

Ab initio MRCI+Q Investigations of Spectroscopic Properties of Several Low-lying Electronic States of S_2^+ Cation

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The complete active space self-consistent field method followed by the internally contracted multireference configuration interaction method has been used to compute the potential energy curves of $X^2\Pi_g$, $a^4\Pi_u$, $A^2\Pi_u$, $b^4\Sigma_g^-$, and $B^2\Sigma_g^-$ states of S_2^+ cation with large correlation-consistent basis sets. Utilizing the potential energy curves computed with different basis sets, the spectroscopic parameters of these states were evaluated. Finally, the transition dipole moment and the Franck-Condon factors of the transition from $A^2\Pi_u$ to $X^2\Pi_g$ were evaluated. The radiative lifetime of $A^2\Pi_u$ is calculated to be 887 ns, which is in good agreement with experimental value of 805 ± 10 ns.

Key Words : Spectroscopic constants, Core-valence correlation, Relativistic correction, Radiative lifetime, S_2^+ cation

Introduction

Sulfur dimer (S_2) and its cation (S_2^+) are important molecules in astrophysics, astrochemistry, and chemical lasers. For example, the spectra of S_2 has been detected in cometary atmospheres,^{1,2} Jupiter's atmosphere,³ and dense molecular clouds.⁴ In addition, S_2^+ cation is always generated from all kinds of industrial and natural plasmas containing sulfur compounds.⁵⁻⁸ Since sulfur compounds play an important role in a variety of research fields, the studies of spectroscopic properties and electronic states of sulfur compounds^{1-4,9-12} have attracted much attention over many years. Compared with extensive investigations of sulfur compounds, there are a few studies on the spectroscopic and transition properties of S_2^+ cation.

Early in 1975, Berkowitz *et al.*¹³ observed the photoelectron spectra of S_2 and Te_2 . Based on the single ionization spectrum of S_2 , they identified the $X^2\Pi_g$, $a^4\Pi_u$, $A^2\Pi_u$, $b^4\Sigma_g^-$, and $B^2\Sigma_g^-$ states of S_2^+ . At the same time, Dyke *et al.*¹⁴ also observed the He(I) photoelectron spectra of S_2 , assigned the $X^2\Pi_g$, $a^4\Pi_u$, $A^2\Pi_u$, $b^4\Sigma_g^-$, and $B^2\Sigma_g^-$ states of S_2^+ , and fitted the spectroscopic parameters of the five electronic states of S_2^+ . Later on, Tsuji *et al.*⁵ made a vibrational analysis of the $A^2\Pi_u$ - $X^2\Pi_g$ transition in S_2^+ . Subsequently, rotational analysis of the S_2^+ ($A^2\Pi_u$ - $X^2\Pi_g$) emission band was reported by Capel *et al.*⁶ and Brabharan *et al.*¹⁵ Recently, the $A^2\Pi_u$ - $X^2\Pi_g$ emission spectrum of S_2^+ was observed through microwave discharge of CS_2 or sulfur vapor in solid neon,⁷ and photolysis of an H_2S_2/Ar matrix in solid argon,⁸ respectively.

However, to the best of our knowledge, only a few theoretical studies were made to investigate the spectroscopic properties of S_2^+ cation. In 1989, the total energy and bond

length of the ground state $X^2\Pi_g$ of S_2^+ are calculated by Balaban *et al.*¹⁰ using *ab initio* method. Recently, Grant *et al.*¹¹ investigated the electronic structure of the ground state for S_2^+ by employing the CCSD(T) theory. The potential energy curve (PEC) of the ground state for S_2^+ was extrapolated to the complete basis set (CBS) by utilizing systematic sequences of correlation-consistent basis sets with an exponential function. Nevertheless, the previously available theoretical calculations are not enough to illuminate the spectroscopic properties of low-lying excited electronic states of S_2^+ cation.

