the values are within the experimental error range. Due to the limitation of the number for observed vibration–rotation levels (only 29 levels observed in the latest experiment), the measurement error of the experiment is relatively large; on the other hand, accurate *ab initio* calculation on the vibration–rotation energy levels is much more important.

Table 1. The comparison of spectroscopic constants of O_2^+ under different approaches. The digits in parentheses are the experimental errors.

Method	R_e/Å	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}
MRCI-F12/CVQZ[a]	1.1144	1927.5385	16.1382	1.6973
MRCI-F12(Π_u)/CVQZ[b]	1.1158	1918.5635	16.1102	1.6933
$\Delta(\Pi_u)$[c]	+0.0014	−8.975	−0.028	−0.004
MRCI-F12+Q/CVQZ[a]	1.1163	1912.6363	16.2723	1.6915
MRCI-F12(Π_u)+Q/CVQZ[b]	1.1167	1909.3300	16.3041	1.6905
$\Delta(\Pi_u)$[d]	+0.0004	−3.3063	0.0318	−0.001
Δ(SR)[e]	+0.0001	−2.7176	−0.0271	−0.0003
MRCI-F12(Π_u)+Q/CVQZ+SR	1.1168	1906.6124	16.2770	1.6902
Δ(SOC)[f]		+0.210	−0.0078	
MRCI-F12(Π_u)+Q/CVQZ+SR+SOC	1.1168	1906.8224	16.2692	1.6902
Expt.[11,29]	1.116877(30)	1905.892(82)	16.489(82)	1.689824(91)
Expt.[10]		1917.8(7)	16.92(2)	

[a]The result of molecular orbital calculations was obtained using the active space CAS-I.
[b]The result of molecular orbital calculations was obtained using the active space CAS-II.
[c]The influence of active space estimated at MRCI-F12 level without Davidson correction.
[d]The influence of active space estimated at MRCI-F12 level with Davidson correction.
[e]The scalar relativistic correction.
[f]The spin–orbit coupling correction.

Table 2. The spectroscopic constants (bond distance R_e, harmonic and anharmonic frequency ($\omega_e, \omega_e\chi_e$), and rotational constant B_e) of ground states of O_2 and O_2^- molecular systems.

	Method	R_e/Å	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}
O_2	MRCI-F12(Π_u)+Q/CVQZ	1.2073	1582.3418	11.4821	1.4461
	MRCI-F12(Π_u)+Q/CVQZ+SR	1.2076	1579.9967	11.4540	1.4456
	MRCI-F12(Π_u)+Q/CVQZ+SR+SOC	1.2076	1579.9738	11.4557	1.4455
	Expt.[7]	1.2075	1580.1	11.9	1.4457
O_2^-	MRCI-F12(Π_u)+Q/CVQZ	1.3496	1118.0814	8.9473	1.1572
	MRCI-F12(Π_u)+Q/CVQZ+SR	1.3501	1116.4072	8.9240	1.1563
	MRCI-F12(Π_u)+Q/CVQZ+SR+SOC	1.3501	1116.4959	8.9237	1.1563
	Expt.[13]	1.35	1090	8 ± 1	
	Expt.[12]	1.348 ± 0.008	1108 ± 20	9	1.161 ± 0.007
	Expt.[14]	1.347 ± 0.005	1173 ± 50		

3.2. Vibrational and rotational levels

On the basis of PECs deduced from the MRCI-F12(Π_u)+Q/CVQZ+SR+SOC computations, the low-lying vibrational terms $G(v)$, rotational constant B_v, and D_v of the ground states for neutral O_2 and ions are obtained and listed in Tables 3, 4, and 5, respectively, with available experimental values for comparison. Table 3 shows the low-lying $v = 0$–11 vibrational energy levels of these molecular systems. The zero-point vibrational energy (ZPVE) of O_2 molecule calculated in this work is 787.8 cm^{-1}, which is in good agreement with the experimental value[9] of 787.2 cm^{-1}. The ZPVE values of the cation and anion are calculated to be 947.8 cm^{-1} and 556.4 cm^{-1}, respectively. In the present calculation, the mean absolute deviation (MAD) of the first 12 vibrational levels $v = 0$–11 is 6.46 cm^{-1} (less than 1%), which is smaller than that of the most recent *ab initio* calculations (12.84 cm^{-1}), indicating the improved accuracy of the present computational scheme for the low-lying vibrational levels of the ground state.

