Accurate *ab initio*-based analytical potential energy function for $S_2(\tilde{a}^1\Delta_g)$ via extrapolation to the complete basis set limit*

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The potential energy curves (PECs) of the first electronic excited state of $S_2(\tilde{a}^1\Delta_g)$ are calculated employing a multi-reference configuration interaction method with the Davidson correction in combination with a series of correlation-consistent basis sets from Dunning: aug-cc-pVXZ (X = T, Q, 5, 6). In order to obtain PECs with high accuracy, PECs calculated with aug-cc-pV(Q, 5)Z basis sets are extrapolated to the complete basis set limit. The resulting PECs are then fitted to the analytical potential energy function (APEF) using the extended Hartree–Fock approximate correlation energy method. By utilizing the fitted APEF, accurate and reliable spectroscopic parameters are obtained, which are consistent with both experimental and theoretical results. By solving the Schrödinger equation numerically with the APEFs obtained at the AV6Z and the extrapolated AV(Q, 5)Z level of theory, we calculate the complete set of vibrational levels, classical turning points, inertial rotation and centrifugal distortion constants.

Keywords: multi-reference configuration interaction method (MRCI), analytical potential energy functions, vibrational levels, spectroscopic parameters

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1. Introduction

It has long been recognized that reduced sulfur-bearing species play an important role in the Earth's atmosphere, in biochemistry, and in combustion chemistry.[1,2] Amongst the various reduced sulfur-bearing species, thiosulfeno radical HS_2,[3,4] hydrogen disulfide H_2S_2,[5] thiozone S_3,[6,7] etc. have aroused considerable interest. Diatomic sulfur S_2, one component of these species, has also been investigated by many groups. Graham[8] was the first to observe the transition of the S_2 $B^3\Sigma_u^- – X^3\Sigma_g^-$ state, and his work was followed by many attempts to interpret this heavily perturbed band system. The ground state $X^3\Sigma_g^-$ of S_2 was well characterized by a combination of electron paramagnetic resonance and microwaves.[9,10] Employing a combination of cavity ring-down spectroscopy and model calculations, Wheeler *et al.* investigated the predissociation of the $B^3\Sigma_u^-$ state[11] and the *B*–*X* band system of S_2 over the range of excited state vibrational levels $10 < v < 22$.[12] Some of the accurate spectroscopic parameters and molecular constants reported in the literature prior to 1979 were summarized by Huber and Herzberg.[13]

Out of a vast body of theoretical work, by carrying out the *ab initio* calculations using self-consistent field (SCF) and configuration interaction (CI) with double zeta quality augmented with polarization functions, Swope *et al.*[14] studied the spectroscopic properties of thirteen low-lying electronic states of S_2. Large scale CI calculations were carried out by Theodorakopoulos and Peyerimhoff[15] to investigate the properties of the $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ states of S_2. Employing the B3LYP functional density theory, Mawhinney and Goddard[16] determined the spectroscopic parameters of these states. Denis[17] calculated the equilibrium geometry and the harmonic vibrational frequency of ground-state S_2 using the coupled cluster theory. Utilizing the global potential energy surface (PES) of $HS_2(X\ A'')$ state, Song *et al.*[3] obtained more accurate spectroscopic parameters of ground-state S_2. Most recently, Xing *et al.*[18] calculated the potential energy curves (PECs) of the ground and some excited states. It is known that $S_2(\tilde{a}^1\Delta_g)$ is involved in many reaction processes of sulfur-containing species, such as $S(^1D) + S_2(^1\Delta_g)$,[9] $H_2S + S(^3P) \rightarrow H_2 + S_2(^1\Delta_g)$,[5] $H(^2S) + S_2(\tilde{a}^1\Delta_g) \rightarrow S(^3P) + SH(\tilde{X}^2\Pi)$,[19] etc. However, less effort has been put into accurately determining the analytical potential energy function (APEF) of $S_2(\tilde{a}^1\Delta_g)$. So we are motivated to carry out more accurate theoretical investigations of $S_2(\tilde{a}^1\Delta_g)$. It could serve as a reference for future studies on the above reactions and as a building block of the global PES for such molecular systems as HS_2, H_2S_2, S_3, etc.

