Excited-states and spectroscopic properties of superoxide anion: a theoretical study including spin–orbit coupling

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ABSTRACT

The potential energy curves (PECs) of 24 $\Lambda-S$ electronic states of superoxide anion (O$_2^-$), which correlated with the first dissociation channel, were calculated using a high-accuracy internally contracted multireference configuration interaction (icMRCI) methodology with the Davidson correction in conjunction with the correlation-consistent basis sets. The core electron correlation and scalar relativistic corrections as well as basis set extrapolation were included. The spin–orbit coupling was also taken into account by using the state interaction approach with the Breit–Pauli Hamiltonian. The PECs of 54 $\Omega$ states generated from the 24 $\Lambda-S$ states were constructed and described in detail. The spectroscopic constants of the seventeen $\Lambda-S$ and 37 $\Omega$ bound states were evaluated and the vibrational properties of some weakly bound states were predicted. Comparing with the available experimental and theoretical data shows that the computational strategy employed is suitable and highly accurate for this system.

1. Introduction

The superoxide anion radical (O$_2^-$) is of special interest because of its important role in the chemistry of the upper atmosphere, specifically that of the D-region. And superoxide anion species is also of interest in many biochemical and industrial applications \cite{1–3}, since it is an important intermediate in a great number of oxidation process activated by enzymes and by industrial catalysts in order to make a triplet dioxygen readily able to accepts electrons \cite{4–6}. A better knowledge of the spectroscopic properties of this species can give insight in aspects related to processes occurring in various environments. Therefore, it has been the subject of numerous experimental \cite{3,7–38} and theoretical studies \cite{39–52} since the 1930s.

The first observation on the electronic structure of the superoxide anion O$_2^-$ was carried out by Neuman \cite{7}...
in 1934. From then on, the stability and spectroscopic properties of the O$_2^-$ ion, as measured by the potential energy curves (PECs) of O$_2^-$ ion and the adiabatic electron affinity (EA) of oxygen, become of great practical and interest. Celotta et al. [8,9] in 1972 studied the transitions from mass-selected O$_2^-$ to vibrational levels of the X$^3\Sigma_g^-$ and a$^1\Delta_g$ states of O$_2$, which was one of the first molecular anions investigated by negative-ion laser photoelectron spectroscopic techniques. They assigned the spectrum of negative-ion O$_2^-$, and determined its equilibrium bond length $R_e$, harmonic frequency $\omega_e$ and dissociation energy $D_0$ for the ground state and estimated the EA of O$_2$. Dolfe [10] in 1978 measured the absorption and excitation spectra of O$_2^-$ in NaCl crystal at 2 K. The PEC of A$^2\Pi_u$ state was constructed with the experimental spectroscopic constants. Numerous earlier spectroscopic experiments had been performed to define the EA of O$_2$ and the spectroscopic structures of anion [11–27]. Most of these studies were summarised by Huber and Herzberg [28] in 1979.

Subsequently, Travers et al. [3] in 1989 detected the spectrum of O$_2^-$ in the gas phase using negative ion photoelectron spectrum technology. They analysed the photoelectron spectra and acquired the $\omega_e$ and $R_e$ of the ground state of O$_2^-$ and the EA of O$_2$. In the experiment of Lavrich et al. [29] in 1993, the excited A$^2\Pi_u$ state of the gas phase superoxide anion O$_2^-$ was observed by photofragmentation spectrum in the range of 4.5 eV, and its potential curve and several spectroscopic constants were evaluated. Lately, Dinu et al. [30] in 2003 applied high-resolution fast beam photofragment spectroscopy on O$_2^-$ molecular ions. Analyzing the kinetic energy release of the photofragments, they reported the relation to the distribution over the six fine-structure dissociation limits O$^-$ ($^2P_{3/2,1/2}$) + O ($^2P_{2,1,0}$) in detail.

The first measurement about the spin–orbit coupling constant for the O$_2^-$ anion was performed by Land et al. [26] in 1973. Later, Stephen et al. in 1986 [31] and Field et al. in 1988 [32] separately reported the spin–orbit splitting values from electron scattering measurements. Schiedt et al. [33] in 1995 resolved the spin–orbit splitting by first using high-resolution photodetachment techniques. Latterly, Ervin et al. [34] in 2003 observed the ultraviolet spectrum and reported 29 vibronic transitions to three low-lying electronic states of neutral O$_2$ ($^X^3\Sigma_g^-$, a$^1\Delta_g$, b$^1\Sigma_g^+$) from the X$^3\Pi_1$ ($J = 3/2$ and 1/2) spin–orbit states of the anion. The energy splitting of the ground state of the anion is determined. They reevaluated the $D_0$, $R_e$, and $\omega_e$ of the ground state for the anion and obtained the EA$_0$ (O$_2$) value. Since 2002, Chen et al. employed the electron-capture detector (ECD) method to carry out a series of studies on the EA of O$_2$ and the PECs of O$_2^-$ anion [35–38]. However, the limitation of the ECD experiments made it unable to provide accurate electron affinities and anion excited-state energies for O$_2$ [34].

On the other hand, a lot of theoretical investigations have been published [39–52] focused on the EA of O$_2$ and PECs of O$_2^-$ anion. The earliest ab initio calculations were made by Michels [39], by Das et al. [40–42], and by Krauss et al. [43] during the 1970s. After that, an extensive systematic theoretical work on O$_2^-$ reported in 1981 is that of Michels [44]. He employed the valence configuration interaction (CI) approach in combine with double-ζ basis and double-ζ-double-polarisation basis sets to calculate the PECs arising from the ground 2$^P$ state of O$^-$ and the ground 3$^P$ and excited 1$^D$ and 1$^S$ state of O atom. The calculations indicated a large number of bound excited-states existed. The spectroscopic constants for these excited-states were also predicted.

Ewig et al. [45] in 1990 constructed the PECs of the ground state and several low-lying excited-states of O$_2^-$ using the MCSCF/CI theoretical method incorporated with a triple-zeta set of contracted Gaussian functions augmented with diffuse primitive d functions (6-311++G(2d)). The transition energy refer to the ground state T$_e$, $R_e$, $\omega_e$ and anharmonic vibrational constants $\omega_e\chi_e$ of the X$^3\Pi_u$, a$^4\Sigma_u^-$ and A$^2\Pi_u$ states were evaluated in vacuo and within a simulated ionic lattice (KCl). At the same year, Børve and coworker [46] paid particular attention to the A$^2\Pi_u$ state and computed its PEC and spectroscopic constants using CASSCF/CI method. In 1992, Nakatsuji et al. [47] characterised the electronic structures of the ground state of the O$_2^-$ species with the single and double excitation configuration interaction (SD-CI) and the symmetry adapted cluster (SAC)/SAC-CI theoretical methods. Spectroscopic constants were derived in the gas phase and on a silver surface. In 1993, González-Luque et al. [48] applied three different methods in a calculation of the EA of the oxygen molecule. At the same time, the spectroscopic constants of the ground state of O$_2^-$ ($^X^3\Pi_u$) were calculated using the CASSCF/MRCI+Q method in combination with an extended ANO-type basis set (7s6p3d2f1g). In 1996, Chandrasekher et al. [49] achieved a comparative study between coupled cluster and quadratic CI approaches. Several spectroscopic constants $R_e$, $\omega_e$, the anharmonic constants $\omega_e\chi_e$, and vibration coupling constant $\alpha_e$ of the ground state of O$_2^-$, O$_2$, and O$_2^+$ were determined using both methods. In 1999, Bruna et al. [50] made the MRCI calculations to study the vertical electronic spectra. They computed the PECs of several ($^X^3\Pi_g$, a$^4\Sigma_u^-$, A$^2\Pi_u$, $^1\Sigma_u^-$) electronic states and obtained some spectroscopic data.

In 2001, Sordo [51] implemented a series of calculations with aug-cc-pVXZ (X = D, T, Q) basis sets at the
CCSDT level of theory on O$_2^-$ and O$_2$ with the purpose of obtaining an accurate value of the EA of O$_2$. Besides EA, using the basis sets extrapolation approach, the $R_e$, $\omega_e$ and dissociation energy $D_e$ of the ground state of the anion were also predicted. In 2003, Ervin et al. [34] calculated the PECs and the transition energy $T_e$, $R_e$ and $\omega_e$ of the $X^2\Pi_g$, $A^2\Pi_u$, $a^3\Sigma_u^-$ states for O$_2^-$ using the CCSD(T) method combined with aug-cc-pVTZ basis set. Recent, Stampfuß et al. [52] in 2003 made the MR-ACPF calculations on the EA of O$_2$ using aug-cc-pVTZ basis set, and reported some spectroscopic constants of O$_2^-$ anion.

Some important corrections on PECs, such as complete basis set (CBS) extrapolation scheme were employed to decrease error brought by basis set truncation. Some important corrections on PECs, such as the core–valence correlation and scalar relativistic corrections were taken into account to enhance the accuracy of calculation. And spin–orbit coupling effect was taken into consideration extensively in calculation. With the PECs obtained, the spectroscopic properties of all the 24 $\Lambda$–S and 54 $\Omega$ states of the O$_2^-$ were described and compared with the recently experimental data and part theoretical results in detail. Through this work, we desire to help understand the experimentally observed results and report unobserved states accurately.