Table 3. The vibrational levels $G(v)$ ($v = 0$–11, $J = 0$) for neutral and ionic molecular systems (in the unit of cm^{-1}).

v	O_2		O_2^+		O_2^-	
	Expt.[9]	This work	Expt.[30]	This work	Expt.[31]	This work
0	0	0	0	0	0	0
1	1556.39	1557.7	1872.97	1874.5	1090(20)	1098.97
2	3089.11	3091.98	3713.13	3716.29		2179.85
3	4598.61	4602.99	5520.56	5525.44		3242.72
4	6084.69	6090.88	7295.34	7301.88		4287.65
5	7547.69	7555.88	9037.51	9045.84		5314.69
6	8988.14	8997.94	10747.12	10757.39		6323.9
7	10406.88	10417.27	12424.17	12436.34		7315.34
8	11801.67	11814.00	14068.68	14082.85		8289.04
9	13173.60	13188.12	15680.61	15696.95		9245.02
10	14523.24	14539.62	17259.94	17278.61		10183.36
11	15852.42	15868.52	18806.6	18827.83		11104.09
MAD		6.46(0.093%)		9.77(0.088%)		
ZPE	787.20	787.82		949.76		556.44

The MAD of $v = 0$–11 vibrational levels for O_2^+ is also small, which is only 9.77 cm^{-1} (0.88%). We note that the absolute deviation increases with the vibrational quantum number v, for instance, the absolute deviation increases to $\sim$ 20 cm^{-1} for $v = 11$. Such an increment in deviation could arise from the accumulation of errors. It may also indicate that the PEC in the range far away from the Franck–Condon region needs to be further improved, for example, considering multiple electron excitation. There are few experimental values of the vibrational levels for the negative ion, and the error bar is large.[12] The $G(v = 1)$ calculated in this paper is 1099 cm^{-1}, which is in reasonable agreement with the experimental value of 1090 ± 20 cm^{-1}. Excited vibrational levels for the ground state of O_2^- are present in this study for the first time, which should be of value for further experimental studies.

The rotational constants B_v and D_v ($v = 0$–11) of these molecular systems are given in Tables 4 and 5, respectively, together with the experimental values listed for comparison. For neutral molecules, the present calculated results of B_v ($v = 0$–11) are in line with the experimental values with 3–4 significant digits, and are in good agreement with the results of the most recent theoretical study.[9] It is worth mentioning that our calculated B_v values are still 3 significant digits in accordance with the experimental results for vibrational levels up to $v = 26$ (data not shown in the table). For example, $B_{16} = 1.18862$ cm^{-1} and $B_{26} = 1.01406$ cm^{-1} of the ground-state O_2 are calculated in this work, which are in good agreement with the corresponding experimental values of 1.18833 cm^{-1} and 1.01537 cm^{-1}.[9] The maximum vibrational level of which the B_v is determined experimentally is $v = 31$, and the deviation of the present computed B_{31} from the experimental value[9] is -0.029 cm^{-1} (0.86410 cm^{-1} vs. 0.89248 cm^{-1}). The D_v ($v = 0$–11) values of the neutral molecule are list in Table 4. The deviation of $10^6 \cdot D_v$ calculated in this work from the experimental value is in the range of 0.02–0.3 cm^{-1}, which is much less than those of the latest calculated results (0.8–1.0 cm^{-1}). The results of $10^6 \cdot D_v$ for excited vibrational states, for example, $v = 16$, 26, and 31, are calculated with errors of 0.171 cm^{-1}, 0.483 cm^{-1}, and 0.765 cm^{-1}, respectively, which are slightly less than those of the latest *ab initio* calculations[9] (0.837 cm^{-1}, 0.667 cm^{-1}, and 1.350 cm^{-1}). The computational results for neutral O_2 indicate that the present computational scheme for low-lying vibration–rotation levels is reliable.