In the present work, by utilizing the multi-reference configuration interaction including the Davidson correction (MRCI(Q)) method,[20] the PECs of the $S_2(\tilde{a}^1\Delta_g)$ radical are calculated with a series of correlation-consistent basis sets from Dunning *et al.*,[21,22] i.e., aug-cc-pVXZ (X = T, Q, 5, 6), which are hereinafter denoted as AVXZ. The uniform singlet- and triplet-pair extrapolation (USTE) protocol[23] is employed to extrapolate the PECs calculated at AV(Q, 5)Z to the com-

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plete basis set (CBS) limit. All the PECs are then fitted to APEFs by using the extended Hartree–Fock approximate correlation energy method (EHFACE).[24] By numerically solving the radial Schrödinger equation of the nuclear motion, the complete vibrational levels, classical turning points, inertial rotation and centrifugal distortion constants are calculated when the rotational quantum number J equals zero. The present results provide more accurate and complete spectroscopic information about $S_2(\tilde{a}^1\Delta_g)$.

The paper is organized as follows. Section 2 describes the theoretical methods, including *ab initio* calculations, the procedure utilized to extrapolate the calculated energies and the APEF formalism. The results and discussion are presented in Section 3. While Section 4 gives our concluding remarks.

2. Theoretical methods

2.1. *Ab initio* calculations

All electronic structure calculations have been carried out at the MRCI(Q) level[20] using the full valence complete-active-space self-consistent field (CASSCF)[25] wave function as the reference, which has recently been applied to many diatomic molecules.[26–28] The AVXZ (X = T, Q, 5, 6) basis sets of Dunning[21,22] have been employed, and the calculations are carried out employing the MOLPRO 2012 package.[29] In the calculation, C_{2v} point group symmetry is adopted, which holds four irreducible representations, namely, A1, B1, B2, and A2. For $S_2(\tilde{a}^1\Delta_g)$, four a1, two b1, and two b2 symmetry molecular orbitals (MOs) are determined as the active space, corresponding to the 3s3p shells of the sulfur atom in the CASSCF and MRCI(Q) calculation. This procedure involves 12 correlated electrons in eight active orbitals (4a1+ 2b1+2b2). For each basis set, the calculations of $S_2(\tilde{a}^1\Delta_g)$ PECs are performed for the internuclear separation ranging from $1.2a_0$ to $20a_0$. Note that all the *ab initio* energies calculated at AVXZ (X = T, Q, 5, 6) basis sets are gathered in Table 1 of the Supplementary Material (SM). The core effects have been neglected by closing the core orbitals in the CASSCF and not correlating them in the MRCI(Q) calculation. A major reason for adopting the frozen core approximation lies in the fact that the raw *ab initio* energies calculated with relatively modest cost (AV(Q, 5)Z) are subsequently extrapolated to the CBS limit, denoted as CBS/AV(Q, 5)Z. The extrapolation is carried out via extrapolation of the electron correlation energy to the CBS limit plus extrapolation to the CBS limit of the CASSCF energy.

2.2. Extrapolation to the CBS limit

The MRCI(Q) electronic energy can be treated in split form, which is written as[23,30]

$$E_X = E_X^{\mathrm{CAS}} + E_X^{\mathrm{dc}}, \tag{1}$$

where the subscript X indicates that the energy has been calculated in the AVXZ basis set, while the superscripts CAS and dc stand for the complete-active space and the dynamical correlation energies, respectively. The X = Q, 5 are adopted in the present work and denoted as USTE(Q, 5).

The CAS energies, which are uncorrelated in the sense of lacking dynamical correlation, are extrapolated to the CBS limit by adopting the two-point extrapolation protocol proposed by Karton and Martin[31]

$$E_X^{\mathrm{CAS}} = E_\infty^{\mathrm{CAS}} + B/X^\alpha, \tag{2}$$

where $\alpha = 5.34$ is an effective decay exponent and E_∞^{CAS} is the energy when $X \to \infty$.

The USTE protocol[23,32] has been successfully applied to extrapolate the dc energies in MRCI(Q) calculations, which is written as

$$E_X^{\mathrm{dc}} = E_\infty^{\mathrm{dc}} + \frac{A_3}{(X+\alpha)^3} + \frac{A_5}{(X+\alpha)^5}, \tag{3}$$

where A_5 is determined by the auxiliary relation

$$A_5 = A_5(0) + cA_3^{5/4}. \tag{4}$$

Here $A_5(0) = 0.0037685459$, $c = -1.17847713$, and $\alpha = -3/8$ are the universal-type parameters.[23,29] Equation (3) is thus transformed into an (E_∞, A_3) two-parameter rule, which is actually used for the practical procedure of extrapolation. The USTE extrapolation scheme has been shown to yield more accurate energies even when the extrapolation is carried out with the cheapest AV(D, T)Z pair.[32] Thus, it is utilized here to extrapolate the dc energies to the CBS limit for the title system.