2. Methodology

The present ab initio calculations were performed using the MOLPRO program version 2010.1 [53]. As the first step, calculations were carried out without the spin–orbit coupling effects. The basis set employed in the calculations was the aug-cc-pV6Z set [54]. In the valence state range, at a given internuclear distance of O$_2^-$, the ground-state molecular orbitals (MOs) were calculated first using the Hartree-Fock self-consistent field (HF-SCF) method. Initial orbitals guessed for the calculation of all states were obtained from the HF orbitals of the ground state. The correlation energy of the anion, with an additional electron, is substantially larger than that of the neutral system and, as a result, high level electron correlation is required. To include, as much as possible, the static correlation effect in the wave functions, then the state-averaged complete active space SCF (CASSCF) [55,56] calculations were made using the HF orbitals as the starting guess. Utilizing the CASSCF energies as reference values, the energies of each electronic state were computed by the internally contracted multireference configuration interaction approach (icMRCI) [57–59]. The static and dynamic correlations are only incorporated with the single and double excitation in MRCI calculations. Then, the effect of triple and quadruple excitation was taken into consideration by using the Davidson procedure (denoted as +Q) [60,61].

All the calculations were performed in the $D_{2h}$ subgroup of $D_{nh}$ point group. Three $^2\!A_u$, one $^2\!B_{1u}$, one $^2\!\Pi_{u,x}$, one $^2\!\Pi_{u,y}$, three $^2\!B_{1g}$, one $^2\!A_g$, one $^2\!\Pi_{g,x}$, one $^2\!\Pi_{g,y}$, three $^4\!A_u$, one $^4\!B_{1u}$, one $^4\!\Pi_{u,x}$, one $^4\!\Pi_{u,y}$, three $^4\!B_{1g}$, one $^4\!A_g$, one $^4\!\Pi_{g,x}$ and one $^4\!\Pi_{g,y}$ were averaged together using the CASSCF averaging procedure. The 24 $\Lambda$–S states, correlating with the first dissociation limit O ($^3\!P$) + O$^-$ ($^2\!P$) of O$_2^-$ anion, were included.

In calculation, eight MOs were put 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 2s2p shell of O atom and O$^-$ anion. The rest of the electrons in the 1s shell were put into two closed-shell core orbitals with one $A_g$ and one $B_{1u}$ MOs. They were not correlated in calculation unless otherwise noted. The active space consisting of thirteen electrons and ten MOs (referred to as CAS (13, 10)) was chosen. That is, we employed ten MOs (3$a_g$, 1$b_{3u}$, 1$b_{2u}$, 3$b_{1u}$, 1$b_{2g}$, and 1$b_5$, in a shorthand notation, [3103110]) to make the PEC calculations. The point spacing interval used here was 0.02 nm for each state, except near the equilibrium position where the point spacing was in 0.005 nm.

The energy extrapolation technique has been employed extensively in high-level quantum chemical calculations [62–64]. Since the correlation-consistent
basis sets, aug-cc-pVXZ \((X = T, Q, 5, 6)\), exhibit basis set convergence toward the complete basis set limit, hence it should be proper to utility in extrapolations [65]. For two successive correlation-consistent basis sets, the total-energy extrapolation formula is written as [63,66]

\[
\Delta E_{\text{total,}\infty} = \frac{\Delta E_{\text{total},X+1}(X + 1)^3 - \Delta E_{\text{total},X}X^3}{(X + 1)^3 - X^3}.
\]

Here, \(\Delta E_{\text{total,}\infty}\) is the total energy extrapolated to the complete basis set limit. \(\Delta E_{\text{total},X+1}\) and \(\Delta E_{\text{total},X}\) are the total energies obtained by the basis sets, aug-cc-pV(X+1)Z and aug-cc-pVXZ, respectively. 

To improve the accuracy of the PECs, the scalar relativistic correction and core–electron correlation effect were included in the molecular energies. At the level of the aug-cc-pCVTZ [67], the difference between the core–valence correlation and the frozen-core approximation energies was used to estimate the core–valence correlation contribution (denoted as +CV). Scalar relativistic effects were taken into account through the third-order Douglas–Kroll Hamiltonian approximation [68–70] (DKH) combined with the relativistic contracted set cc-PV5Z [62]. The difference between the cc-pV5Z energy with and without DKH approximation forms the scalar relativistic contribution (denoted as +DK). All these corrections were calculated with the icMRCI method.

The spin–orbit couplings were computed using the state interaction approach with the Breit–Pauli Hamiltonian [71]. The Breit–Pauli Hamiltonian can be written as

\[
\hat{\Delta} = \frac{e^2}{2m_e^2c^2} \sum_i \left[ \sum_{\alpha} \frac{Z_\alpha}{r_{i\alpha}} \left( \vec{r}_{i\alpha} \times \vec{p}_i \right) \right] \cdot \vec{s}_i - \sum_{j \neq i} \frac{1}{r_{ij}} \left[ \vec{r}_{ij} \times \vec{p}_i \right] \left( \vec{s}_i \times 2 \vec{s}_j \right).
\]

Here Roman subscripts \(i\) and \(j\) refer to the electrons, Greek subscript \(\alpha\) denotes the nuclei, respectively. And the other symbols have the usual meanings. Such as, \(Z_\alpha\) is the nuclear charge number of the \(\alpha\)th nucleus, \(e\) is the electronic charge, \(m_e\) is the mass of the electron, and \(c\) is the velocity of light. \(s_i\) is the spin operator for the \(i\)th electron, \(\vec{r}_{i\alpha}\) is the position vector between the \(i\)th electron and the \(\alpha\)th nucleus, \(\vec{p}_i\) is the momentum vector of \(i\)th electron, \(r_{ij}\) is the distance of the \(i\)th electron with respect to the \(j\)th electron.

The spin–orbit coupling contributions were computed by diagonalisation of the electronic Hamiltonian and the Breit–Pauli spin–orbit coupling Hamiltonian in a basis of the electronic eigenfunctions. All 24 \(\Lambda–S\) states which correlate with the lowest dissociation limit were included in the spin–orbit coupling calculations.

Based on the calculated PECs of bound \(\Lambda–S\) and \(\Omega\) electronic states of \(O_2^-\) anion, they were fitted to an analytic form by cubic splines. Then the ro-vibrational Schrödinger equation was solved using the Numerov’s method [72]. That is, the ro-vibrational constants were determined from the analytic potential by solving the ro-vibrational Schrödinger equation first, and then the spectroscopic parameters were evaluated by fitting the vibrational levels. The spectroscopic constants, \(R_e\), \(\omega_e\), \(\omega_a x_e\), \(\alpha_e\), \(B_e\), \(\beta_e\), and \(T_e\) were evaluated. The dissociation energies \(D_e\) were estimated by comparing the molecular energies at \(R_e\) and at a relatively large separation for all electronic states.

## 3. Results and discussion

All 24 valence \(\Lambda–S\) states of \(O_2^-\) generated from the interaction of the ground state \(O(1^3\Pi_g, 2s^22p^4)\) with the ground-state \(O^- (2^3\Pi_u, 2s^22p^5)\) are studied. These states have doublet and quartet spin multiplicities. The dissociation correlations between the atomic and \(\Lambda–S\) states are shown in Table 1.

We first explore the sensitivity of the computational results to the basis set and discuss their convergence behaviour at the icMRCI+Q level of theory. All the basis sets used in calculations were the consistent-consistent basis sets, and the complete basis set limit energies were estimated by the total energy extrapolation scheme aforementioned. In order to provide an initial assessment of the quality of the basis sets used in this work, the spectroscopic constants were calculated for all 24 \(\Lambda–S\) states.

Due to the length limitation, only the main spectroscopic constants, \(T_e\), \(R_e\), \(\omega_e\) and \(D_e\) of \(1^2\Sigma_g^+, 1^4\Delta_g, 1^2\Delta_u\) and \(1^4\Pi_u\) states are listed in Table 2 for comparison. It should be pointed out that the CBS results listed in Table 2 are those derived from the extrapolation of the two largest successive basis sets, aug-cc-pV5Z and aug-cc-pV6Z.
As shown in Table 2, it can be found that the spectroscopic constants systemically vary with the quality of correlation-consistent basis sets. The $T_e$, $R_e$, $\omega_e$, and $D_e$ values converge toward the CBS limit when increasing cardinal number X in basis set for all four electronic states. Take the $1^4\Delta_g$ state as an example, the basis sets from the aug-cc-pVTZ to aug-cc-pVQZ, from the aug-cc-pVQZ to aug-cc-pVQZ, and from the aug-cc-pVQZ to aug-cc-pVQZ increase the $T_e$ by 588.41, 227.82, and 147.48 cm$^{-1}$, respectively. Similarly, with the increasing of basis sets, the $R_e$ increases, while the $\omega_e$ and $D_e$ increase to some extent. Overall, the change trend of the spectroscopic constants for the other three states is as same as that of the $1^4\Delta_g$ state with the cardinal number increasing. In general, the results in Table 2 demonstrate that the $T_e$, $R_e$, $\omega_e$, and $D_e$ of $1^2\Sigma_g^-$, $1^2\Delta_u$, $1^4\Delta_g$, and $1^4\Pi_u$ states are convergent with respect to the basis set at the icMRCI+Q level of theory. Whereas, even the largest aug-cc-pVQZ set appears to have very larger basis set incompleteness error [73]. Therefore, calibration by extrapolation of basis sets does seem warranted since the differences between CBS and aug-cc-pVQZ are found to be very larger in the present work for all electronic states of the $O_2^-$ anion. This would eliminate one of the major sources of errors in $ab$ initio calculations.