In the present study, we performed *ab initio* calculations on the low-lying electronic states of S_2^+ . The core-valence correlation and scalar relativistic (mass-velocity and Darwin term) corrections were taken into account. The PECs of 5 Λ -

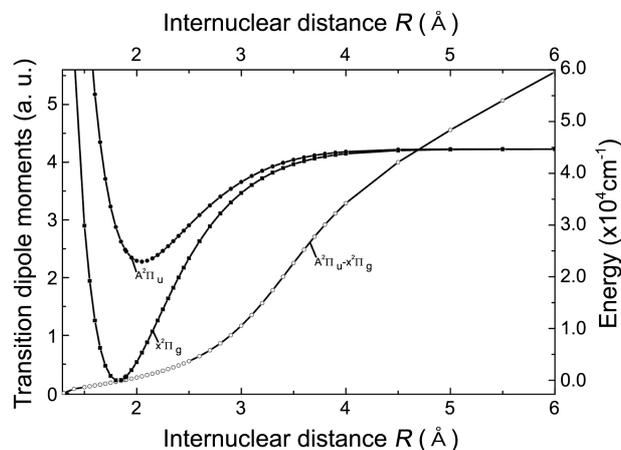


Figure 1. The PECs of $X^2\Pi_g$ and $A^2\Pi_u$ states determined by the MRCI+Q/CBS+CV+DK calculations (top and right axes), and the transition dipole moment of $A^2\Pi_u$ - $X^2\Pi_g$ (bottom and left axes).

S states ($X^2\Pi_g$, $a^4\Pi_u$, $A^2\Pi_u$, $b^4\Sigma_g^-$, and $B^2\Sigma_g^-$) were calculated with high-level multireference methods. In order to eliminate errors due to the incomplete basis set, the PECs were computed with a series of correlation-consistent basis sets and extrapolated to the CBS limit. On the basis of PECs of the bound Λ -S and Ω electronic states, the spectroscopic constants of the bound states were determined by numerically solving the nuclear-motion Schrödinger equations. Finally, the transition dipole moment (TDM) and the radiative lifetime of $A^2\Pi_u$ were obtained. The spin-orbit coupling (SOC) effect was included in computations on transition properties of $X^2\Pi_g$ - $A^2\Pi_u$.

Methods and Computational Details. In the present work, the electronic structure computations were performed with MOLPRO 2010 quantum chemical package designed by Werner *et al.*¹⁶ The point group of the S_2^+ cation is $D_{\infty h}$. Nevertheless, owing to the limit of the MOLPRO procedure, all of the computations were carried out in the D_{2v} subgroup of the $D_{\infty h}$ point group. The correlating relationships for the irreducible representations of the $D_{\infty h}$ and D_{2v} are $\Sigma_g^+ = A_g$, $\Sigma_g^- = B_{1g}$, $\Sigma_u^+ = B_{1u}$, $\Sigma_u^- = A_u$, $\Pi_g = B_{2g} + B_{3g}$, and $\Pi_u = B_{2u} + B_{3u}$. In the subsequent calculations, the PECs of $X^2\Pi_g$, $a^4\Pi_u$, $A^2\Pi_u$, $b^4\Sigma_g^-$, and $B^2\Sigma_g^-$ electronic states of S_2^+ were calculated through the complete active space self-consistent field (CASSCF) method.^{17,18} In the CASSCF computations, active space was made up of eight MOs: two A_g , one B_{3u} , one B_{2u} , two B_{1u} , one B_{2g} , one B_{3g} symmetric MOs. The 3s3p valence electrons of S were placed into the active space. The other twenty electrons of S_2^+ were distributed into the closed orbitals, *i.e.*, three A_g , one B_{3u} , one B_{2u} , three B_{1u} , one B_{2g} , and one B_{3g} symmetric MOs, which correspond to inner-shell orbitals 1s2s2p of S. Furthermore, all configurations in the configuration interaction (CI) expansions of the CASSCF wave functions were used as reference for internally contracted multireference configuration interaction method¹⁹ (MRCI) and MRCI with the Davidson correction (MRCI+Q).²⁰ Additionally, the core-valence (CV) correlation induced by $n = 2$ orbital of S atom was estimated by combining the MRCI+Q method and the aug-cc-pwCVQZ basis set.²¹ The 1s core orbital of sulfur atom was excluded in CV computations. In order to improve the quality of spectroscopic constants, the scalar relativistic effect was taken into account *via* the second-order Douglas-Kroll-Hess (DKH) one-electron integrals in the PECs calculations. The scalar relativistic effect (denoted as DK) was produced by the difference between the energies with DKH and without DKH using an aug-cc-pVQZ-dk²² basis set at the MRCI+Q level. The sensitivity of calculated electronic states to the basis set was investigated by using a series of correlation consistent basis sets (aug-cc-pV($n + d$)Z, $n = Q(4), 5, 6$).²³ For the sake of brevity, the basis set is abbreviated to aVnZ. The dynamical correlation energy was extrapolated to the CBS limit by n^{-3} extrapolation formula²⁴⁻²⁷ with $n = Q, 5$.