2.3. APEF of $S_2(\tilde{a}^1\Delta_g)$

The diatomic PECs of $S_2(\tilde{a}^1\Delta_g)$, which show the correct behavior at both the asymptotic limits $R \to 0$ and $R \to \infty$, have been modeled using the EHFACE model,[24] which takes the following form:

$$V = V_{\mathrm{EHF}}(R) + V_{\mathrm{dc}}(R), \tag{5}$$

where $V_{\mathrm{EHF}}(R)$ and $V_{\mathrm{dc}}(R)$ denote the extended Hartree–Fock (EHF) and the dynamical correlation parts of the potential energy. The latter term is modeled by

$$V_{\mathrm{dc}}(R) = -\sum_{n=6,8,10} C_n \chi_n(R) R^{-n}, \tag{6}$$

with the damping functions for the dispersion coefficients assuming the form

$$\chi_n(R) = \left[1 - \exp\left(-A_n R/\rho - B_n R^2/\rho^2\right)\right]^n, \tag{7}$$

where A_n and B_n are auxiliary functions and defined as

$$A_n = \alpha_0 n^{-\alpha_1}, \tag{8}$$

$$B_n = \beta_0 \exp(-\beta_1 n), \tag{9}$$

with α_0, β_0, α_1, and β_1 being universal dimensionless parameters for all isotropic interactions: $\alpha_0 = 16.36606$, $\beta_0 = 17.19338$, $\alpha_1 = 0.70172$, $\beta_1 = 0.09574$. Moreover, $\rho/a_0 = 5.5 + 1.25R_0$, $R_0 = 2\left(\langle r_A^2\rangle^{1/2} + \langle r_B^2\rangle^{1/2}\right)$ is the LeRoy parameter,[33] $\langle r_A^2\rangle$ and $\langle r_B^2\rangle$ are the expectation values of squared radii for the outermost electron in atoms A and B, respectively.

The EHF-type energy term in Eq. (5) is written as

$$V_{\rm EHF}(R) = -\frac{D}{R}\left(1 + \sum_{i=1}^{n} a_i r^i\right)\exp(\gamma r), \tag{10}$$

where $\gamma = \gamma_0[1 + \gamma_1 \tanh(\gamma_2 r)]$, with $r = R - R_e$, is the displacement from the equilibrium diatomic geometry; D, $a_i\,(i = 1,\ldots,n)$, and $\gamma_i\,(i = 0,1,2)$ are adjustable parameters to be obtained from a least-square fitting procedure.

3. Results and discussion

3.1. The potential energy function

We compare in Fig. 1 the *ab initio* PECs of $S_2(\tilde{a}^1\Delta_g)$ calculated at AV6Z and extrapolated to the CBS limit using AV(Q, 5)Z results. It can be seen that both PECs show a smooth and converged behavior. The difference between these two PECs is small, with the well depths of the global minimum differing only $\sim 0.001E_h$. The AV6Z is considered an expensive basis set, with higher computational cost than AVQZ and AV5Z. With the extrapolation using the USTE(Q, 5) scheme, the accurate CBS PEC can be obtained at a much lower computational cost. Note that this extrapolation procedure was also successfully employed by Liu *et al.*[34] recently to obtain an accurate PEC of $CO(X^1\Sigma^+)$, with results comparing favorably with the experimental ones.

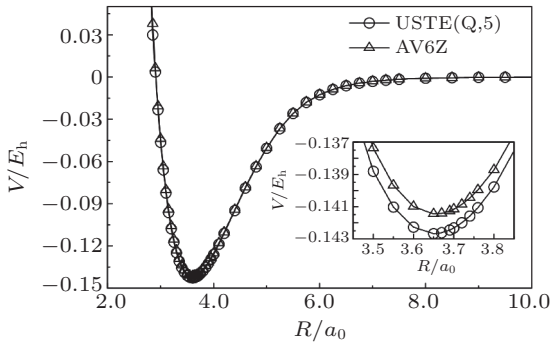


Fig. 1. Comparison of the PECs of $S_2(\tilde{a}^1\Delta_g)$ calculated at AV6Z and extrapolated to the CBS limit using AV(Q, 5)Z results.