Then we go on to discuss the effects on the spectroscopic constants by core–electron correlation and scalar relativistic corrections. Due to the limitation of coverage, here we only optionally take the $1^2\Sigma_g^-$, $1^4\Pi_u$, $1^2\Sigma_g^-$ and $1^4\Delta_g$ states as examples. Table 3 collects the spectroscopic constants, $T_e$, $R_e$, $\omega_e$, and $D_e$ results of the $1^2\Sigma_g^-$, $1^4\Pi_u$, $1^2\Sigma_g^-$ and $1^4\Delta_g$ states computed at the icMRCI+Q/AV6Z level of theory as well as their corresponding changes caused by the two corrections.

Focusing on the effect on $T_e$ by core–valence correlation and/or scalar relativistic corrections, it is found that, the core–valence correlation contribution to the $T_e$ is equal to $-478.02$ (1.71%), $-576.78$ (2.20%), $-573.48$ (2.25%) and $-266.45$ (0.85%) cm$^{-1}$ for the $1^2\Sigma_g^-$, $1^2\Pi_u$, $1^4\Delta_g$ and $1^4\Pi_u$ $\Lambda$–$\Sigma$ states, respectively. The scalar relativistic correction makes their $T_e$ values separately decline

### Table 2. Spectroscopic parameters of four electronic states: convergence observations of basis sets at the icMRCI+Q level of theory.

|              | $T_e$/cm$^{-1}$ | $R_e$/nm | $\omega_e$/cm$^{-1}$ | $D_e$/eV | $T_e$/cm$^{-1}$ | $R_e$/nm | $\omega_e$/cm$^{-1}$ | $D_e$/eV |
|--------------|----------------|----------|----------------------|----------|----------------|----------|----------------------|----------|
| $1^2\Sigma_g^-$ | 26,884.98     | 0.2197   | 336.27               | 0.7372   | 24,580.06     | 0.2134   | 379.20               | 1.0706   |
| $1^4\Delta_g$ | 27,494.68     | 0.2793   | 345.18               | 0.7619   | 25,168.47     | 0.2142   | 385.69               | 1.0931   |
| $1^4\Delta_g$ | 27,726.23     | 0.2762   | 347.28               | 0.7656   | 25,396.29     | 0.2186   | 387.56               | 1.0987   |
| $1^4\Delta_g$ | 27,874.38     | 0.2749   | 348.00               | 0.7681   | 25,543.77     | 0.2175   | 388.14               | 1.1007   |
| CBS          | 28,079.36     | 0.2731   | 349.01               | 0.7715   | 25,748.11     | 0.2160   | 388.95               | 1.1033   |

### Table 3. Effect on spectroscopic parameters ($T_e$, $R_e$, $\omega_e$, and $D_e$) by core–valence correlation correction and/or relativistic correction at the icMRCI+Q/AV6Z level of theory.

|              | $T_e$/cm$^{-1}$ | $R_e$/nm | $\omega_e$/cm$^{-1}$ | $D_e$/eV | $T_e$/cm$^{-1}$ | $R_e$/nm | $\omega_e$/cm$^{-1}$ | $D_e$/eV |
|--------------|----------------|----------|----------------------|----------|----------------|----------|----------------------|----------|
| $1^2\Sigma_g^-$ | 26,884.98     | 0.2197   | 336.27               | 0.7372   | 24,580.06     | 0.2134   | 379.20               | 1.0706   |
| $1^4\Delta_g$ | 27,494.68     | 0.2793   | 345.18               | 0.7619   | 25,168.47     | 0.2142   | 385.69               | 1.0931   |
| $1^4\Delta_g$ | 27,726.23     | 0.2762   | 347.28               | 0.7656   | 25,396.29     | 0.2186   | 387.56               | 1.0987   |
| $1^4\Delta_g$ | 27,874.38     | 0.2749   | 348.00               | 0.7681   | 25,543.77     | 0.2175   | 388.14               | 1.1007   |
| CBS          | 28,079.36     | 0.2731   | 349.01               | 0.7715   | 25,748.11     | 0.2160   | 388.95               | 1.1033   |
by 58.82, 47.63, 56.18, and 58.52 cm\(^{-1}\). Although this improvement is not more than 60 cm\(^{-1}\), it is by no means negligible to achieve the goal of spectroscopic accuracy. Obviously, of the two corrections, the most significant correction is the inclusion of the core–valence correlation. When both corrections are taken into account at the same time, the smallest change of \(T_e\) is 325.27 cm\(^{-1}\) (1.04\%) for the 1\(^4\)\(\Pi\)_\(u\) state and the largest one is 629.66 cm\(^{-1}\) (2.47\%) for the 1\(^4\)\(\Delta\)_\(g\) state. So it is significant and should be considered in calculation.

The effect on equilibrium bond length by the core–valence correlation contribution is more notable, being 0.00110 nm on average and a maximum of 0.00183 nm at the same time, the smallest change of \(T_e\) is 325.27 cm\(^{-1}\) (1.04\%) for the 1\(^4\)\(\Pi\)_\(u\) state and the largest one is 629.66 cm\(^{-1}\) (2.47\%) for the 1\(^4\)\(\Delta\)_\(g\) state. So it is significant and should be considered in calculation.

According to the above analysis, we can conclude that the core–valence correlation and scalar relativistic effects are important in obtaining accurate PECs and spectroscopic properties for the \(O_2^-\) anion and cannot be dismissed in highly-accurate calculation.

Unless otherwise noted, all results presented below refer to the icMRCI+Q level of approximation with inclusion of core–electron correlation and scalar relativistic corrections at the CBS limit with or without spin–orbit coupling splitting. In addition, all the extrapolation calculations were carried out employing the largest successive correlation-consistent basis sets, aug-cc-pV6Z and aug-cc-pV5Z.

### 3.1 Spectroscopic properties of 17 \(\Lambda–S\) bound states

Using the aforementioned methods, the PECs of all 24 \(\Lambda–S\) electronic states of \(O_2^-\) anion, corresponding to the first dissociation channel, \(O(3\,^3\Pi_g) + O^- (2\,^3\Sigma_u^-)\), were calculated for internuclear separation from 0.10 to 1.2 nm. For more clarity, we depict these curves in Figures 1 and 2 with the internuclear separation from 0.10 to 0.52 nm. Meanwhile, the PEC of \(X^2\Pi_g\) state is plotted in both figures for comparative purposes.

From Figures 1 and 2, we can find that the PECs of all the 24 \(\Lambda–S\) electronic states are correlated to the same asymptote. Seventeen electronic states, \(X^2\Pi_g\), \(A^2\Pi_u\), \(1^2\Delta_u\), \(1^2\Sigma_u^+\), \(1^2\Sigma_u^-\), \(1^2\Sigma_g^-\), \(1^2\Sigma_g^+\), \(1^2\Delta_g\), \(2^2\Pi_g\), \(1^4\Sigma_u^-\), \(1^4\Delta_g\), \(1^4\Sigma_g^+\), \(1^4\Pi_u\), \(1^4\Sigma_g^-\), \(2^4\Pi_u\), and \(1^4\Pi_g\), are found to be bound states, while the others, \(2^2\Sigma_u\), \(2^2\Pi_u\), \(1^4\Delta_u\), \(2^4\Sigma_g\), \(2^4\Sigma_u\), \(2^4\Pi_g\), and \(1^4\Sigma_u^+\), are repulsive.

According to the above analysis, we can conclude that the core–valence correlation and scalar relativistic effects are important in obtaining accurate PECs and spectroscopic properties for the \(O_2^-\) anion and cannot be dismissed in highly-accurate calculation.

### 3.1.1 Spectroscopic constants of \(X^2\Pi_g\) and \(A^2\Pi_u\) states

Based on the PECs obtained, the spectroscopic constants for the 17 \(\Lambda–S\) bound state were evaluated. For convenience of discussion, we divide them into two groups. One is the \(X^2\Pi_g\) and \(A^2\Pi_u\) states, which are the only two
L–S states having the experimental data. The other states have no corresponding spectroscopic measurements exist so far. The present results are presented in Tables 5 and 6, respectively. Since the experimental data before 1979 had been summarised in the work of Huber and Herzberg [28], therefore, here we only gather the data of the literature [28] and part of the later experimental data and the previous theoretical results in Tables 5 and 6 for comparison.

For the ground state \( \chi^2 \Pi_g \), we find excellent quantitative agreement between our calculation and the available experimental data. The present \( R_e \) of 0.13457 nm and \( B_e \) of 1.1601 cm\(^{-1}\) are in good accordance with the recent experimental values [34] of 0.1348 nm and 1.161 cm\(^{-1}\), respectively. The computed \( \omega_e \) value is of 112.68 cm\(^{-1}\), which is fallen into the error range of the recent measurements [34], however, somewhat larger than the prior experimental value [28].

Ervin et al. [34] and Sordo [51] both employed coupled-cluster theory [CCSD(T) and CCSDT] method in conjunction with correlation-consistent basis set to calculate several spectroscopic constants for the ground state of \( \text{O}_2^- \). The quality of the present \( R_e \) and \( \omega_e \) is equivalent to them when compared with the recent experiment [34].