The SOC was calculated by employing the state interaction method with the full Breit-Pauli (BP) operator,²⁸ which means that the spin-orbit eigenstates are determined by diagonalizing $\hat{H}^{el} + \hat{H}^{SO}$ in the basis eigenfunctions of

\hat{H}^{el} . On the basis of PECs obtained by MRCI + Q/CBS + CV + DK + SOC level, we then solved the nuclear-motion Schrödinger equations utilizing the numerical integration LEVEL program²⁹ designed by Le Roy to obtain the corresponding vibrational wave functions, vibrational energy levels, Franck-Condon factors (FCFs), and spectroscopic constants.

Results and Discussion

Spectroscopic Parameters. In order to obtain more accurate PECs, the point spacing interval of the calculated electronic states was 0.05 Å for $R = 1.3$ -2.4 Å, 0.1 Å for $R = 2.5$ -4.0 Å, and 0.5 Å for $R = 4.5$ -6.0 Å. Table 1 lists the calculated parameters of S_2^+ , including adiabatic transition energies T_e , vibrational constants (ω_e and $\omega_e x_e$), rotational constants B_e , and equilibrium distances R_e . In Table 1, the spectroscopic constants were evaluated with the MRCI method utilizing the AVQZ and aV5Z basis sets. Table 1 also lists the previously available experimental results. Compared with previous accurate experimental results,¹⁵ the ω_e , $\omega_e x_e$, B_e , and R_e of $X^2\Pi_g$ and $A^2\Pi_u$ states evaluated with the AVQZ basis set are accurate with deviations of 50.961, 0.5905, 0.0453 cm^{-1} , and 0.0131 Å, but the spectroscopic constants of the two states evaluated with the AV5Z basis set are accurate to within 9.65, 0.0768, 0.00275 cm^{-1} , and 0.0114 Å, respectively. For $A^2\Pi_u$ state, the T_e value calculated with the AVQZ basis set differs from experimental result¹⁵ by 331.63 cm^{-1} , and the T_e value calculated with the AV5Z basis set is only 307.25 cm^{-1} larger than experimental data.¹⁵ On the whole, the spectroscopic parameters obtained by the AV5Z basis set are more accurate. Thus, we use the AV5Z basis set to calculate the Davidson correction (MRCI+Q). Table 1 also lists the spectroscopic parameters derived from the PECs including CV and DK effects. As shown in Table 1, the T_e values of $a^4\Pi_u$, $A^2\Pi_u$, $b^4\Sigma_g^-$, and $B^2\Sigma_g^-$ states obtained with the MRCI+Q method are 17817.16, 22013.82, 30773.25, and 38898.84 cm^{-1} , respectively, which are 228.07, 638.88, 716.91, and 900.67 cm^{-1} smaller than those calculated by the MRCI method. When only the core-valence correlation correction is taken into account in the present MRCI+Q calculations, T_e is increased by 157.00, 526.03, 464.99, and 547.14 cm^{-1} for $a^4\Pi_u$, $A^2\Pi_u$, $b^4\Sigma_g^-$, and $B^2\Sigma_g^-$ states, respectively; ω_e is increased by 6.79, 4.31, 7.14, 3.93, and 5.20 cm^{-1} for $X^2\Pi_g$, $a^4\Pi_u$, $A^2\Pi_u$, $b^4\Sigma_g^-$, and $B^2\Sigma_g^-$ states, respectively. When only the relativistic correction is taken into account in the present MRCI+Q calculations, the influence of DK correction on the spectroscopic constants is evidently smaller than that with the core-valence correlation correction. For example, the DK correction makes the values of T_e shift only by 86.38, 116.74, 106.52, and 79.06 cm^{-1} for $a^4\Pi_u$, $A^2\Pi_u$, $b^4\Sigma_g^-$, and $B^2\Sigma_g^-$ states, respectively. Even though the influence of the DK correction on spectroscopic constants is relatively small, it cannot be omitted in high-level *ab initio* computations.