The EHFACE model is then employed to obtain the APEFs for $S_2(\tilde{a}^1\Delta_g)$ by least-square fitting the PECs calculated using AVXZ (X = T, Q, 5, 6). The APEF is also obtained by fitting the PECs extrapolated to the CBS limit using the result calculated from AV(Q, 5)Z basis sets, hereinafter denoted as CBS/USTE(Q, 5) APEF. The parameters a_i, D, R_e, and γ_i are obtained from the least-square fitting procedure. We have tried $n = 3$ to $n = 9$ for the total numbers of coefficients a_i with the purpose of getting a satisfactory result. By comparing the spectroscopic constants with the experimental and other theoretical data, the best results are obtained with $n = 7$. All parameters of APEFs for $S_2(\tilde{a}^1\Delta_g)$ in Eqs. (6) and (10) are collected in Table 1, while the *ab initio* and the fitted CBS/USTE(Q, 5) PECs are displayed in Fig. 2. As can be seen, the modeled potential accurately mimics the *ab initio* energies, with the maximum error being smaller than 0.05 kcal/mol.

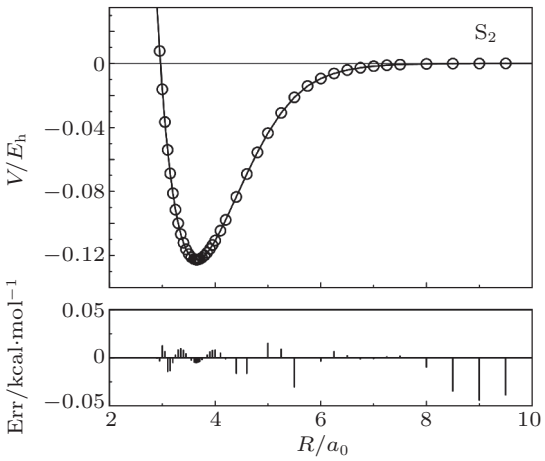


Fig. 2. The extrapolated CBS/USTE(Q, 5) PECs for $S_2(\tilde{a}^1\Delta_g)$. The circles indicate the *ab initio* energies, while the line is from the fitted APEF. The differences between them are charted in the bottom panel.

Table 1. Fitted parameters of $S_2(\tilde{a}^1\Delta_g)$ APEFs in Eqs. (6) and (10).

Basis set	AVTZ	AVQZ	AV5Z	AV6Z	USTE(Q, 5)
R_e/a_0	3.65054	3.62319	3.60897	3.60484	3.60071
D/E_h	0.39440	0.41949	0.43231	0.43639	0.44014
a_1/a_0^{-1}	1.23239	1.70342	1.38442	1.52880	1.64029
a_2/a_0^{-2}	–0.11708	0.46088	0.03153	0.21175	0.40683
a_3/a_0^{-3}	0.58250	0.45736	0.43332	0.40330	0.46036
a_4/a_0^{-4}	–0.17925	0.05444	–0.08250	–0.01765	0.03532
a_5/a_0^{-5}	0.16671	0.03317	0.08731	0.058693	0.05489
a_6/a_0^{-6}	–0.09951	–0.04654	–0.06044	–0.05487	–0.05496
a_7/a_0^{-7}	0.027782	0.01826	0.01797	0.01835	0.02016
γ_0/a_0^{-1}	0.82511	1.30369	0.98878	1.13506	1.24722
γ_1/a_0^{-1}	4.15409	1.66477	4.64026	4.08810	1.90732
γ_2/a_0^{-1}	0.14044	0.15422	0.08179	0.07346	0.14832
$C_6/E_h a_0^{-6}$	120.2491	117.8233	115.9064	114.6994	114.5670
$C_8/E_h a_0^{-8}$	3581.574	3509.326	3452.232	3416.279	3412.335
$C_{10}/E_h a_0^{-10}$	139745.4	136926.4	134698.7	133295.9	133142.0
$\Delta E_{\rm RMSD}/\mathrm{kal\cdot mol^{-1}}$	0.02201	0.02079	0.01860	0.018300	0.01764

To evaluate the fitting quality of the fitted PECs, we calculate the root-mean square derivation ($\Delta E_{\rm RMSD}$) using the following equation:

$$\Delta E_{\rm RMSD} = \sqrt{\frac{1}{N}\left\{\sum_{i=1}^{N}[V_{\rm APEF}(i) - V_{\rm ab}(i)]^2\right\}}, \tag{11}$$

where $V_{\rm APEF}(i)$ and $V_{\rm ab}(i)$ are the i-th energies from fitting and from the *ab initio* calculation, respectively; N

is the number of points employed in the fitting procedure ($N = 79$). The values of ΔE_{RMSD} are also gathered in Table 1. This table shows the ΔE_{RMSD} for APEFs obtained from fitting the *ab initio* PECs of MRCI(Q)/AVTZ, MRCI(Q)/AVQZ, MRCI(Q)/AV5Z, MRCI(Q)/AV6Z, and the extrapolated CBS/USTE(Q, 5) are 0.02201 kcal/mol, 0.2079 kcal/mol, 0.01860 kcal/mol, 0.01830 kcal/mol, and 0.01764 kcal/mol, respectively. The ΔE_{RMSD} shows a decreasing trend as the size of the basis set increases, and the CBS/USTE(Q, 5) APEF gives the smallest RMSD, which shows that the fitting process is of a high quality.