By analyzing the compositions of icMRCI wave functions, we find that the \( \chi^2 \Pi_g \) state is characterised mainly by the configuration \( 2 \sigma_{g}^{2} 2 \sigma_{u}^{2} 3 \sigma_{g}^{2} 1 \tau_{u}^{1} 1 \pi_{u}^{1} 3 \pi_{u}^{4} \) near the equilibrium internuclear separation. The rest configurations are indeed insignificant, such as \( 2 \sigma_{g}^{2} 2 \sigma_{u}^{2} 3 \sigma_{g}^{2} 1 \tau_{u}^{1} 1 \pi_{u}^{1} 3 \pi_{u}^{4} \) as seen in Table 4. That is to say, the ground state has no strong interaction with other states around the equilibrium position. So it is not surprise that the single-reference coupled-cluster theory method could describe its spectroscopic properties properly.

In contrast, the MCSF method estimates a relative longer \( R_e \) [41,42,45] and larger \( \omega_e \) [42,45] when compared with the recent experimental values [34]. However, Das et al. [41] reported a smaller \( \omega_e \) with the same method which differs from the trend presented by the other calculations. The main reason may lie in the different choice of configurations in their calculations.

The spectroscopic constants of the ground state of \( \text{O}_2^- \) (\( \chi^2 \Pi_g \)) were computed by González-Luque et al. [48] employed the MRCI+Q method combined with the

### Table 4. Leading configurations of 17 L–S bound states near the equilibrium position.

| States | Valence electronic configurations | \( \langle r^2 \rangle \) (nm\(^2\)) |
|--------|---------------------------------|-------------------|
| \( \chi^2 \Pi_g \) | \( 2 \sigma_{g}^{2} 2 \sigma_{u}^{2} 3 \sigma_{g}^{2} 1 \tau_{u}^{1} 1 \pi_{u}^{1} 3 \pi_{u}^{4} \) | \( 0.8767 \) |
| \( \Delta \Sigma_g^+ \) | \( 2 \sigma_{g}^{2} 2 \sigma_{u}^{2} 3 \sigma_{g}^{2} 1 \tau_{u}^{1} 1 \pi_{u}^{1} 3 \pi_{u}^{4} \) | \( 0.9829 \) |
| \( \Delta \Sigma_g^- \) | \( 2 \sigma_{g}^{2} 2 \sigma_{u}^{2} 3 \sigma_{g}^{2} 1 \tau_{u}^{1} 1 \pi_{u}^{1} 3 \pi_{u}^{4} \) | \( 0.7609 \) |
| \( \Sigma_g^0 \) | \( 2 \sigma_{g}^{2} 2 \sigma_{u}^{2} 3 \sigma_{g}^{2} 1 \tau_{u}^{1} 1 \pi_{u}^{1} 3 \pi_{u}^{4} \) | \( 0.7261 \) |
| \( \Sigma_u^+ \) | \( 2 \sigma_{g}^{2} 2 \sigma_{u}^{2} 3 \sigma_{g}^{2} 1 \tau_{u}^{1} 1 \pi_{u}^{1} 3 \pi_{u}^{4} \) | \( 0.6628 \) |
| \( \Sigma_u^- \) | \( 2 \sigma_{g}^{2} 2 \sigma_{u}^{2} 3 \sigma_{g}^{2} 1 \tau_{u}^{1} 1 \pi_{u}^{1} 3 \pi_{u}^{4} \) | \( 0.6238 \) |

\( ^a \)The value in parentheses is the square of a configuration coefficient.
Table 5. Spectroscopic constants of the $X^2 \Pi_\alpha$ and $A^2 \Pi_\alpha$ states of $O_2^{-}$ anion.

| $X^2 \Pi_\alpha$ | $A^2 \Pi_\alpha$ |
|-----------------|-----------------|
| $T_v$ (cm$^{-1}$) | $R_v$ (nm) | $\omega_v$ (cm$^{-1}$) | $\omega_x$ (cm$^{-1}$) | $\omega_{xy}$ (cm$^{-1}$) | $B_v$ (cm$^{-1}$) | $10^6 \omega_x$ (cm$^{-1}$) | $10^6 \beta_\alpha$ (cm$^{-1}$) | $D_v$ (eV) |
| This work | 0.0 | 0.13457 | 1122.22 | 8.85 | 1.1601 | 1.31 | 0.0665 | 4.2764 |
| Exp. [34] | 0.0 | 0.1348(8) | 1108(20) | [9] | 1.161 | – | – | 4.1724 |
| Exp. [29] | 0.0 | – | – | – | – | – | – | 4.2484 |
| Exp. [28] | 0.0 | 0.135 | 1090 | 8.0(1) | – | – | – | 4.1573 |
| Exp. [3] | 0.0 | 0.1347(5) | 1073(50) | – | – | – | – | 4.00 |
| Cal. [47] | 0.0 | 0.144 | – | – | – | – | – | 4.0762 |
| Cal. [51] | 0.0 | 0.13481 | 1132 | – | – | – | – | 4.129 |
| Cal. [34] | 0.0 | 0.1356 | 1112 | – | – | – | – | 4.210 |
| Cal. [42] | 0.0 | 0.1356 | 1098 | 9.04 | 1.135 | 1.51 | – | 3.93 |
| Cal. [45] | 0.0 | 0.13544 | 1163 | 9.2 | – | – | – | 4.056 |
| Cal. [46] | 0.0 | 0.13653 | – | – | – | – | – | 4.0813 |
| Cal. [50] | 0.0 | 0.13732 | 1065 | 8.8 | – | – | – | 4.084 |
| Cal. [48] | 0.0 | 0.1362 | 1107.2 | 13.06 | 1.1361 | 1.37 | – | 4.056 |

*The value of $\nu_0$.  

Table 6. Spectroscopic constants of the 15 $\Lambda$–$S$ states of $O_2^{-}$ anion.

| $a^2 \Sigma_\alpha ^{-}$ (1st well) | $a^2 \Sigma_\alpha$ (2nd well) | $A^2 \Delta_\alpha ^{-}$ (1st well) | $A^2 \Delta_\alpha$ (2nd well) |
|-----------------|-----------------|-----------------|-----------------|
| $T_v$ (cm$^{-1}$) | $R_v$ (nm) | $\omega_v$ (cm$^{-1}$) | $\omega_x$ (cm$^{-1}$) | $\omega_{xy}$ (cm$^{-1}$) | $B_v$ (cm$^{-1}$) | $10^6 \omega_x$ (cm$^{-1}$) | $10^6 \beta_\alpha$ (cm$^{-1}$) | $D_v$ (eV) |
| This work | 0.0 | 0.13457 | 1122.22 | 8.85 | 1.1601 | 1.31 | 0.0665 | 4.2764 |
| Exp. [34] | 0.0 | 0.1348(8) | 1108(20) | [9] | 1.161 | – | – | 4.1724 |
| Exp. [29] | 0.0 | – | – | – | – | – | – | 4.2484 |
| Exp. [28] | 0.0 | 0.135 | 1090 | 8.0(1) | – | – | – | 4.1573 |
| Exp. [3] | 0.0 | 0.1347(5) | 1073(50) | – | – | – | – | 4.00 |
| Cal. [47] | 0.0 | 0.144 | – | – | – | – | – | 4.0762 |
| Cal. [51] | 0.0 | 0.13481 | 1132 | – | – | – | – | 4.129 |
| Cal. [34] | 0.0 | 0.1356 | 1112 | – | – | – | – | 4.210 |
| Cal. [42] | 0.0 | 0.1356 | 1098 | 9.04 | 1.135 | 1.51 | – | 3.93 |
| Cal. [45] | 0.0 | 0.13544 | 1163 | 9.2 | – | – | – | 4.056 |
| Cal. [46] | 0.0 | 0.13653 | – | – | – | – | – | 4.0813 |
| Cal. [50] | 0.0 | 0.13732 | 1065 | 8.8 | – | – | – | 4.084 |
| Cal. [48] | 0.0 | 0.1362 | 1107.2 | 13.06 | 1.1361 | 1.37 | – | 4.056 |

*The value of $\nu_0$.  

*Note: $\omega$, $\omega_x$, $\omega_{xy}$, $B$, $\omega_x$, $\beta_\alpha$, $D_v$ refer to the spectroscopic constants in the usual notation.
(7s6p3d2f1g) valence basis set. Among those constants they obtained, the $\omega_e$ of 1107.2 cm\(^{-1}\) is the best one, which excellently agrees with the recent experimental value \[34\]. While the other spectroscopic constants, $R_e$, $\omega_eX_e$, $R_a$, and $D_a$ are inferior to the present ones when compared with the recent experiment \[34\]. Bruna et al. \[50\] performed MRCl calculations and obtained the $R_e$, $\omega_e$, and $\omega_eX_e$ of the $X^2\Pi_g$ state. Their $R_e$ is slightly longer and $\omega_e$ is a little larger than the recent experiment \[34\].

As for the $D_e$, the present result is about 0.07 eV higher than the experiment value of 4.1716 eV (2.49\%) by Ervin et al. \[34\], however, more closely to the one of 4.2428 eV (0.66\%) by Lavrich et al. \[29\]. To clarify, the $D_e$ \[29\] is derived from the $D_0$ \[29\] and the recent $\omega_e$ and $\omega_eX_e$ \[34\]. Sometimes, the notable discrepancies among the reported experimental results make it difficult to assess the accuracy of theoretical predictions. Whereas, we believe that the present $D_e$ result is the most accurate one since variously significant factors are taken into account in the calculations as illustrated in the previous section.