By incorporating the Davidson correction as well as the CV and DK corrections into the present study, we calculate the spectroscopic constants which agree very well with the

Table 1. The spectroscopic constants of low-lying electronic states of S_2^+ with the AVQZ and AV5Z basis sets including core-valence correlation and relativistic corrections

		T_e (cm ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	B_e (cm ⁻¹)	R_e (Å)
X ² Π _g	MRCI					
	AVQZ	0	857.06	3.9876	0.3623	1.8357
	AV5Z	0	801.92	3.3934	0.3143	1.8318
	MRCI+Q	0	799.96	3.4042	0.3140	1.8325
	+CV	0	806.75	3.4397	0.3163	1.8260
	+DK	0	795.08	3.3976	0.3138	1.8330
	+CV+DK	0	802.07	3.4432	0.3161	1.8264
	Expt. ^a	0	–	–	–	1.82(5)
	Expt. ^b	0	807(3)	3.5(3)	–	–
	Expt. ^c	0	805.9(2)	3.38(2)	0.3175	1.8226
	Expt. ^d	0	806.099(11)	3.3971(18)	0.316974(53)	1.8239(1)
Expt. ^e	–	806.10(1)	3.3971(18)	–	–	
Expt. ^f	0	800(10)	3.0(5)	–	–	
a ⁴ Π _u	MRCI					
	AVQZ	17595.42	563.14	2.7384	0.2505	2.0518
	AV5Z	18045.23	566.22	2.6613	0.2513	2.0485
	MRCI+Q	17817.16	566.82	2.7039	0.2513	2.0483
	+CV	17974.16	571.13	2.6712	0.2533	2.0403
	+DK	17730.78	560.48	2.6520	0.2505	2.0519
	+CV+DK	17891.14	564.69	2.6127	0.2525	2.0436
A ² Π _u	MRCI					
	AVQZ	22013.82	542.24	3.3157	0.2490	2.0581
	AV5Z	22652.70	543.07	3.2133	0.2494	2.0564
	MRCI+Q	22013.82	542.24	3.3157	0.2490	2.0581
	+CV	22539.85	549.38	3.2109	0.2516	2.0474
	+DK	22130.56	539.63	3.1988	0.2490	2.0578
	+CV+DK	22453.03	542.31	3.1523	0.2507	2.0511
	Expt. ^a	–	–	–	–	2.04
	Expt. ^b	22580(3)	551(3)	3.1(3)	–	–
Expt. ^c	22344.69(58)	552.72(5)	3.14(20)	0.2524(3)	2.0441(13)	
Expt. ^d	22345.450(30)	552.635(11)	3.1365(24)	0.252150(52)	2.0450(2)	
Expt. ^f	22120(50)	560(10)	3.0(5)	–	–	
b ⁴ Σ _g ⁻	MRCI					
	AVQZ	30603.32	596.16	4.3829	0.2787	1.9451
	AV5Z	31490.16	595.24	4.2270	0.2789	1.9444
	MRCI+Q	30773.25	600.51	4.3224	0.2798	1.9413
	+CV	31238.24	604.44	4.2925	0.2818	1.9344
	+DK	30879.77	591.30	4.3719	0.2788	1.9447
	+CV+DK	31347.80	595.30	4.3426	0.2808	1.9377
B ² Σ _g ⁻	MRCI					
	AVQZ	38747.79	527.84	4.5073	0.2686	1.9816
	AV5Z	39799.51	523.87	4.2786	0.2677	1.9847
	MRCI+Q	38898.84	533.47	4.4653	0.2698	1.9770
	+CV	39445.98	538.67	4.5165	0.2710	1.9728
	+DK	38977.90	522.02	4.4071	0.2685	1.9821
	+CV+DK	39527.00	527.13	4.4352	0.2697	1.9778

Note: For the experimental values, the inaccuracy of measurement is depicted in the bracket. ^aReference 14. ^bReference 5. ^cReference 6. ^dReference 15. ^eReference 7. ^fReference 8.