3.2. Spectroscopic constants

Based on the APEFs obtained by fitting the raw MRCI(Q)/AVTZ, MRCI(Q)/AVQZ, MRCI(Q)/AV5Z, MRCI(Q)/AV6Z, and the extrapolated CBS/USTE(Q, 5) PECs, we calculate the spectroscopic constants of $S_2(\tilde{a}^1\Delta_g)$. Some other theoretical and experimental studies have published spectroscopic constants of $S_2(\tilde{a}^1\Delta_g)$. Among them, Swope *et al.*[14] calculated R_e, ω_e, B_e, and α_e from the SCF and CI calculations. Compared with the experimental value, their vibrational frequency is too large. By carrying out the MRCI(Q) level of theory calculation with a series of Dunning's basis set, Peterson *et al.*[6] calculated R_e, ω_e and $\omega_e\chi_e$. Xing *et al.*[18] calculated the PECs of the ground state and some excited states, and gave more complete spectroscopic constants of $S_2(\tilde{a}^1\Delta_g)$. The values of D_e, R_e, ω_e, B_e, α_e, and $\omega_e\chi_e$ are collected in Table 2 together with the other theoretical and experimental data[13] for convenient comparison.[6,14,18] As we can see from the table, the dissociation energy increases monotonically as the basis set increases from AVTZ to AV6Z, and the largest value is obtained at CBS/USTE(Q, 5) APEF, differing $0.0012E_h$ from that at the AV6Z APEF. The equilibrium bond length is calculated from CBS/USTE(Q, 5) APEF to be $3.6007a_0$, which is only $0.0127a_0$ longer than the experimental value,[13] and $0.0035a_0$ longer than the most recent value obtained by Xing *et al.*,[18] showing a high accuracy. The vibrational frequency is calculated to be 700.81 cm^{-1}, which differs from the experimental[13] and the theoretical[18] values by 1.54 $\mathrm{cm}^{-1}$and 1.13 cm^{-1}, respectively. The spectroscopic constant B_e from CBS/USTE(Q, 5) APEF is smaller than that of Ref. [18], which must be due to the fact that B_e is inversely proportional to R_e. However, the spectroscopic constants α_e and $\omega_e\chi_e$ can be affected by B_e, ω_e, and the force constants (quadratic f_2, cubic f_3, and quartic f_4). All of these parameters can cause the values of $\alpha_e$and $\omega_e\chi_e$ to be larger than those of Refs. [6] and [18]. Comparing the results from the present CBS/USTE (Q, 5) APEF with those of AV6Z, the deviations of D_e, R_e, ω_e, B_e, α_e, and $\omega_e\chi_e$ are 0.852%, 0.11%, 0.23%, 0.24%, 0.52%, and 0.38%, respectively. The spin–orbital coupling effect on the diatomic PEC and nonadiabatic reaction dynamics were investigated and reported in Refs. [35] and [36], as it is known that the spin–orbital coupling effect is big when crossing exists or the avoidance of crossing among the PECs. Although the spin–orbital coupling may affect the diatomic PECs and the spectroscopic constants, the spin–orbital coupling effect is not included in the current work, since we do not find the crossing or avoided crossing between the $\tilde{a}^1\Delta_g$ state and the ground state or the higher excited states.

Table 2. Spectroscopic constants compared with experimental and others' theoretical data for the $S_2(\tilde{a}^1\Delta_g)$ molecule. The dissociation energies are in E_h, equilibrium bondlength in a_0, while B_e, α_e, and $\omega_e\chi_e$ are in cm^{-1}.

