

## ARTICLE

# Accurate Theoretical Study of LiS Radical and Its Singly Charged Cation and Anion in their Ground Electronic State

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Potential energies of  $\text{LiS}(^2\Pi)$ ,  $\text{LiS}^-(^1\Sigma^+)$  and  $\text{LiS}^+(^3\Sigma^-)$  are calculated by using the multi-reference configuration interaction method including Davidson correction and the augmented correlation-consistent basis sets aug-cc-PV( $X+d$ )Z ( $X=T, Q$ ). Such obtained potential energies are subsequently extrapolated to the complete basis set limit. Both the core-valence correction and the relativistic effect are also considered. The analytical potential energy functions are then obtained by fitting such accurate energies utilizing a least-squares fitting procedure. By using such analytical potential energy functions, we obtain the accurate spectroscopic parameters, complete set of vibrational levels and classical turning points. The present results are compared well with the experimental and other theoretical work.

**Key words:** Analytical potential energy function, Spectroscopic constants, Vibrational energy levels

## I. INTRODUCTION

Metal oxide species play a major role in a variety of environments, including catalysis, high temperature reactions, and stellar atmospheres [1, 2], which have received an appreciable amount of studies [3]. The alkali metal monosulfide, LiS, was addressed by Partridge *et al.* [4] who deduced that the  $^2\Pi$  state is the ground state of LiS. By analyzing the observed millimeter/sub-millimeter spectrum, Brewster and Ziurys [5] obtained spectroscopic constants and equilibrium bond length in the ground state of  $\text{LiS}(X^2\Pi)$ . Lee and Wright [6] calculated a set of potential energy curves (PECs) of LiS which were then extrapolated to complete basis set (CBS) using the two-point extrapolation formula developed by Helgaker *et al.* [7, 8]. By employing LeRoy's LEVEL 7.5 program [9], the spectroscopic constants were also calculated. By using the full valence complete active self-consistent field (CASSCF) method [10] which was then followed by the internally contracted multi-reference configuration interaction approach (MRCI) [11, 12], Khadri *et al.* [13] carried out detailed studies of  $\text{LiS}^+$  with the correlation-consistent basis sets of Dunning, cc-PV5Z [14, 15]. They obtained the spectroscopic constants of the lowest electronic states of  $\text{LiS}^+$ , including the harmonic and anharmonic vibrational frequencies, rotational constants, and dissociation energies. Boldyrev *et al.* [16] reported a study of the electronic ground state of  $\text{LiS}^-(^1\Sigma^+)$  with polarized

split-valence basis sets (6-311+G\*) [17–20] at correlated second-order (MP2) levels and self-consistent field method (SCF). The equilibrium geometries were used to evaluate electron correlation in the frozen-core approximation by full fourth order [21] moller-pleeset perturbation theory and the (U)Q-CISD(T) method [22] for  $\text{LiM}^n$  ( $n=+1, 0, -1$ ;  $M=\text{Li, Be, P, C, N, O, F}$ ).

In order to obtain the accurate PECs of  $\text{LiS}^n$  ( $n=-1, 0, +1$ ), by employing the MRCI(Q) method [23], we carried out detailed studies of  $\text{LiS}^n$  ( $n=-1, 0, +1$ ) systems with the standard augmented correlation-consistent basis sets, aug-cc-PV(T+d)Z (AVTdZ) and aug-cc-PV(Q+d)Z (AVQdZ). The core-valence (CV) correlation is carried out with the CV basis set aug-cc-PCVQZ, and the relativistic correction is also taken into account by using the aug-cc-PVQZ-DK basis set. In particular, the uniform singlet-pair and triplet-pair extrapolation (USTE) protocol [24–26] is employed to extrapolate the PECs calculated at AVXdZ ( $X=T, Q$ ) to the CBS limit. All the PECs are then fitted to analytical potential energy function (APEFs) by using the formalism developed by Aguado and Paniagua [27, 28]. By numerically solving the radical Schrodinger equation of the nuclear motion, we obtained vibrational levels, classical turning points, rotation and centrifugal distortion constants.