previous experimental values.^{8,15} For instance, the differences between our calculated T_e of the A²Π_u state and the experimental values^{8,15} are 107.58–333.03 cm⁻¹. Regarding the vibrational frequencies of X²Π_g and A²Π_u, our calculated

values of ω_e and $\omega_e x_e$ differ by less than 10.33 and 0.0461 cm⁻¹ from the accurate experimental results.^{7,15} For the rotational constants of X²Π_g and A²Π_u, our calculated B_e values differ by less than 0.00145 cm⁻¹ from experimental

Table 2. Spectroscopic constants of low-lying electronic states of S_2^+ determined by MRCI+Q computations at the AV5Z and CBS

	T_e (cm $^{-1}$)	ω_e (cm $^{-1}$)	$\omega_e x_e$ (cm $^{-1}$)	B_e (cm $^{-1}$)	R_e (Å)
$X^2\Pi_g$					
AV5Z	0	799.96	3.4042	0.3140	1.8325
CBS	0	804.51	3.3895	0.3152	1.8290
CBS+cv	0	813.73	3.3909	0.3180	1.8210
CBS+dk	0	799.38	3.4069	0.3150	1.8298
CBS+cv+dk	0	808.75	3.4111	0.3178	1.8217
Calc. ^a		816.9	3.1		1.8240
$a^4\Pi_u$					
AV5Z	17817.16	566.82	2.7039	0.2513	2.0483
CBS	18063.19	570.46	2.6753	0.2523	2.0443
CBS+cv	18695.01	574.74	2.6423	0.2543	2.0362
CBS+dk	17915.14	564.13	2.6219	0.2514	2.0478
CBS+cv+dk	18449.35	568.31	2.5828	0.2535	2.0395
$A^2\Pi_u$					
AV5Z	22219.99	546.74	3.2610	0.2499	2.0542
CBS	22450.26	551.11	3.2145	0.2510	2.0498
CBS+cv	23146.01	553.29	3.1448	0.2527	2.0428
CBS+dk	22299.86	543.71	3.1237	0.2501	2.0532
CBS+cv+dk	22996.89	546.45	3.0862	0.2518	2.0465
$b^4\Sigma_g^-$					
AV5Z	30773.25	600.51	4.3224	0.2798	1.9413
CBS	30963.96	605.65	4.3086	0.2811	1.9375
CBS+cv	31804.18	609.53	4.2713	0.2831	1.9305
CBS+dk	31008.86	596.63	4.3662	0.2801	1.9408
CBS+cv+dk	31851.20	600.57	4.3291	0.2821	1.9337
$B^2\Sigma_g^-$					
AV5Z	38898.84	533.47	4.4653	0.2698	1.9770
CBS	39072.23	539.54	4.4632	0.2713	1.9716
CBS+cv	39996.19	544.86	4.5435	0.2725	1.9675
CBS+dk	39091.04	528.26	4.4149	0.2699	1.9767
CBS+cv+dk	40016.04	533.58	4.4775	0.2712	1.9724

^aReference12

results.¹⁵ Compared with the experimental values,^{14,15} the calculated results of R_e of the two states are accurate, only with deviations of less than 0.0061 Å.

Table 2 lists spectroscopic constants obtained from MRCI+Q PECs at aV5Z and CBS levels. Compared with spectroscopic constants determined by the MRCI+Q/aV5Z calculations, the extrapolation to the CBS limit (excluding the CV and DK effects) makes T_e increase by 246.03, 230.27, 190.71, and 173.39 cm $^{-1}$ for $a^4\Pi_u$, $A^2\Pi_u$, $b^4\Sigma_g^-$, and $B^2\Sigma_g^-$ states, respectively. Compared with spectroscopic constants determined at the MRCI+Q/aV5Z+CV+DK level, the extrapolation to the CBS limit makes T_e increase by 558.21, 543.86, 503.4, and 489.04 cm $^{-1}$, respectively, for $a^4\Pi_u$, $A^2\Pi_u$, $b^4\Sigma_g^-$, and $B^2\Sigma_g^-$ states. As to the $A^2\Pi_u$ state, the T_e obtained by the MRCI+Q/CBS+CV+DK calculations is larger than previously available experimental data¹⁵ by 651.44 cm $^{-1}$, the deviations of ω_e , $\omega_e x_e$, B_e , and R_e determined at the MRCI+Q/CBS+CV+DK level from the experimental values^{14,15} are only 6.185 cm $^{-1}$, 0.0503 cm $^{-1}$, 0.00035 cm $^{-1}$, and 0.0015 Å, respectively. As to the $X^2\Pi_g$ state, the deviations of ω_e ,