As seen from Table 4, the A$^2\Pi_u$ state can be essentially represented by one main configuration, $2\sigma_g^2 2\pi_u^2 3\pi_g^1 \sigma_u^4$ mixed with $2\sigma_g^2 2\pi_u^2 2\sigma_g^1 2\pi_u^1 \pi_g^1 \sigma_u^3 1\pi_g^4$, which is reasonable agreement with the prior observation by Dinu et al. \[30\]. Although the latter configuration is basically unimportant for the A$^2\Pi_u$ state, we think that its multireference character is more obvious than that of the X$^2\Pi_g$ state. As one electron from 1$\pi_u$ bonding orbital of X$^2\Pi_g$ is stimulated to the antibonding 1$\pi_u$ orbit, the A$^2\Pi_u$ state can be generated.

Three group measurements \[10,28,29\] were performed for the A$^2\Pi_u$ state of O$_2^-$ anion. However, the obvious difference of $T_e$, $R_e$, $\omega_e$, and $\omega_eX_e$ exists among the three experiments. Therefore, none of their results are conclusive to some extent. It should be noted that the present $T_e$, $\omega_e$, and $\omega_eX_e$ agree with those of the measurement data \[28\] in general. The present transition energy is estimated to be 25707.72 cm\(^{-1}\), which is about 407.72 cm\(^{-1}\) higher than the measurement of 25300 cm\(^{-1}\) \[28\] and 1602.28 cm\(^{-1}\) lower than the reported $\nu_{00}$ of 27305 cm\(^{-1}\) \[10\]. The present calculation overestimates the $R_e$ value about 0.005 \[10\] and 0.0010 nm \[29\] than the experimental bonding length, which is similar to the predictions reported by the other authors \[34,41,42,44-46,50\]. Therefore, we infer that the experimental equilibrium bond length of the A$^2\Pi_u$ state \[10,29\] is a bit on the low side than the true $R_e$ value. Only the $\omega_e$ result calculated by Ervin et al. \[34\] is equivalent to the present one in quality when compared with the measurements \[28\].

From the above analyses, we find that, on the one hand, most of the previous calculations only limited in the valence range, and the important effects of the core–valence correlation and relativistic effects were neglected; on the other hand, the truncation of basis sets brings notable error, however, to our knowledge, no studies took the issue into consideration except for one reported by Sordo \[51\]. In this work, not only the high-level iCM-MRCI+Q level of theory was employed to calculate the energy for the O$_2^-$ anion, but the important contributions of the core–valence correlation and scalar relativistic effects and CBS extrapolation were also included. Comparison with available experimental data and the prior theoretical calculations shows that the present PECs and spectroscopic constants of the X$^2\Pi_g$ and A$^2\Pi_u$ states of O$_2^-$ anion are the most accurate predictions made so far. These prove that the computational strategy employed here is justified to be suitable for the O$_2^-$ anion system. So, we can conclude that, the spectroscopic constants of those excited A–S states shown below, obtained at the same method, are expected to be the reliable predictions.

### 3.1.2. Spectroscopic constants of the 15 A–S excited bound states

The spectroscopic constants of 1$^2\Sigma^+_g$, a$^4\Sigma_u^-$, 1$^2\Delta_u$, 1$^4\Delta_g$, 1$^4\Sigma^+_g$, 1$^2\Sigma_u^+$, 1$^2\Sigma_u^-$, 1$^2\Sigma_g^-$, 1$^2\Pi_u$, 2$^2\Sigma_g^-$, 1$^2\Delta_g$, 1$^4\Sigma^+_g$, 2$^2\Pi_g$, 2$^4\Pi_u$, and 1$^4\Sigma^+_u$ are also estimated and tabulated in Table 6, whereas no measurements can be found in the literature up to date.

As can be seen from Figure 2, we find that the PEC of a$^4\Sigma_u^-$ state holds a double well. The present calculation supports the prediction by Ervin et al. \[34\], who estimated that the a$^4\Sigma_u^-$ state had a secondary minimum near 0.12 nm not being observed previously. The two potential wells are located approximately at 0.11940 and 0.18316 nm, and the energies at the bottom of both wells are 16046.23 cm\(^{-1}\) and 6853.09 cm\(^{-1}\) lower than that of the A$^2\Pi_u$ state at the equilibrium bond distance. Therefore, the first excited-state of O$_2^-$ anion is a quartet $^4\Sigma_u^-$ state, which is confirmed again according to the values listed in Tables 5 and 6. This order differs from the record of Huber and Herzberg \[28\], who identified the first excited-state of O$_2^-$ as the A$^2\Pi_u$ state \[28\]. The dominant configurations of both wells are mainly characterised by the same two configurations, $2\sigma_g^2 2\pi_u^2 3\pi_g^1 \Omega_u^4 1\pi_u^2 3\sigma_u^1$ and $2\sigma_g^2 2\pi_u^2 3\sigma_g^1 2\pi_u^1 \pi_g^1 4\sigma_u^1$, only with different contribution coefficient.

A barrier appears on the PEC of a$^4\Sigma_u^-$ state between the two wells around 0.12547 nm, and is lower than the dissociation limit. So a$^4\Sigma_u^-$ is a stable electronic state. The prior theoretical studies \[41,44,45,50\] did not report the internal potential well maybe since their PECs calculations were performed only within a relative narrow
internuclear separation range. To our surprise, although the depth of inner well is about 13680.07 cm\(^{-1}\) relative to the top of the barrier, it only possesses nine vibrational levels. However, the depth of the external potential well is 15156.70 cm\(^{-1}\) relative to the dissociation limit and it holds forty vibrational states. Thus, observations of the second well should be easier than that of the first one.

For the two close-lying quartets, \(1^4\Delta_g\) and \(1^4\Sigma_g^+\) are predicted to be about 25032.62 and 25324.30 cm\(^{-1}\) above the ground state. Their dominated configuration originates from the same electron transition \(1\pi_u \rightarrow 3\sigma_u\) from the ground state. Their PECs are almost congruent as can be seen from Figure 2. The spectroscopic constants for both states are found to be very similar. They are stable with many vibrational levels. Thus both of them are relatively easy to observe in experiments.

Three doublets states (\(1^2\Sigma_u^-, 1^2\Delta_u\) and \(1^2\Sigma_u^+\)) can be basically represented by one dominant configuration, \(2\sigma_g^22\sigma_u^23\sigma_g^-1\pi_u^+1\pi_g^-3\sigma_u^-\) mixed with another secondary configuration. The dominant electronic transitions between the \(X^2\Pi_g\) and the three states can be regarded as the \(1\pi_g^-3\sigma_u^+\) promotions. The transition energies is evaluated to be 25744.15 cm\(^{-1}\), 27043.01 and 29783.15, respectively. The well depth of the three states is separately 8578.51, 7356.58 and 2751.16 cm\(^{-1}\). For the \(1^2\Sigma_u^-\) state, its bond length of 0.19121 nm is the shortest one among the three states, and it possesses a barrier at 0.34360 nm with a height of 261.17 cm\(^{-1}\) above the dissociation limit due to the avoided crossing with the higher \(2^2\Sigma_u^-\) state (see Figure 3). While \(2^2\Sigma_u^-\) state forms a repulsive. The \(1^2\Sigma_u^-\) state possesses 7 vibrational states, with vibrational levels of 218.20, 647.22, 1064.49, 1467.71, 1854.60, 2222.86, and 2570.20 cm\(^{-1}\) for \(\nu = 0 – 6\). The \(1^2\Delta_u\) and \(1^2\Sigma_u^+\) states have more than forty vibrational states. From this point of view, the \(1^2\Sigma_u^-\) state should be difficult to observe than the \(1^2\Delta_u\) and \(1^2\Sigma_u^+\) states.

The \(1^2\Sigma_u^-\)-\(X^2\Pi_g\) transition may be observed around 27500 cm\(^{-1}\). The \(1^2\Sigma_u^-\) state is mostly characterised by the configuration, \(2\sigma_g^22\sigma_u^2\ 3\sigma_g^-1\pi_u^+1\pi_g^-3\sigma_u^-\) as with the \(1^4\Delta_g\) and \(1^4\Sigma_g^+\) states. The computed \(R_e\) and \(\omega_e\) results for the \(1^2\Sigma_g^-\) state are 0.21615 nm and 358.9 cm\(^{-1}\), respectively. And it holds many vibrational levels. So it can be observed though it has a shallow well.

Similar to the \(a^4\Sigma_g^-\) state, \(1^2\Sigma_g^+\) state also has a double well on its PEC. The first well is at 0.17576 nm and 2636.11 cm\(^{-1}\) above the dissociation limit, which holds only one vibration state with one vibrational level of 265.08 cm\(^{-1}\). Therefore, it is quite unstable. Between the two wells, there is a barrier at 0.19500 nm and it is 3457.60 cm\(^{-1}\) higher than the dissociation limit. The second well is rather shallow with a depth of 35 cm\(^{-1}\) below the dissociation limit, whereas it possesses five vibration states with vibrational levels of 4.18, 11.70, 18.38, 24.56, 30.59 cm\(^{-1}\) for \(\nu = 0 – 4\). Both wells should be difficult to be observed due to few vibration states.

The \(1^4\Pi_u\) state is represented by a dominant \(2\sigma_g^22\sigma_u^23\sigma_g^-1\pi_u^+1\pi_g^-3\sigma_u^-\) configuration around the equilibrium internuclear distance of 0.23885 nm, which arises from the transition \(3\sigma_g^- \rightarrow \sigma_u\) from the ground state. In the present study, it is predicted to be 31221.58 cm\(^{-1}\) higher than the ground \(X^2\Pi_g\) state. This state was identified to be the first quartet state of O\(_2\) by Herzberg in 1979 [28]. Actually, its transition energy is larger than that of the \(a^4\Sigma_g^-\) state. The depth of its potential well is 3069.74 cm\(^{-1}\), and this state holds 22 vibrational states. Therefore, it is a stable bound state that can be observed easily.