## II. COMPUTATIONAL DETAIL

### A. *Ab initio* calculations

The *ab initio* calculations are carried out by using MOLPRO 2012 program [29]. In order to obtain the high-level PECs of  $\text{LiS}^n$  ( $n=-1, 0, 1$ ), the potential energies are calculated for the internuclear separation

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ranging from  $0.5 a_0$  to  $35 a_0$  with the interval of  $0.05 a_0$ , which declines to  $0.01 a_0$  in the vicinity of the equilibrium geometries. All calculations are carried out at the MRCI(Q) level using the CASSCF wave function [10–12] as the reference, which has been applied to many diatomic molecules [30–32]. In the *ab initio* calculations of PECs of  $\text{LiS}^n$  ( $n=-1, 0, 1$ ), the AVXdZ ( $X=\text{T}, \text{Q}$ ) atomic basis sets of Dunning [14, 15] is employed for Li atom. For sulfur atom, the AVXdZ ( $X=\text{T}, \text{Q}$ ) basis set is chosen, which includes high-exponent core-polarization d functions as performed for the second row atoms. Both the core-valence correction and the relativistic effect are considered. The core-valence (CV) correction is taken into account with the CV basis set aug-cc-PCVQZ, and the relativistic correction is carried out with the aug-cc-PVQZ-DK basis set, respectively. We employ  $C_{2v}$  point group symmetry in the *ab initio* calculations, which includes four irreducible representations, namely  $A_1, B_1, B_2$  and  $A_2$ , respectively. For  $\text{LiS}^n$  ( $n=-1, 0, 1$ ), 8 orbitals ( $4a_1+2b_1+2b_2$ ) are confirmed as the active space. Thus, in order to select molecular state, we choose the  $A_1$  irreducible representation of the  $C_{2v}$  point group and carry out the two-state average calculation.

## B. Extrapolation to CBS limit

The MRCI(Q) electronic energy can be treated in spilt form, which can be written as [33]

$$E_X = E_X^{\text{CAS}} + E_X^{\text{dc}} \quad (1)$$

where the subscript  $X$  indicates that the energy has been calculated in the AVXdZ ( $X=\text{T}, \text{Q}$ ) basis sets, while the superscripts dc and CAS stand for the dynamical correlation energy and the complete-active space energy, respectively.

By utilizing the two-point extrapolation protocol proposed by Karton and Martin [34], the CAS energies are extrapolated to CBS limit.

$$E_X^{\text{CAS}} = E_\infty^{\text{CAS}} + \frac{B}{X^a} \quad (2)$$

where  $E_\infty^{\text{CAS}}$  is the energy when  $X \rightarrow \infty$  and  $a=5.34$  is an effective decay exponent.

The USTE technique [24–26] has been successfully performed to extrapolate the dc energies in MRCI(Q) calculations, which takes the following form:

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

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

where  $A_5(0)=0.0037685459$ ,  $c=-1.17847713$  and  $\alpha=-3/8$  are the universal-type parameters [25]. Thus, Eq.(3) is then transformed into an  $(E_\infty, A_3)$  two-parameter rule, which is actually used for the practical procedure of extrapolation [30, 33, 35]. Thus, the dc energies were extrapolated to the CBS limit by utilizing USTE extrapolation scheme.

TABLE I Fitted parameters of  $\text{LiS}^-(^1\Sigma^+)$ ,  $\text{LiS}(^2\Pi)$  and  $\text{LiS}^+(^3\Sigma^-)$  APEFs in Eqs.(6) and (7).

	$\text{LiS}^-(^1\Sigma^+)$	$\text{LiS}(^2\Pi)$	$\text{LiS}^+(^3\Sigma^-)$
$\beta_1$	0.239	2.078	0.21
$\beta_2$	1.097	0.582	1.010
$a_0$	$-0.72182167 \times 10^0$	$0.40040660 \times 10^2$	$-0.23022750 \times 10^0$
$a_1$	$-0.10846881 \times 10^1$	$-0.11570447 \times 10^0$	$-0.080174377 \times 10^0$
$a_2$	$-0.51650233 \times 10^2$	$0.13341602 \times 10^2$	$0.13455433 \times 10^2$
$a_3$	$0.32051904 \times 10^4$	$-0.51699120 \times 10^3$	$0.21294347 \times 10^3$
$a_4$	$-0.74264190 \times 10^5$	$0.69600871 \times 10^4$	$-0.10912527 \times 10^5$
$a_5$	$0.10577021 \times 10^7$	$-0.50863924 \times 10^5$	$0.22183465 \times 10^6$
$a_6$	$-0.99294670 \times 10^7$	$0.22861362 \times 10^6$	$-0.24793086 \times 10^7$
$a_7$	$0.62845961 \times 10^8$	$-0.66068864 \times 10^6$	$0.16900161 \times 10^8$
$a_8$	$-0.26457271 \times 10^9$	$0.12321755 \times 10^7$	$-0.72433952 \times 10^8$
$a_9$	$0.70633102 \times 10^9$	$-0.14329597 \times 10^7$	$0.19138850 \times 10^9$
$a_{10}$	$-0.10772305 \times 10^{10}$	$0.94435635 \times 10^6$	$-0.28534443 \times 10^9$
$a_{11}$	$0.71287920 \times 10^9$	$-0.26902331 \times 10^6$	$0.18365533 \times 10^9$