	D_e	R_e	ω_e	B_e	α_e	$\omega_e\chi_e$
AVTZ	0.128767	3.6505	674.90	0.2826	0.00197	4.029
AVQZ	0.136479	3.6232	690.51	0.2869	0.00194	3.979
AV5Z	0.140352	3.6090	696.49	0.2891	0.00194	3.937
AV6Z	0.141464	3.6048	699.18	0.2898	0.00194	3.936
CBS/USTE(Q, 5)	0.142679	3.6007	700.81	0.2905	0.00193	3.921
Theory[6]	–	3.6070	697.0	–	–	3.07
Theory[14]	–	3.605	746	0.2897	0.0014	–
Theory[18]	0.141963	3.5972	699.68	0.2911	0.00168	3.102
Experiment[13]	–	3.588	702.35	0.2926	0.00173	3.09

It can be concluded from the above discussion that the present spectroscopic constants of the $S_2(\tilde{a}^1\Delta_g)$ electronic state calculated from the CBS/USTE(Q, 5) APEF are in better agreement with the experiments and other theoretical results[6,13,14,18] than those from the AVXZ ($X = \mathrm{T}, \mathrm{Q}, 5, 6$) APEFs. It is worth noting that the computational cost of the CBS/USTE(Q, 5) scheme is much lower than that of AV6Z, while it provides more accurate results.

3.3. Vibrational manifolds

By solving the radial Schrödinger equation of the nuclear motion with the program Level 7.5,[37] we obtain the vibrational energy levels. The radial Schrödinger equation of the nuclear motion is written as

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{\hbar^2}{2\mu r^2}J(J+1)+V(r)\right]\psi_{v,J}(r) = E_{v,J}\psi_{v,J}(r), \tag{12}$$

where $\psi_{v,J}(r)$ and $E_{v,J}$ are the eigenfunctions and eigenvalues of the potential $\frac{\hbar^2}{2\mu r^2}J(J+1)+V(r)$, respectively, and $V(r)$ is the rotationless APEF, r is the internuclear distance of diatom S_2, μ is the reduced mass of the molecule, and v and J are the vibrational and the rotational quantum numbers, respectively. For a given vibrational level, the rotational sublevels can be written as

$$\begin{aligned} E_{v,J} = {} & G(v)+B_v[J(J+1)]+D_v[J(J+1)]^2 \\ & +H_v[J(J+1)]^3+L_v[J(J+1)]^4 \\ & +M_v[J(J+1)]^5+N_v[J(J+1)]^6 \\ & +O_v[J(J+1)]^7, \end{aligned} \tag{13}$$

where $G(v)$ is the vibrational level, $B(v)$ is the inertial rotation constant, and D_v, H_v, L_v, M_v, N_v, and O_v are the centrifugal distortion constants, respectively.

By solving Eq. (12) numerically, we obtain the complete set of vibrational states for $S_2(\tilde{a}^1\Delta_g)$ when the rotational quantum number J equals 0. Due to the length limitation, we tabulate the results of only the first 21 vibrational states, while the complete set of vibrational states can be found in Tables 2 and 3 of SM. For each vibrational state, one vibrational level $G(v)$ and its classical turning points, one inertial rotation constant $B(v)$, and six centrifugal distortion constants D_v, H_v, L_v, M_v, N_v, and O_v are obtained. Table 3 presents the vibrational levels $G(v)$, the classical turning points R_{min} and R_{max}, and the inertial rotation constants $B(v)$ calculated from both the CBS/USTE(Q, 5) and AV6Z APEF. As we can see from Table 3, the CBS/USTE(Q, 5) APEF predicts slightly bigger vibrational levels $G(v)$ than AV6Z APEF does. The difference is only 0.257 cm^{-1} when $v = 0$ and the difference becomes bigger as the vibrational number v increases, with the largest difference being found to be 18.891 cm^{-1} when $v = 20$. The maximal difference for the inertial rotation constants $B(v)$ is found at $v = 20$ with the value of 1.93×10^{-4} cm^{-1}. Moreover, the classical turning points differ at a magnitude of $10^{-3}a_0$, showing good accordance with each other.

Table 3. Vibrational levels $G(v)$ (in cm^{-1}) , classical turning points (in a_0), and rotational constant B_v (in cm^{-1}) of the first 21 vibrational states for $S_2(\tilde{a}^1\Delta_g)$ when $J = 0$, predicted by the CBS/USTE(Q, 5) and AV6Z APEFs.