The remaining six excited bound states, \(2^2\Pi_g\), \(2^2\Sigma_g^-\), \(1^4\Sigma_g^-\), \(1^4\Pi_g\), \(2^4\Pi_u\) and \(1^2\Delta_g\), could be found in the range of 33571.40-34200 cm\(^{-1}\). Their transition energies are 33870.42, 33784.61 cm\(^{-1}\), 33882.14, 33914.10, 34163.64, and 34190.64 cm\(^{-1}\), respectively. The energy separation of the six states is only 406.03 cm\(^{-1}\) near the equilibrium positions. Thus, they present a strong multireference configuration character except for the \(2^4\Pi_u\) and \(1^4\Pi_g\) states. Among the six electronic states, each has a long bond length, but a small vibrational frequency. The potential wells of them are all very shallow, with the largest depth of 658.95 cm\(^{-1}\) for the \(2^2\Pi_g\) state. The \(2^2\Pi_g\) state holds sixteen vibrational states with vibrational levels of 79.28, 216.56, 327.75, 415.58, 482.79, 532.11, 566.28, 588.04, 600.11, 605.24, 606.16, 605.60, 606.31, 611.01, 622.44, and 643.34 cm\(^{-1}\) for \(\nu = 0 – 15\). Therefore, it is not difficult to be observed in an experiment. The \(4\Sigma_g^-\) possesses only three vibrational states with vibrational levels of 57.41, 162.12 and 253.16 cm\(^{-1}\) for \(\nu = 0 – 2\). As with the \(2^2\Sigma_g^-\) and \(1^4\Sigma_g^-\) states, the \(1^4\Pi_g\) is a weakly bound state which possesses only three vibrational states with vibrational levels of 24.84, 658.95 and 89.11 cm\(^{-1}\) for \(\nu = 0 – 2\). Neither of the \(4\Sigma_g^-\) and \(1^4\Pi_g\) states can be discovered in experiments easily. The \(2^4\Pi_u\) states has only one main
configuration $2\sigma^22\sigma^22\pi^11\pi_g^11\pi_u^13\sigma_u^1$ just like the $1^4\Pi_u$ state. It has ten vibrational states with vibrational levels of 44.60, 119.81, 178.63, 223.72, 257.78, 283.50, 303.55, 320.63, 337.41, and 356.59 cm$^{-1}$ for $\nu = 0$–9. The $1^2\Delta_u$ is a weakly bound state which has the smallest vibrational frequency of 13.3 cm$^{-1}$ among the 17 $\Lambda$–$S$ bound states. However, it is surprising that the state holds eight vibrational states with vibrational levels of 4.69, 12.97, 20.09, 26.45, 32.44, 38.45, 44.89, 52.14, and 60.59 cm$^{-1}$ for $\nu = 0$–8 as well. Both of the $1^2\Delta_u$ and $2^4\Pi_u$ states need to use great effort to find through experiments.

To our knowledge, no available experimental data can be found in the literature thus far except for the $X^2\Pi_g$ and $A^2\Pi_u$ states. Therefore, we cannot compare the present results with them directly.

### 3.2. Spectroscopic properties of the 37 $\Omega$ bound states

With the spin–orbit coupling interaction, the lowest dissociation limit, arising from the ground state O ($3^3P_g$) and O$^-$ ($2^3P_g$), splits into six closely dissociation limits with a separation of only 405 cm$^{-1}$, which correlates with 54 $\Omega$ states generated from the 24 $\Lambda$–$S$ states of the $O_2^-$ anion. The dissociation relationships for the possible $\Omega$ states and corresponding energy separations are given in Table 7. The PECs of the 22 $\Omega = 1/2$ states and their dissociation relationships are displayed in Figures 4 and 5, and that of the $\Omega = 3/2(18), 5/2(8), 7/2(2), -1/2(4)$ states are drawn in Figures I–IV in supplementary part limited by space.

The spin–orbit interaction causes different $\Lambda$–$S$ states that have common $\Omega$ states to recombine. The dissociation limits of the present 54 $\Omega$ states generated from the 24 $\Lambda$–$S$ states are the $O(3^3P_g) + O^{-}(2^3P_g)$ for the $1^4\Delta_g, 7/2$, $1^4\Delta_u, 7/2$, $1^4\Sigma_g, 5/2$, $1^2\Delta_u, 5/2$, $1^4\Pi_g, 5/2$, $X^2\Pi_g, 3/2$, $a^4\Sigma_u^-, 3/2$, $1^2\Sigma_g^-, 3/2$, $1^4\Sigma_g^+, 3/2$, $1^2\Delta_u, 3/2$, $2^1\Sigma_u^-, 3/2$, $1^2\Sigma_u^+, 1/2$, $1^4\Sigma_g^-, 1/2$, $2^1\Pi_u, 1/2$, $a^4\Sigma_u^+, 1/2$, $1^2\Sigma_u^-, 1/2$, $2^2\Sigma_u^-, 1/2$, and $1^4\Sigma_g^+, 1/2$ states, the $O(3^3P_g) + O^{-}(2^3P_g)$ for the $X^2\Pi_g, 1/2$, $1^4\Pi_u, 1/2$, $1^4\Pi_u, -1/2$, $2^2\Pi_g, -1/2$, $1^2\Sigma_u^+, 1/2$, $2^1\Pi_u, 1/2$, and $1^4\Sigma_g^+, 1/2$ states, the $O(3^3P_g) + O^{-}(2^3P_g)$ for the $X^2\Pi_g, 1/2$, $1^4\Pi_u, 1/2$, $1^2\Delta_u, 5/2$, $2^4\Pi_u, 5/2$, and $1^4\Pi_u, 5/2$ states, the $O(3^3P_g) + O^{-}(2^3P_g)$ for the $X^2\Pi_g, 1/2$, $1^4\Pi_u, 1/2$, $1^2\Delta_u, 5/2$, $2^4\Pi_u, 5/2$, and $1^4\Pi_u, 5/2$ states, the $O(3^3P_g) + O^{-}(2^3P_g)$ for the $X^2\Pi_g, 1/2$, $1^4\Pi_u, 1/2$, $1^2\Delta_u, 5/2$, $2^4\Pi_u, 5/2$, and $1^4\Pi_u, 5/2$ states.

### Table 7. Dissociation relationships between $\Omega$ states and atomic states of O$_2^-$ anion.

| Atomic states | Relative energy/cm$^{-1}$ |
|---------------|---------------------------|
| (O + O$^-$)   |                           |
| $1^2P_g + ^2P_g$ | 7/2(2), 5/2(24), 3/2(6), 1/2(8) | 0.0 |
| $3^2P_g + ^2P_g$ | 5/2(2), 3/2(4), 1/2(6) | 159.49 |
| $3^2P_g + ^2P_g$ | 5/2(2), 3/2(4), 1/2(4) | 181.81 |
| $3^2P_g + ^2P_g$ | 3/2(2), 1/2(2) | 221.11 |
| $3^2P_g + ^2P_g$ | 3/2(2), 1/2(4) | 335.77 |
| $3^2P_g + ^2P_g$ | 1/2(2) | 404.51 |

Figure 4. PECs of 11 $\Omega = 1/2$ states of O$_2^-$ anion. 1$^1\Pi_g^3/2$, 2$^2\Sigma_g^+, 1/2$, 3$^2\Sigma_u^-, 3/2$, 4$^1\Pi_g^3/2$, 5$^2\Sigma_g^-, 1/2$, 6$^2\Sigma_u^-, 1/2$, 7$^2\Sigma_u^-, 3/2$, 8$^2\Sigma_u^-, 1/2$, 9$^2\Pi_g^3/2$, 10$^2\Sigma_u^-, 3/2$, 11$^1\Delta_u$.

Figure 5. PECs of 11 $\Omega = 1/2$ states of O$_2^-$ anion. 1$^1\Pi_g^3/2$, 2$^2\Sigma_g^+, 1/2$, 3$^2\Sigma_u^-, 3/2$, 4$^1\Pi_g^3/2$, 5$^2\Sigma_g^-, 1/2$, 6$^2\Sigma_u^-, 1/2$, 7$^2\Sigma_u^-, 3/2$, 8$^2\Pi_g^3/2$, 9$^2\Sigma_g^+, 1/2$, 10$^2\Pi_g^3/2$, 11$^1\Delta_u$. 156.73 (3$^3P_g^3P_g$ of O) and 221.91 (3$^3P_g^3P_g$ of O), and 180.50 cm$^{-1}$ (2$^3P_g^2P_g$ of O$^-$), in excellent agreement with the observed values of 158.27 and 226.98 [75], and 177.08 cm$^{-1}$ [76], respectively. This indicates that the present calculations could describe the dissociation properties of O$_2^-$ anion properly.

Among the 54 $\Omega$ states of O$_2^-$ anion, 37 are bound states. Based on the PECs obtained, their spectroscopic
constants are fitted and separately shown in Tables 8–10 along with the main components of Λ–S states near the equilibrium positions. To facilitate this discussion, the spectroscopic constants of the 18 Ω states generated from the X2Πg, A2Πu, 14Πu, 23Πg, 24Πu, and 141Πg Λ–S states are listed in Table 8. Those of the 11 Ω states originated from the 8 Σ Λ–S states are summarised in Table 9. And those of the 8 Ω states produced from the 14Δg, 12Δu, and 12Δg states are tabulated in Table 10.