## C. APEFs of $\text{LiS}^n$ ( $n=-1, 0, 1$ )

The APEFs of  $\text{LiS}^n$  ( $n=-1, 0, 1$ ) are written as the formalism developed by Aguado and Paniagua [27, 28], which is expressed as a sum of two terms corresponding to the short-range and long-range potentials,

$$V_{\text{LiS}}^{(2)} = V_{\text{short}}^{(2)} + V_{\text{long}}^{(2)} \quad (5)$$

$$V_{\text{long}}^{(2)} = \sum_{i=1}^n a_i (R_{\text{LiS}} e^{-\beta_2^{(2)} R_{\text{LiS}}})^i \quad (6)$$

where the diatomic potentials which tend to zero as  $R_{\text{LiS}} \rightarrow \infty$ . The short-range potentials which tend to infinite value when  $R_{\text{LiS}} \rightarrow 0$  takes the following expression

$$V_{\text{short}}^{(2)} = \frac{a_0}{R_{\text{LiS}}} e^{-\beta_1^{(2)} R_{\text{LiS}}} \quad (7)$$

The parameters in Eqs.(6) and (7) are obtained by fitting the *ab initio* energies calculated using AVXdZ ( $X=\text{T}, \text{Q}$ ), which are then extrapolated to the CBS limit. Moreover, both the CV and DK are also considered, which are added to the CBS results and then employed to model the APEFs, here and after denoted as CBS+CV+DK APEFs. The nonlinear parameters  $\beta_i$  ( $i=1, 2$ ) and linear parameters  $a_i$  ( $i=0, 1, 2, \dots, n$ ) in Eq.(6) and Eq.(7) are gathered in Table I.

## III. RESULTS AND DISCUSSION

### A. The PECs

The results of  $\text{LiS}^-(^1\Sigma^+)$ ,  $\text{LiS}(^2\Pi)$  and  $\text{LiS}^+(^3\Sigma^-)$  PECs calculated at CBS+CV+DK level are shown in Fig.1. It shows that the CBS+CV+DK PEC of  $\text{LiS}^-(^1\Sigma^+)$  is deeper than the CBS one. While, it can be seen through the other two figures that the CBS

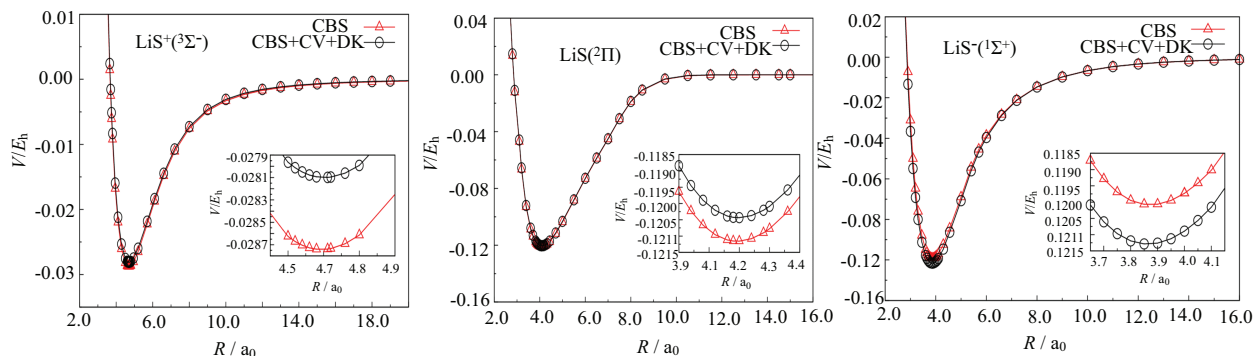


FIG. 1 PECs of  $\text{LiS}^+(\text{}^3\Sigma^-)$ ,  $\text{LiS}(\text{}^2\Pi)$ , and  $\text{LiS}^-(\text{}^1\Sigma^+)$ . The PECs of  $\text{LiS}(\text{}^2\Pi)$  obtained from the CBS APEF and the CBS+CV+DK APEFs.