v	CBS/USTE(Q, 5)				AV6Z			
	$G(v)$	R_{min}	R_{max}	B_v	$G(v)$	R_{min}	R_{max}	B_v
0	185.172	3.52782	3.67880	0.081213	184.815	3.53187	3.68302	0.081027
1	554.265	3.47753	3.73954	0.080967	553.046	3.48152	3.74384	0.080781
2	921.599	3.44432	3.78325	0.080721	919.521	3.44827	3.78761	0.080535
3	1287.176	3.41815	3.81998	0.080474	1284.238	3.42208	3.82438	0.080289
4	1650.999	3.39609	3.85265	0.080227	1647.198	3.40000	3.85709	0.080042
5	2013.068	3.37683	3.88258	0.079980	2008.401	3.38071	3.88707	0.079795
6	2373.387	3.3596	3.91052	0.079732	2367.848	3.36347	3.91505	0.079547
7	2731.955	3.34395	3.93694	0.079483	2725.539	3.34781	3.94151	0.079299
8	3088.775	3.32957	3.96214	0.079235	3081.474	3.33342	3.96676	0.079050
9	3443.849	3.31624	3.98635	0.078986	3435.653	3.32007	3.99101	0.078800
10	3797.177	3.30379	4.00973	0.078736	3788.078	3.30761	4.01444	0.078551
11	4148.762	3.2921	4.03241	0.078486	4138.749	3.29591	4.03717	0.078301
12	4498.605	3.28107	4.05448	0.078236	4487.665	3.28487	4.05929	0.078050
13	4846.708	3.27061	4.07603	0.077986	4834.828	3.27441	4.08089	0.077799
14	5193.07	3.26067	4.09713	0.077735	5180.236	3.26447	4.10204	0.077547
15	5537.694	3.2512	4.11781	0.077484	5523.892	3.25498	4.12278	0.077296
16	5880.581	3.24213	4.13814	0.077232	5865.795	3.24592	4.14316	0.077043
17	6221.731	3.23345	4.15815	0.076980	6205.944	3.23723	4.16323	0.076790
18	6561.144	3.22511	4.17787	0.076728	6544.341	3.22889	4.18301	0.076537
19	6898.822	3.21709	4.19734	0.076475	6880.984	3.22086	4.20254	0.076283
20	7234.765	3.20936	4.21657	0.076222	7215.874	3.21313	4.22183	0.076029

Table 4. Centrifugal distortion constants (in cm^{-1}) of the first 21 vibrational states for $S_2(\tilde{a}^1\Delta_g)$ when $J = 0$, calculated from the CBS/USTE(Q, 5) APEF.

v	$D_v/10^{-8}$	$H_v/10^{-16}$	$L_v/10^{-22}$	$M_v/10^{-28}$	$N_v/10^{-34}$	$O_v/10^{-40}$
0	1.56665	–8.95691	–8.25129	–5.08739	–2.36233	–1.75398
1	1.57004	–9.27506	–8.25552	–5.14787	–2.51306	–1.94317
2	1.57340	–9.59090	–8.26979	–5.22525	–2.68695	–2.14477
3	1.57674	–9.90520	–8.29530	–5.32102	–2.88650	–2.37081
4	1.58007	–10.21875	–8.33329	–5.43681	–3.11267	–2.60739
5	1.58337	–10.53241	–8.38504	–5.57420	–3.36701	–2.85517
6	1.58667	–10.84707	–8.45185	–5.73479	–3.65089	–3.10489
7	1.58995	–11.16364	–8.53505	–5.9201	–3.96602	–3.36851
8	1.59323	–11.48311	–8.63602	–6.13196	–4.31302	–3.57035
9	1.59650	–11.80646	–8.75613	–6.37168	–4.69446	–3.79589
10	1.59978	–12.13474	–8.89678	–6.64096	–5.11172	–4.01575
11	1.60306	–12.46900	–9.05942	–6.94164	–5.56539	–4.11601
12	1.60635	–12.81037	–9.24549	–7.27516	–6.05834	–4.19887
13	1.60965	–13.15996	–9.45647	–7.64324	–6.59358	–4.28826
14	1.61298	–13.51895	–9.69389	–8.04798	–7.16731	–3.95498
15	1.61633	–13.88854	–9.95922	–8.49025	–7.79045	–4.00788
16	1.61971	–14.26994	–10.25408	–8.97336	–8.45635	–3.24847
17	1.62313	–14.66442	–10.57999	–9.49803	–9.17441	–2.62293
18	1.62659	–15.07326	–10.93858	–10.06606	–9.94908	–2.37387
19	1.63010	–15.49778	–11.33159	–10.6814	–10.77300	–0.82122
20	1.63367	–15.93931	–11.76061	–11.34443	–11.66060	0.34910