Now, we discuss the effect on the spectroscopic constants by the spin–orbit coupling. As can be seen from Table 8, with the spin–orbit coupling included, each 2 Π splits into two components, 2Π1/2 and 2Π3/2. Although the compositions of the two components of the X2Πg state are pure at the equilibrium internuclear separation, the energy of the X2Πg, 3/2 component decreases by 77.26 cm⁻¹ and of the X2Πg, 1/2 component increases by 77.03 cm⁻¹ when compare with that of the Λ–S state. The spin–orbit splitting between the two spin components is 154.29 cm⁻¹ at the equilibrium internuclear separation, which compares very well with the experimental value of 161±4 cm⁻¹ [33] and 151±11 [34] reported previously.

Table 8. Spectroscopic constants of 18 Ω states generated from the six Π Λ–S states of O₂⁻ anion.

| Ω | Tₜ/cm⁻¹ | Rₑ/nm | ωₑ/cm⁻¹ | Δₑ/eV | Λ–S state compositions near Rₑ (%) |
|---|---------|-------|---------|-------|-----------------------------------|
| X2Π 3/2 | 0.0 | 0.13527 | 1123.34 | 4.2663 | X2Π (100.00) |
| X2Π 1/2 | 154.29 | 0.13528 | 1093.64 | 4.2485 | X2Π (100.00) |
| A2Π 1/2 | 25.725.94 | 0.17850 | 550.50 | 0.9681 | A2Π (99.88), 12Δu (0.12) |
| A2Π 3/2 | 25.844.45 | 0.17848 | 551.40 | 0.9754 | A2Π (99.88), 12Δu (0.12) |
| 14Π 1/2 | 31.224.44 | 0.23880 | 240.87 | 0.3844 | 14Π (100.00) |
| 14Π 3/2 | 31.273.82 | 0.23876 | 240.29 | 0.3820 | 14Π (99.98), 14Δg (0.02) |
| 14Π 1/2 | 31.322.32 | 0.23835 | 237.18 | 0.3808 | 14Π (99.98), 14Δg (0.02) |
| 14Π 3/2 | 31.371.48 | 0.23842 | 237.23 | 0.3799 | 14Π (99.98), 14Δg (0.02) |
| 23Π 1/2 | 33.860.99 | 0.40094 | 188.54 | 0.0797 | 23Π (90.87), 22Σg (7.91), 14Π (1.22) |
| 23Π 3/2 | 33.892.59 | 0.40120 | 184.12 | 0.0870 | 23Π (89.09), 22Σg (8.95), 14Π (1.96) |
| 24Π 1/2 | 33.933.85 | 0.47647 | 151.63 | 0.0442 | 24Π (98.90), 14Δg (0.72), 14Σg (0.39) |
| 24Π 3/2 | 33.946.63 | 0.47864 | 150.73 | 0.0452 | 24Π (98.60), 14Δg (0.87), 14Σg (0.53) |
| 141Π 1/2 | 33.967.94 | 0.47739 | 153.22 | 0.0438 | 24Π (100.00) |
| 141Π 3/2 | 34.000.35 | 0.47687 | 149.84 | 0.0445 | 24Π (98.60), 14Δg (0.99), 14Σg (0.42) |
| 141Π 1/2 | 34.153.98 | 0.45730 | 52.434 | 0.0135 | 14Π (99.96), 23Π (1.00), 14Δg (0.03) |
| 141Π 3/2 | 34.217.41 | 0.45800 | 50.497 | 0.0136 | 14Π (97.99), 23Π (2.01) |
| 141Π 1/2 | 34.255.16 | 0.45843 | 50.873 | 0.0134 | 14Π (76.66), 23Π (17.75), 14Σg (6.59) |
| 141Π 3/2 | 34.267.45 | 0.45862 | 52.358 | 0.0135 | 14Π (87.69), 22Σg (11.05), 23Π (1.59) |

Table 9. Spectroscopic constants of 11 Ω states generated from the eight Σ Λ–S states of O₂⁻ anion.

| Ω | Tₜ/cm⁻¹ | Rₑ/nm | ωₑ/cm⁻¹ | Δₑ/eV | Λ–S state compositions near Rₑ (%) |
|---|---------|-------|---------|-------|-----------------------------------|
| a4Σ 1/2 | 973.71 | 0.11940 | 1612.29 | 1.8779 | 14Σ (99.99), 14Σ (0.01) |
| a4Σ 1/2 | 983.66 | 0.18316 | 546.14 | 1.6963 | 14Σ (100.00) |
| a4Σ 1/2 | 978.75 | 0.11941 | 1612.42 | 1.8790 | 14Σ (100.00) |
| a4Σ 1/2 | 1893.66 | 0.18315 | 546.62 | 1.6961 | 14Σ (99.99) |
| a4Σ 1/2 | 25396.95 | 0.21342 | 391.69 | 1.3388 | 14Σ (98.80), 14Σ (0.20) |
| a4Σ 1/2 | 25401.55 | 0.21342 | 391.75 | 1.4066 | 14Σ (100.00) |
| a4Σ 1/2 | 27117.63 | 0.20267 | 366.68 | 0.9170 | 14Σ (99.99) |
| a4Σ 1/2 | 27222.20 | 0.21614 | 359.02 | 0.8040 | 14Σ (99.98), 14Σ (0.01) |
| a4Σ 1/2 | 29862.16 | 0.19123 | 446.97 | 0.4100 | 14Σ (99.98), 14Σ (0.02) |
| a4Σ 1/2 | 33861.86 | 0.27839 | 118.16 | 0.0378 | 14Σ (100.00) |
| a4Σ 1/2 | 33861.84 | 0.27841 | 118.16 | 0.0384 | 14Σ (100.00) |
| a4Σ 1/2 | 33922.97 | 0.44686 | 151.89 | 0.0223 | 22Σg (99.98), 14Δg (0.01) |
| a4Σ 1/2 | 36889.73 | 0.17577 | 525.43 | 0.0108 | 14Σ (100.00) |
| a4Σ 1/2 | 34796.12 | 0.63481 | 9.12 | 0.0075 | 14Σ (99.97), 14Δg (0.02) |
from photoelectron spectroscopy and those of 160±16 [26], 160±8 [31], and 149±8 cm⁻¹ [32] from electron scattering measurements.

When comparing with the \(X^2\Pi_g\), the equilibrium bond lengths for two components elongate about 0.00070 nm, the \(\omega_e\) of \(X^2\Pi_g\) increases 1.12 cm⁻¹, while, of \(X^2\Pi_g\) decreases 28.57 cm⁻¹. And the \(D_c\) values for two components reduce by 81.46 and 225.03 cm⁻¹, respectively. No experimental data were reported for both \(\Omega\) components except for the spin–orbit coupling constant of the \(X^2\Pi_g\) state [26,31–34].

As for the \(A^2\Pi_u\) state, its spin–orbit coupling constant is predicted to be 118.51 cm⁻¹, whereas the \(R_c\), \(\omega_e\) and \(D_c\) separation between the two components is only 0.00002 nm, 0.90 and 58.87 cm⁻¹. The two components of the \(2^2\Pi_g\) state have an energy splitting of 31.60 cm⁻¹ at the equilibrium internuclear separation. The \(R_c\) of both components are slightly elongated and the \(\omega_e\) decrease not more than 4.68 cm⁻¹ compare with the corresponding \(\Lambda–S\) state. Different from \(X^2\Pi_g\) state, the two components of the \(A^2\Pi_u\) and \(2^2\Pi_g\) states split in a regular order. The dominant \(\Lambda–S\) compositions of \(A^2\Pi_u\) and \(1^2\Delta_u\) states mix with each other slightly near their equilibrium internuclear separation.

As we know, each \(^4\Pi\) splits into four components, \(4\Pi_{1/2}, 4\Pi_{3/2}\) and \(4\Pi_{5/2}\). Thus, twelve \(\Omega\) states generate from \(1^4\Pi_u, 2^4\Pi_u\), and \(3^4\Pi_g\) states. Among them, four components of \(1^4\Pi_u\) are separated within 147.04 cm⁻¹ in a regular order. The \(R_c\) of four \(\Omega\) components shorten by 0.00005–0.00050 nm, and the \(\omega_e\) decrease several cm⁻¹ compared with the \(1^4\Pi_u\) state. As for the \(2^4\Pi_u\) state, the energy separations of the \(2^4\Pi_u\) are 12.78, 21.31 and 32.41 cm⁻¹, respectively. The overall splitting among the four components of the second \(2^4\Pi_u\) is only 66.50 cm⁻¹ at the equilibrium geometry. As with the \(1^4\Pi_u\) state, the four components of \(2^4\Pi_u\) are predicted to be in a regular order. The \(R_c\), \(\omega_e\) and \(D_c\) of four \(\Omega\) components of \(2^4\Pi_u\) separately change in the range of 0.00034–0.00159 nm, of 0.37–2.12 and of 0.80–8.87 cm⁻¹ compared with that of the corresponding \(\Lambda–S\) state. For the \(1^4\Pi_g\) state, the calculated spin–orbit coupling constant of 113.47 cm⁻¹ is between that of \(1^2\Pi_u\) and \(2^4\Pi_u\). The equilibrium bond lengths of the four components for the \(1^4\Pi_g\) state also shorten due to the contributions of \(2^2\Pi_g\) and \(3^2\Sigma_g^–\) states. Differently from \(1^4\Pi_u\) and \(2^4\Pi_u\) states, the \(1^4\Pi_g\) state splits into four components with \(\Omega = 5/2\), lying the lowest. The order of transition energy to the ground state is \(1^4\Pi_g, 5/2 < 1^4\Pi_g, 3/2 < 1^4\Pi_g, 1/2 < 1^4\Pi_g, –1/2\). The \(1^4\Pi_g, 5/2\) and \(1^4\Pi_g, 3/2\) components are separated from one another by the intervening components of the second well of the \(1^2\Sigma_g^+, 1/2\) component, and \(1^4\Pi_g, 3/2\) and \(1^4\Pi_g, 1/2\) are separated by the \(1^2\Delta_g, 5/2\) component as well.