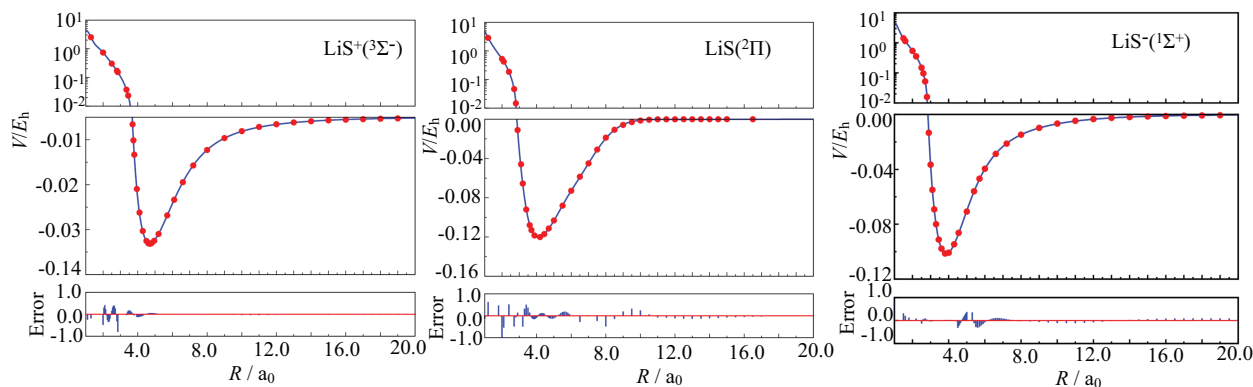


FIG. 2 APEFs of  $\text{LiS}^+(\text{}^3\Sigma^-)$ ,  $\text{LiS}(\text{}^2\Pi)$ , and  $\text{LiS}^-(\text{}^1\Sigma^+)$ . The circles indicate the MRCI(Q)/CBS+CV+DK energies, while lines are from the fitted the APEFs.

PECs of  $\text{LiS}(\text{}^2\Pi)$  and  $\text{LiS}^+(\text{}^3\Sigma^-)$  are both deeper than CBS+CV+DK PECs. For comparison, both the fitted MRCI(Q)/CBS+CV+DK APEFs and the *ab initio* energies are displayed in Fig.2. Shown in this figure are also the difference between APEFs and the *ab initio* energies. As can be seen from this figure, the modeled APEFs accurately mimic the *ab initio* energies. To evaluate the fitting quality of the fitted APEFs, we calculated the root-mean square derivation (RMSD) using the following equation:

$$\Delta E_{\text{RMSD}} = \frac{1}{N} \left\{ \left[ \sum_{i=1}^N (V_{\text{fit}} - V_{\text{ab}})^2 \right] \right\}^{1/2} \quad (8)$$

where  $N$  is the number of points utilized in the fitting process,  $V_{\text{fit}}$  are the energies obtained from the fitted APEFs and  $V_{\text{ab}}$  are MRCI(Q)/CBS+CV+DK energies, respectively. The values of  $\Delta E_{\text{RMSD}}$  are 0.1086, 0.1423, and 0.1335 kcal/mol for  $\text{LiS}^-(\text{}^1\Sigma^+)$ ,  $\text{LiS}(\text{}^2\Pi)$  and  $\text{LiS}^+(\text{}^3\Sigma^-)$  respectively, showing high accuracy of the fitted APEFs.

## B. Spectroscopic constants

By utilizing APEFs of  $\text{LiS}^-(\text{}^1\Sigma^+)$ ,  $\text{LiS}(\text{}^2\Pi)$  and  $\text{LiS}^+(\text{}^3\Sigma^-)$ , the spectroscopic constants are calculated,

which are tabulated in Table II. The other theoretical results [4, 6, 13, 16] are also tabulated in Table II for convenient comparison. It can be seen from Table II that the values of  $R_e$ ,  $D_e$ ,  $\omega_e$ ,  $\omega_e\chi_e$ ,  $B_e$ , and  $\alpha_e$  of  $\text{LiS}(\text{}^2\Pi)$  together with the other experiment [5] and theoretical data [4, 6, 16] for convenient comparison. The  $R_e$  of  $\text{LiS}(\text{}^2\Pi)$  decreases as the basis set increases from AVTdZ to CBS+CV+DK APEF. The values of  $D_e$  calculated from CBS+CV+DK APEF is 3.2776 eV, which differs from the experimental [5] value by 0.022 eV. Comparing the results calculated from CBS+CV+DK APEF with those of experimental [5] and theoretical data [6], the deviation of  $\omega_e$  and  $B_e$  are 0.39% and 1.14%, 0.14% and 0.46%, respectively. The values of  $\omega_e\chi_e$  and  $\alpha_e$  calculated from CBS+CV+DK APEF differ from those of CBS APEF, by 4.3% and 2.8%, respectively.