Table 5. Centrifugal distortion constants (in cm^{-1}) of the first 21 vibrational states for $S_2(\tilde{a}^1\Delta_g)$ when $J = 0$, calculated from AV6Z APEF.

v	$D_v/10^{-8}$	$H_v/10^{-16}$	$L_v/10^{-22}$	$M_v/10^{-28}$	$N_v/10^{-34}$	$O_v/10^{-40}$
0	1.56317	–8.9723800	–8.28434	–5.45150	–2.86599	–2.09230
1	1.56659	–9.3326478	–8.35264	–5.52570	–3.01006	–2.26506
2	1.57001	–9.6905871	–8.42828	–5.61347	–3.17299	–2.44633
3	1.57343	–10.046775	–8.51225	–5.71621	–3.35755	–2.64588
4	1.57685	–10.401835	–8.60561	–5.83548	–3.56515	–2.85515
5	1.58028	–10.756432	–8.70946	–5.97287	–3.79766	–3.07270
6	1.58371	–11.111272	–8.82495	–6.13002	–4.05691	–3.29388
7	1.58716	–11.467106	–8.95330	–6.30854	–4.34502	–3.52844
8	1.59061	–11.824726	–9.09577	–6.51022	–4.66371	–3.75602
9	1.59408	–12.184964	–9.25366	–6.73689	–5.01533	–3.96240
10	1.59756	–12.548700	–9.42834	–6.99031	–5.40049	–4.10439
11	1.60107	–12.916852	–9.62120	–7.27239	–5.82277	–4.19250
12	1.60459	–13.29038	–9.83371	–7.58493	–6.28464	–4.27008
13	1.60814	–13.670289	–10.06735	–7.92979	–6.78922	–4.42659
14	1.61172	–14.057624	–10.32372	–8.30985	–7.33465	–4.08569
15	1.61534	–14.453472	–10.60436	–8.72587	–7.93090	–4.17647
16	1.61899	–14.858963	–10.91100	–9.18162	–8.57278	–3.53648
17	1.62269	–15.275267	–11.24530	–9.67824	–9.26948	–3.03344
18	1.62643	–15.703598	–11.60900	–10.21825	–10.02695	–2.77913
19	1.63023	–16.145214	–12.00401	–10.80488	–10.83568	–1.57803
20	1.63408	–16.601412	–12.43214	–11.44002	–11.71439	–0.70514

The other six centrifugal distortion constants D_v, H_v, L_v, M_v, N_v, and O_v obtained from the CBS/USTE(Q, 5) and AV6Z APEF are tabulated in Tables 4 and 5, respectively, with the difference between them being small. Unfortunately, as far as we know, there is no experimental or theoretical work reported on the vibrational levels, classical turning points, inertial rotation and centrifugal distortion constants. Thus, a direct comparison cannot be made between them. However, according to the high-quality fitting of the APEF and the excellent agreement between the present spectroscopic parameters and the available results reported in the literature,[6,13,14,18] we have reason to believe that the results collected in Tables 4 and 5 are accurate and reliable. Furthermore, although the CBS/USTE(Q, 5) scheme is less costly, the APEF obtained from this scheme can give results as good as those at the AV6Z level. Thus the CBS/USTE(Q, 5) APEF can describe the interaction potential energy of $S_2(\tilde{a}^1\Delta_g)$ well.

4. Conclusions

The PECs of the $\tilde{a}^1\Delta_g$ electronic state of the S_2 molecule have been calculated using the CASSCF as the reference wave function followed by the MRCI(Q) approach in combination with a series of correlation-consistent AVXZ (X = T, Q, 5, 6) basis sets. The USTE(Q, 5) scheme is employed to extrapolate the PEC to the CBS limit. The PECs so obtained are subsequently fitted to APEFs using the EHFACE model. Based on the APEFs of $S_2(\tilde{a}^1\Delta_g)$, the spectroscopic constants D_e, R_e, ω_e, B_e, α_e, and $\omega_e\chi_e$ are calculated. In comparison with the available experimental data, the results obtained from the CBS/USTE(Q, 5) and AV6Z APEF exhibit high accuracy. Thus, they are used to perform the calculations of vibrational manifolds. By numerically solving the radial Schrödinger equation of the nuclear motion, the complete set of vibrational states have been obtained for the first time. For each vibrational state, one vibrational level and its corresponding classical turning points, one inertial rotation constant and six centrifugal distortion constants are also produced. As a whole, the present results provide a more accurate and complete investigations of the spectroscopic parameters and vibrational manifolds of the $S_2(\tilde{a}^1\Delta_g)$ molecule.

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