| \(T_c/cm^{-1}\) | \(R_c/nm\) | \(\omega_e/cm^{-1}\) | \(D_e/eV\) | Dominant \(\Lambda–S\) state compositions near \(R_c\) (%) |
|----------------|--------------|----------------|-----------|----------------------------------|
| \(1^4\Delta_g, 7/2\) | 25,013.30 | 0.21253 | 397.39 | 1.1184 | \(1^4\Delta_g\) (100.00) |
| \(1^4\Delta_g, 5/2\) | 25,091.22 | 0.21256 | 397.31 | 1.1146 | \(1^4\Delta_g\) (100.00) |
| \(1^4\Delta_g, 3/2\) | 25,211.93 | 0.21253 | 395.57 | 1.1133 | \(1^4\Delta_g\) (100.00) |
| \(1^4\Delta_g, 1/2\) | 25,290.28 | 0.21259 | 393.75 | 1.1115 | \(1^4\Delta_g\) (100.00) |
| \(2^4\Delta_u, 7/2\) | 25,820.31 | 0.19476 | 426.27 | 1.0660 | \(2^4\Delta_u\) (99.50), \(2^4\Delta_u\) (0.05) |
| \(2^4\Delta_u, 5/2\) | 25,894.06 | 0.19431 | 423.62 | 1.0613 | \(2^4\Delta_u\) (99.83), \(2^4\Delta_u\) (0.16) |
| \(2^4\Delta_u, 3/2\) | 34,218.95 | 0.66575 | 13.008 | 0.0066 | \(2^4\Delta_u\) (99.96), \(1^2\Sigma_g^+, 3/2\) (0.04) |
| \(2^4\Delta_u, 1/2\) | 34,356.34 | 0.66488 | 9.5474 | 0.0108 | \(2^4\Delta_u\) (99.98), \(1^2\Sigma_g^+, 1/2\) (0.02) |

Table 10. Spectroscopic constants of \(8 \Omega\) states generated from the three \(\Delta \Lambda–S\) states of \(O_2^-\) anion.

No splitting appears with the spin–orbit interaction. Their PECs and spectroscopic constants are almost the same as those of the corresponding \(\Lambda–S\) states except for the \(T_c\). Take the \(3^2\Sigma_g^+\) state for example, the calculated \(T_c\), \(R_c\), \(\omega_e\) and \(D_c\) values of the \(3^2\Sigma_g^+, 1/2\) state are 27622.20 cm⁻¹, 0.21614 nm, 359.02 cm⁻¹, and 0.8040 eV, which are 81.86 cm⁻¹, 0.0001 nm, 0.09 and 37 cm⁻¹ different from the \(1^2\Sigma_g^+, 1/2\) state, respectively. The same situation is observed for the other \(3^2\Sigma_g^+\) states. On a whole, the effects of spin–orbit coupling on \(R_c\), \(\omega_e\) and \(D_c\) are rather small for all five \(2^2\Sigma\) states.

Each \(4^2\Sigma\) state splits into two components, \(4^2\Sigma_{1/2}\) and \(4^2\Sigma_{3/2}\). The dominant \(\Lambda–S\) state composition remains almost pure at the equilibrium internuclear separations for each \(\Omega\) state of the \(1^4\Sigma_g^+, 1^4\Sigma_g^–, 1^4\Sigma_u^–\) states. Therefore, the spin–orbit coupling makes small change on their spectroscopic constants. With the spin–orbit coupling included, the energy separation of two components of each \(4^2\Sigma\) state is not more than 4.6 cm⁻¹; the \(R_c\) of two \(\Omega\) components of each \(4^2\Sigma\) state is almost the same as those of the corresponding \(\Lambda–S\) state; the change of \(\omega_e\) of two \(\Omega\) components of each \(4^2\Sigma\) state is less than 1 cm⁻¹ compared with the corresponding \(\Lambda–S\) state; and the largest
change of $D_e$ relate to the $\Lambda$–$S$ state is only 28.23 cm$^{-1}$ of the $1^4\Sigma_g^+$ state is in an inverted order among the three $4\Sigma$ bound states when the spin–orbit coupling effect is included.

The spectroscopic constants of the 8 $\Omega$ states produced from three $\Delta$ states $\Lambda$–$S$ are presented in Table 10. Four components of $1^4\Delta_g$ are separated within 277.75 cm$^{-1}$ with $1^4\Delta_g,1/2$ lying the lowest. The spin components of the $1^2\Delta_g$ and $1^2\Delta_u$ states split in an inverted order with a spin–orbit splitting of 73.75 and 137.39 cm$^{-1}$, respectively. Among the eight $\Omega$ states, the largest deviations of $D_e$, $R_e$ and $\omega_e$ from the corresponding $\Lambda$–$S$ state are observed to be 20.97 cm$^{-1}$, 0.00303 nm and 3.75 cm$^{-1}$ for the $1^2\Delta_g,3/2$ state, respectively. The main reason may be that the potential well of the $1^2\Delta_g$ state is rather shallow, small spin–orbit coupling effect can bring about obvious PEC change. As expected, the spectroscopic constants of the $1^4\Delta_g$, $1^2\Delta_g$ and $1^2\Delta_u$ states change quite tiny because of the almost pure $\Lambda$–$S$ composition contribution in the spin–orbit coupling calculations except for the $T_e$ values.

From the analyses above, although the spin–orbit coupling effect lowers the energy of the system, the spin–orbit coupling contribution causes no significant change in the shape of the PECs. Therefore, no obvious impact appears on most of the spectroscopic constants for $\Omega$ states except for the $T_e$. However, now we have a rudimentary knowledge on SOC of the superoxide anion species which is the necessary information to explain spin flip in O$_2$ activation [4–6].

Since no experimental spectroscopic constants of the $\Omega$ states and low-lying excited $\Lambda$–$S$ states of O$_2^-$ anion can be found in the literature to our knowledge, therefore, we cannot make direct comparison between theory and experiment. However, a very nice agreement is found between the present predictions and the available experimental ones for the ground state and $A^2\Pi_g$ states. Thus, we believe that, with reasons, the PECs and spectroscopic constants of 37 $\Omega$ and 16 $\Lambda$–$S$ excited bound states should be reliable.

4. Conclusions

The entire 54 $\Omega$ states derived from the 24 $\Lambda$–$S$ states of the first dissociation limit of O$_2^-$ anion are studied using the CASSCF approach followed by the icMRCI method with the Davidson correction. Basis sets extrapolation technique is applied in all calculations to acquire the CBS limit energy. Core–valence correlation and scalar relativistic corrections are taken into consideration to correct the molecular energy. The spin–orbit coupling effect is extensively investigated employing the Breit–Pauli Hamiltonian.

With these calculations, we find that, (1) seventeen states of the 24 $\Lambda$–$S$ states of O$_2^-$ anion are bound states within 37000 cm$^{-1}$ and six of the 16 bound excited $\Lambda$–$S$ states are predicted for the first time; (2) the $a^4\Sigma_u^+$ state is the first excited–state. It possesses two potential wells on its PEC and the positions of both wells are ascertained. $1^2\Sigma_g^+$ state has a double well as well as the $a^4\Sigma_u^+$ state; (3) $A^2\Pi_u$ is the first doublet excited–state, which is 16046.23 cm$^{-1}$ higher than the $a^4\Sigma_u^-$ state. The equilibrium bond length of the $A^2\Pi_u$ state is consistently larger with the value of the other calculations than the available experimental values; (4) some potential wells are rather shallow and can only support several vibrational states, such as the $2^2\Sigma_g^-,1^4\Sigma_g^-,1^4\Pi_g,2^2\Pi_u$, and both wells of $1^2\Sigma_g^+$ states. Therefore, the spectra of them would be difficult to be observed in experiments; (5) the spin–orbit splitting of the ground state of the anion is estimated to be 154.29 cm$^{-1}$. And the overall largest spin–orbit splitting is predicted to be 276.98 cm$^{-1}$ for the $1^4\Delta_g$ state; (6) the spin–orbit coupling effect is not significantly large. Hence, most of the spectroscopic constants do not change greatly except for the $T_e$. Seven bound states ($\chi^2\Pi_g,1^2\Delta_g,1^4\Delta_g,1^4\Pi_g,1^4\Delta_u,1^4\Sigma_g^+$, and $1^2\Delta_u$) are in inverted order with the spin–orbit coupling included.

These natures of the PECs and spectroscopic properties of the low-lying excited–state of O$_2^-$ anion provide useful information for the future laboratory research.

Disclosure statement

No potential conflict of interest was reported by the authors.

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