For  $\text{LiS}^+(\text{}^3\Sigma^-)$ , the equilibrium  $R_e$  obtained from the AVTdZ, AVQdZ, CBS and CBS+CV+DK APEFs are 2.5147, 2.4883, 2.4874, and 2.4857 Å, respectively. As can be seen from this table that the equilibrium bond lengths predicted from the CBS and CBS+CV+DK APEFs are only 0.0414 and 0.0397 Å larger than the theoretical data in Ref.[6]. The dissociation energy ( $D_e$ ) calculated from CBS+CV+DK APES is 0.7625 eV,

TABLE II Spectroscopic constants of LiS( $^2\Pi$ ), LiS $^+$ ( $^3\Sigma^-$ ), and LiS $^-$ ( $^1\Sigma^+$ ).

		$R_e/\text{\AA}$	$D_e/\text{eV}$	$\omega_e/\text{cm}^{-1}$	$\omega_e\chi_e/\text{cm}^{-1}$	$B_e/\text{cm}^{-1}$	$\alpha_e/\text{cm}^{-1}$
LiS( $^2\Pi$ )	AVTdZ	2.1719	3.0951	570.761	3.262	0.6263	0.0053
	AVQdZ	2.1676	3.1956	571.928	3.173	0.6228	0.0052
	CBS	2.1617	3.2956	580.037	3.171	0.6332	0.0051
	CBS+CV+DK	2.1603	3.2776	582.247	3.206	0.6331	0.0052
	Theor.[4]	2.147	3.300	583			
	Theor.[6]	2.145		589	3.96	0.634	0.0067
	Theor.[16]	2.147		597			
	Expt.[5]	2.1497		580		0.634	0.00679
LiS $^+$ ( $^3\Sigma^-$ )	AVTdZ	2.5147	0.7781	317.046	4.004	0.4672	0.0080
	AVQdZ	2.4883	0.7797	334.744	4.454	0.4791	0.0084
	CBS	2.4874	0.7816	338.032	4.524	0.4775	0.0084
	CBS+CV+DK	2.4857	0.7625	326.984	4.436	0.4782	0.0085
	Theor.[6]	2.446		353	5.07	0.489	0.0094
	Theor.[13]	2.43	0.831	376	4.50	0.562	0.011
LiS $^-$ ( $^1\Sigma^+$ )	AVTdZ	2.0582	2.5540	675.712	5.541	0.6975	0.0079
	AVQdZ	2.0540	2.6324	669.084	5.271	0.7003	0.0077
	CBS	2.0495	2.6968	655.262	4.935	0.7034	0.0075
	CBS+CV+DK	2.0437	2.7636	655.211	4.815	0.7037	0.0074
	Theor.[16]	2.058	2.4414	660			

which is only 0.0191 and 0.0685 eV smaller than the CBS value and theoretical data [13]. The vibration frequency is calculated to be 326.984  $\text{cm}^{-1}$  at the CBS+CV+DK level, which differs from the theoretical values in Refs.[6] and [13] only by 26.016 and 49.016  $\text{cm}^{-1}$ , respectively. Comparing the results from the present CBS+CV+DK APEF with CBS APEF, the deviations of  $\omega_e$ ,  $B_e$ ,  $\alpha_e$ , and  $\omega_e\chi_e$  are 3.268%, 0.143%, 0.521% and 3.934%, respectively.

For the LiS $^-$ ( $^1\Sigma^+$ ), as shown in Table II,  $D_e$  increases monotonically from AVTdZ to CBS APEFs, and the deepest well depth is obtained from CBS+CV+DK APEF, with the difference of 0.0668 and 0.3222 eV from those of the CBS APEF and theoretical results [16].  $R_e$  decreases and  $B_e$  increases from the result of AVTdZ to CBS+CV+DK APEFs. The differences of vibrational frequency  $\omega_e$  obtained from CBS+CV+DK APEFs are 0.051 and 4.738  $\text{cm}^{-1}$ , compared with CBS and theoretical results [16], respectively. Comparing the results from the present CBS APEF with the those of CBS+CV+DK APEF, the deviation of  $R_e$ ,  $\omega_e$ ,  $\omega_e\chi_e$ ,  $B_e$ ,  $\alpha_e$  are 0.283%, 0.0078%, 2.4%, 0.57% and 1.29%, respectively.