Table 3. Spectroscopic constants of the $X^2\Pi_g$ and $A^2\Pi_u$ states of S_2^+ including the spin-orbit coupling effect

	T_e (cm $^{-1}$)	ω_e (cm $^{-1}$)	$\omega_e x_e$ (cm $^{-1}$)	B_e (cm $^{-1}$)	R_e (Å)
$X^2\Pi_{g1/2}$	0	808.98	3.4048	0.3178	1.8217
$X^2\Pi_{g3/2}$	425.61	808.51	3.4170	0.3178	1.8217
$A^2\Pi_{u1/2}$	23221.38	546.31	3.0921	0.2518	2.0466
$A^2\Pi_{u3/2}$	23197.99	546.59	3.0804	0.2518	2.0464

$\omega_e x_e$, B_e , and R_e determined by the MRCI+Q/CBS+CV+DK calculations from the experimental values^{14,15} are also only 2.651 cm $^{-1}$, 0.014 cm $^{-1}$, 0.000826 cm $^{-1}$, and 0.0022 Å, respectively. Our calculated ω_e , $\omega_e x_e$, and R_e of $X^2\Pi_g$ state are 808.75 cm $^{-1}$, 3.4111 cm $^{-1}$, and 1.8217 Å, respectively, which also agree well with those of previous theoretical values¹¹ of 816.9 cm $^{-1}$, 3.1 cm $^{-1}$, 1.8240 Å. In comparison to previous experimental and theoretical results,^{14,15} we can conclude that the spectroscopic constants determined by the MRCI+Q/CBS+CV+DK calculations are more accurate, even if the spectroscopic constants obtained by the MRCI+Q/AV5Z+CV+DK calculation also agree well with experimental data. Additionally, the spectroscopic constants for $a^4\Pi_u$, $b^4\Sigma_g^-$, and $B^2\Sigma_g^-$ states have not been measured in experiments. However, we believe that the spectroscopic constants of these states are also accurate owing to the good consistence with experimental results for the $X^2\Pi_g$ and $A^2\Pi_u$ states.

Effect of Spin-Orbit Coupling on PECs of $X^2\Pi_g$ and $A^2\Pi_u$ States. The SOC effect generally results in the splitting of multiplet electronic states. The spin-orbit splitting of the $X^2\Pi_g$ and $A^2\Pi_u$ states has been determined experimentally⁶ utilizing a rotational analysis of the A-X emission band. Table 3 lists the spectroscopic constants of the $X^2\Pi_g$ and $A^2\Pi_u$ states determined by the MRCI+Q/CBS+CV+DK calculations including the SOC effect. The calculated spin-orbit splitting of the $X^2\Pi_g$ and $A^2\Pi_u$ states are 425.61 and 23.39 cm $^{-1}$, respectively, which are in reasonable agreement with experimental data of 469.7 ± 2.3 and 13.5 ± 2.7 cm $^{-1}$.⁶ For the $X^2\Pi_g$ state, the modifications caused by the SOC effect are only 0.23 cm $^{-1}$, -0.0063 cm $^{-1}$, 0 cm $^{-1}$, and 0 Å, for spectroscopic constants ω_e , $\omega_e x_e$, B_e , and R_e , respectively. For the $A^2\Pi_u$ state, the modifications caused by the SOC effect are only 0.14 cm $^{-1}$, -0.0058 cm $^{-1}$, 0 cm $^{-1}$, 0 Å, and 55.89 cm $^{-1}$ for these spectroscopic parameters, respectively. According to the above discussion, we can conclude that the SOC effect cannot bring obvious modification to the spectroscopic parameters of $X^2\Pi_g$ and $A^2\Pi_u$.