In the O_2^+ system, the deviation of our computed B_v and $10^6 \cdot D_v$ values for $v = 0$–11 are in the range of < 0.01 cm^{-1} and 0.01–0.02 cm^{-1}, respectively, which are close to the errors of recent extrapolated results with the MRCI method.[27] For $v = 18$, 19 levels in $^{16}O_2^+$, the experimental values[28] of B_v are 1.3167 cm^{-1} and 1.2949 cm^{-1}, respectively, which agree well with our computed values 1.3182 cm^{-1} and 1.2966 cm^{-1}, respectively. The experimental values[29] of $10^6 \cdot D_v$ are

6.3876 ± 0.0086 cm^{-1} and 6.4825 ± 0.0085 cm^{-1}, respectively, which are also in accordance with the present computed values, 6.3080 cm^{-1} and 6.4114 cm^{-1}, respectively. For the $v = 20$ vibrational level of $^{16}O_2^+$, our computed values of B_v and $10^6 \cdot D_v$ (1.2746 cm^{-1} and 6.5212 cm^{-1}) are also in agreement with recent experimental values[29] (1.272884(11) cm^{-1} and 6.596 ± 0.018 cm^{-1}), respectively.

Table 4. The rotational constants B_v values for vibrational levels $v = 0$–11 (in the unit of cm^{-1}).

v	O_2		O_2^+		O_2^-
	Expt.[9]	This work	Expt.[30]	This work	This work
0	1.43771	1.43766	1.68	1.68056	1.14931
1	1.42196	1.42189	1.66	1.66118	1.13536
2	1.40630	1.40619	1.64	1.64176	1.12145
3	1.39070	1.39056	1.62	1.62229	1.10758
4	1.37550	1.37497	1.60	1.60279	1.09374
5	1.36040	1.35942	1.59	1.58314	1.07993
6	1.34430	1.34396	1.56	1.56352	1.06614
7	1.32857	1.32846	1.54	1.54379	1.05236
8	1.31311	1.31302	1.52	1.52398	1.03860
9	1.29776	1.29758	1.50	1.50402	1.02485
10	1.28221	1.28217	1.48	1.48398	1.01108
11	1.26610	1.26672	1.47	1.46380	0.99733

Table 5. The rotational constants D_v values for vibrational levels $v = 0$–11 (in the unit of 10^{-6} cm^{-1}).

v	O_2		O_2^+		O_2^-
	Expt.[9]	This work	Expt.[32]	This work	This work
0	4.854	4.831	5.33 ± 0.05	5.3244	4.9525
1	4.957	4.830	5.36 ± 0.05	5.3549	4.9478
2	5.000	4.830	5.40	5.3867	4.9445
3	5.000	4.830	5.43	5.4240	4.9429
4	5.049	4.828	5.47	5.4541	4.9431
5	5.145	4.835	5.50	5.4895	4.9451
6	5.006	4.835	5.54	5.5388	4.9471
7	4.953	4.835	5.59	5.5742	4.9531
8	4.990	4.845	5.63	5.6140	4.9644
9	5.012	4.858	5.6 ± 0.8	5.6592	4.9665
10	4.990	4.869	5.7 ± 0.8	5.7068	4.9777
11	4.951	4.884		5.7677	4.9927

To the best of our knowledge, there are no experimental results for the B_v and D_v of O_2^- anions. Our calculated values of B_v and D_v ($v = 0$–11) are listed in Tables 4 and 5, respectively. Since the same computational scheme as that for the neutral and cation is adopted for the anion, we expect that the results of low-lying vibrational and rotational spectrum information would have similar accuracy, which could help further experimental investigations on O_2^- anions.

4. Conclusions

In this paper, we provide a computational scheme to obtain accurate spectroscopic constants and vibration–rotation spectra of the ground electronic states of O_2 and its ions, using the explicitly correlated MRCI-F12 approach. The computed PECs of the ground states at the MRCI-F12(Π_u)+Q/CVQZ +SR+SOC level, as well as the spectroscopic constants and low-lying vibration–rotation levels are in good agreement with available experimental values. We also discuss the effects of various corrections, including the Davidson correction, active space dependence, scalar relativistic correction, and spin–orbit coupling, on the accurate calculation of spectroscopic constants. The reasonable feasibility of MRCI-F12(Π_u)+Q/CVQZ +SR+SOC method to calculate oxygen molecular systems is proved. The accurate results provided in the present study would be valuable for further spectroscopic measurements and for understanding the electronic states of these molecular systems.

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