### C. Vibrational energy levels

By solving the radical Schrödinger equation of the nuclear motion with LEVEL 7.5 program [9], the vibrational energy levels are calculated. The radical

Schrödinger equation is written as

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2}{2\mu r^2} J(J+1) + V(r) \right] \Psi_{\nu,J}(r) = E_{\nu,J} \Psi_{\nu,J}(r) \quad (9)$$

where  $E_{\nu,J}$  is eigenvalues,  $\Psi_{\nu,J}$  is eigenfunction,  $V(r)$  is the potential energy,  $J$  and  $\nu$  are the rotational and vibrational quantum number,  $r$  and  $\mu$  are the internuclear distance and the reduced mass of the molecule, respectively. For a given vibrational level, the rotational sublevels can written as

$$E_{\nu,J} = G(\nu) + B_\nu[J(J+1)] - D_\nu[J(J+1)]^2 + H_\nu[J(J+1)]^3 + L_\nu[J(J+1)]^4 + M_\nu[J(J+1)]^5 + N_\nu[J(J+1)]^6 + O_\nu[J(J+1)]^7 \quad (10)$$

where  $G(\nu)$  is the vibrational level,  $B_\nu$  is inertial rotation constant, and  $D_\nu$ ,  $H_\nu$ ,  $L_\nu$ ,  $M_\nu$ ,  $N_\nu$ , and  $O_\nu$  are the centrifugal distortion constants, respectively.

The complete set of vibrational states for of LiS $^n$  ( $n=-1, 0, 1$ ) are calculated when  $J=0$ , by solving Eq.(10) numerically. Table III–IV gather the classical turning points ( $R_{\min}$ ,  $R_{\max}$ ), the inertial rotation constants  $B_\nu$  and the vibrational levels  $G(\nu)$  calculated from the CBS+CV+DK APEFs for LiS, LiS $^-$  and LiS $^+$  respectively. Here, due to the length limitation, we only tabulate the result of 21 vibrational states. In Table III, we present the corresponding results of LiS( $^2\Pi$ ). It can be found that vibrational levels  $G(\nu)$  of CBS+CV+DK APEF show small difference from the CBS APEF, the

TABLE III The vibrational levels  $G(\nu)$ , classical turning points  $R$ , and rotational constant  $B_\nu$  of the first 21 vibrational states for  $\text{LiS}(^2\Pi)$  when  $J=0$  predicted by the CBS+CV+DK APEF and CBS APEF.

CBS+CV+DK					CBS				
$\nu$	$G(\nu)/\text{cm}^{-1}$	$R_{\min}/a_0$	$R_{\max}/a_0$	$B_\nu/\text{cm}^{-1}$	$\nu$	$G(\nu)/\text{cm}^{-1}$	$R_{\min}/a_0$	$R_{\max}/a_0$	$B_\nu/\text{cm}^{-1}$
0	288.558	3.90696	4.28891	0.622875	0	287.948	3.90828	4.29045	0.622594
1	856.420	3.79460	4.46124	0.613558	1	855.864	3.79397	4.46038	0.614210
2	1414.851	3.72335	4.58953	0.605277	2	1415.145	3.72123	4.58675	0.606571
3	1965.707	3.66841	4.69895	0.597831	3	1967.011	3.66511	4.69479	0.599539
4	2510.084	3.62274	4.79704	0.591021	4	2512.219	3.61848	4.79196	0.592978
5	3048.546	3.58318	4.88745	0.584673	5	3051.189	3.57816	4.88179	0.586769
6	3581.311	3.54802	4.97234	0.578651	6	3584.099	3.54239	4.96636	0.580812
7	4108.380	3.51623	5.05316	0.572845	7	4110.973	3.51010	5.04703	0.575024
8	4629.613	3.48712	5.13093	0.567174	8	4631.727	3.48059	5.12476	0.569344
9	5144.797	3.46021	5.20641	0.561575	9	5146.218	3.45335	5.20027	0.563722
10	5653.677	3.43516	5.28020	0.556002	10	5654.265	3.42804	5.27411	0.558120
11	6155.995	3.41170	5.35275	0.550424	11	6155.681	3.40438	5.34670	0.552515
12	6651.497	3.38963	5.42443	0.544820	12	6650.286	3.38216	5.41839	0.546891
13	7139.963	3.36879	5.49551	0.539179	13	7137.922	3.36121	5.48943	0.541240
14	7621.213	3.34906	5.56620	0.533504	14	7618.469	3.34139	5.56002	0.535567
15	8095.122	3.33031	5.63667	0.527803	15	8091.851	3.32259	5.63030	0.529880
16	8561.628	3.31246	5.70700	0.522094	16	8558.049	3.30471	5.70036	0.524198
17	9020.740	3.29543	5.77724	0.516401	17	9017.106	3.28767	5.77024	0.518545
18	9472.543	3.27915	5.84739	0.510755	18	9469.129	3.27140	5.83394	0.512947
19	9917.194	3.26536	5.91740	0.505188	19	9914.289	3.25582	5.90941	0.507435
20	10354.921	3.24859	5.98720	0.499734	20	10352.818	3.24088	5.97861	0.502039

TABLE IV The vibrational levels  $G(\nu)$ , classical turning points, and rotational constant  $B_\nu$  of the first 21 vibrational states for  $\text{LiS}^+(^3\Sigma^-)$  when  $J=0$  predicted by the CBS+CV+DK APEF.

CBS+CV+DK					CBS				
$\nu$	$G(\nu)/\text{cm}^{-1}$	$R_{\min}/a_0$	$R_{\max}/a_0$	$B_\nu/\text{cm}^{-1}$	$\nu$	$G(\nu)/\text{cm}^{-1}$	$R_{\min}/a_0$	$R_{\max}/a_0$	$B_\nu/\text{cm}^{-1}$
0	162.121	4.47246	4.96545	0.469308	0	167.296	4.47069	4.97216	0.469257
1	79.608	4.32457	5.20657	0.459675	1	495.108	4.32501	5.20331	0.460603
2	788.881	4.23483	5.39103	0.450166	2	813.842	4.23473	5.38213	0.451773
3	1089.761	4.16806	5.55444	0.440719	3	1123.251	4.16703	5.54116	0.442769
4	1382.063	4.11441	5.70705	0.431287	4	1423.114	4.11243	5.69161	0.433592
5	1665.602	4.06949	5.85364	0.421831	5	1713.244	4.06665	5.83652	0.424244
6	1940.199	4.03089	5.99701	0.412322	6	1993.482	4.02728	5.97903	0.414729
7	2205.687	3.99713	6.13903	0.402735	7	2263.698	3.99287	6.12089	0.405051
8	2461.909	3.96722	6.28109	0.393051	8	2523.793	3.96241	6.26338	0.395214
9	2708.725	3.94048	6.42429	0.383254	9	2773.696	3.93522	6.40752	0.385227
10	2946.009	3.91640	6.56958	0.373330	10	3013.369	3.91077	6.55415	0.375098
11	3173.656	3.89460	6.71779	0.363273	11	3242.803	3.88866	6.70401	0.364837
12	3391.579	3.87479	6.86974	0.353075	12	3462.020	3.86860	6.85778	0.354458
13	3599.714	3.85672	7.02620	0.342731	13	3671.076	3.85033	7.01608	0.343975
14	3798.019	3.84022	7.18793	0.332241	14	3870.054	3.83364	7.17953	0.333403
15	3986.479	3.82512	7.35572	0.321606	15	4059.073	3.81838	7.34872	0.322761
16	4165.105	3.81128	7.53039	0.310832	16	4238.277	3.80440	7.52423	0.312068
17	4333.936	3.79861	7.71280	0.299927	17	4407.842	3.79157	7.70666	0.301344
18	4493.045	3.78700	7.90383	0.288902	18	4567.970	3.77980	7.89661	0.290612
19	4642.534	3.77636	8.10446	0.277773	19	4718.887	3.76898	8.09469	0.279891
20	4782.542	3.76663	8.31568	0.266559	20	4860.842	3.75905	8.30156	0.269203

TABLE V The vibrational levels, classical turning points, and rotational constant of the first 21 vibrational states for  $\text{LiS}^-(^1\Sigma^+)$  when  $J=0$  predicted by the CBS+CV+DK APEF and CBS APEF.

CBS+CV+DK					CBS				
$\nu$	$G(\nu)/\text{cm}^{-1}$	$R_{\min}/a_0$	$R_{\max}/a_0$	$B_\nu/\text{cm}^{-1}$	$\nu$	$G(\nu)/\text{cm}^{-1}$	$R_{\min}/a_0$	$R_{\max}/a_0$	$B_\nu/\text{cm}^{-1}$
0	325.905	3.69232	4.05126	0.698439	0	325.829	3.70374	4.06273	0.694255
1	972.833	3.57969	4.20347	0.692256	1	972.453	3.59180	4.21576	0.687728
2	1613.847	3.50745	4.31585	0.685996	2	1612.874	3.52012	4.32891	0.681193
3	2248.536	3.45180	4.41229	0.679646	3	2246.717	3.46495	4.42605	0.674623
4	2876.540	3.40583	4.49976	0.673195	4	2873.605	3.41938	4.51419	0.667992
5	3497.366	3.36640	4.58149	0.666630	5	3493.160	3.38029	4.59656	0.661279
6	4110.749	3.33174	4.65928	0.659944	6	4105.003	3.34594	4.67498	0.654466
7	4716.290	3.30079	4.73431	0.653128	7	4708.758	3.31524	4.75064	0.647536
8	5313.637	3.27280	4.80736	0.646175	8	5304.054	3.28748	4.82435	0.640475
9	5902.446	3.24726	4.87903	0.639076	9	5890.520	3.26213	4.89673	0.633270
10	6482.384	3.22378	4.94978	0.631828	10	6467.790	3.23883	4.96824	0.625909
11	7053.126	3.20207	5.01997	0.624422	11	7035.505	3.21729	5.03927	0.618382
12	7614.356	3.18191	5.08992	0.616855	12	7593.310	3.19727	5.11015	0.610679
13	8165.767	3.16311	5.15988	0.609123	13	8140.858	3.17861	5.18116	0.602791
14	8707.064	3.14552	5.23008	0.601219	14	8677.809	3.16115	5.25255	0.594712
15	9237.959	3.12902	5.30075	0.593142	15	9203.834	3.14478	5.32456	0.586434
16	9758.177	3.11351	5.37207	0.584888	16	9718.615	3.12940	5.39740	0.577953
17	10267.453	3.09890	5.44424	0.576455	17	10221.847	3.11492	5.47127	0.569265
18	10765.537	3.08512	5.51742	0.567840	18	10713.242	3.10127	5.54638	0.560389
19	11252.190	3.07210	5.59178	0.559045	19	11192.528	3.08838	5.62292	0.551262
20	11727.190	3.05979	5.66749	0.550068	20	11659.458	3.07621	5.70106	0.541948

deviations of  $v=0, 1, 2, 3,$  and  $4$  are 0.21%, 0.065%, 0.021%, 0.067% and 0.085%, respectively. It can be seen from Table IV, the differences between the CBS and CBS+CV+DK APEFs of  $\text{LiS}^+(^3\Sigma^-)$  are only 3.69%, 3.1%, 3.06%, 4.1% and 2.88% for  $v=0, 1, 2, 3,$  and  $4,$  respectively. Table V demonstrates the vibrational levels  $G(\nu)$  of  $\text{LiS}^-(^1\Sigma^+)$  from CBS APEF and CBS APEF, showing the deviations for  $v=0, 1, 2, 3,$  and  $4$  are 0.023%, 0.040%, 0.060%, 0.080% and 0.10%, respectively. Whereas, according to the high quality of CBS+CV+DK APEF, the results are accurate and reliable. As a result, the present work provides more accurate and complete investigation on the  $\text{LiS}^n$  ( $n=-1, 0, 1$ ) system.

#### IV. CONCLUSION

The PECs, spectroscopic constants, classical turning points and vibrational levels are studied for  $\text{LiS}, \text{LiS}^-$  and  $\text{LiS}^+$  systems. The *ab initio* energies are calculated at the MRCI/AVXdZ ( $X=T, Q$ ) levels of the theory which are then extrapolated to the CBS limit. The the relativistic effect and core-valence correlation are also considered. Excellent agreement on spectroscopic parameters is obtained between the present result and other theoretical and experimental results. It can be concluded that the present work provide more accurate

and complete investigations on the spectroscopic constants and vibrational manifolds of  $\text{LiS}(^2\Pi), \text{LiS}^-(^1\Sigma^+)$  and  $\text{LiS}^+(^3\Sigma^-)$ , respectively.

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