Transition Dipole Moment and Radiative Lifetime of $A^2\Pi_u$ State. The electronic transition dipole moment (TDM) function of the $A^2\Pi_u$ - $X^2\Pi_g$ transition was computed. For the sake of clarity, the TDM of $A^2\Pi_u$ - $X^2\Pi_g$ as a function of the internuclear distance and PECs of the two states are plotted in Figure 1. It is found from Figure 1. that the TDM increases monotonously as the internuclear distance increases from 1.35 to 6.0 Å, and equals 0.29 a. u. (1 a. u. = 2.542 Debye) at the equilibrium distance of the $A^2\Pi_u$ state. On the basis of the PECs obtained by the MRCI+Q/CBS+CV+DK+SOC

Table 4. $G(v)$ and B_v values of the $X^2\Pi_g$ and $A^2\Pi_u$ states of S_2^+

v	$X^2\Pi_g$				$A^2\Pi_u$			
	$G(v) (cm^{-1})$		$B_v (cm^{-1})$		$G(v) (cm^{-1})$		$B_v (cm^{-1})$	
	This work	Expt. ^a	This work	Expt. ^a	This work	Expt. ^a	This work	Expt. ^a
0	403.7317	402.336	0.31691	0.31623	272.8086	275.528	0.25085	0.25130
1	1205.8977	1201.662	0.31516	0.31440	812.6406	821.866	0.24903	0.24356
2	2001.3019	1994.130	0.31341	0.31264	1346.4115	1361.906	0.24731	0.24779
3	2790.0386	2779.840	0.31167	0.31094	1874.7000	1895.605	0.24552	0.24593
4	3571.8724	3558.753	0.30991	0.30923	2396.3422	2422.921	0.24372	0.24424
5	4346.7829	4330.781	0.30815	0.30750	2911.9229	2943.875	0.24196	0.24253
6	5114.8205	5096.041	0.30639	0.30567	3421.4136	3458.419	0.24017	0.24075
7	5876.0047	5854.427	0.30464	0.30397	3924.4728	3966.528	0.23835	0.23904
8	6630.4602	6606.057	0.30288	0.30219	4421.1328	4468.250	0.23654	0.23712
9	7378.1632	7350.800	0.30111	0.30042	4911.5683	4963.298	0.23473	0.23538
10	8119.0423	8088.640	0.29934	0.29861	5395.7421	5451.910	0.23289	0.23346

^aReference15.

calculations, we evaluated the spectroscopic constants, vibrational wave functions, and vibrational energy levels of $X^2\Pi_g$ and $A^2\Pi_u$. The spectroscopic constants of the two states have been analyzed in above Section, and vibrational level $G(v)$, vibration-dependent rotational constant B_v of the first 11 vibrational states for the two states are listed in Table 4. For the $X^2\Pi_g$ state, the largest deviation of $G(v)$ and B_v from experimental values¹⁵ are only 30.4023 cm^{-1} (0.38% for $v = 10$) and 0.0008 cm^{-1} , respectively. For the $A^2\Pi_u$ state, the largest deviation of $G(v)$ and B_v from experimental values¹⁵ are only 56.1679 cm^{-1} (1.03% for $v = 10$) and 0.0055 cm^{-1} , respectively. On the whole, our calculated values of $G(v)$ and B_v of the $X^2\Pi_g$ and $A^2\Pi_u$ states agree well with the previous experimental results. Subsequently, we evaluated the Franck-Condon factors (FCFs) from the vibrational level $v = 0-6$ of the upper electronic state ($A^2\Pi_u$) to the vibrational level $v' = 0-6$ of the lower ground state ($X^2\Pi_g$), as listed in

Table 5. It is found that the maximum FCFs of $v'-v''$ transitions in $A^2\Pi_u-X^2\Pi_g$ system are 6.67×10^{-2} (6-0), 9.45×10^{-2} (5-1), 1.02×10^{-1} (3-2), 1.07×10^{-1} (2-3), 1.26×10^{-1} (1-4), 1.40×10^{-1} (0-5), and 1.74×10^{-1} (0-6) for $v'' = 0-6$ vibrational energy levels, respectively, which agree well with the corresponding experimental values: 7.24×10^{-2} , 9.53×10^{-2} , 1.02×10^{-1} , 1.11×10^{-1} , 1.05×10^{-1} , 1.51×10^{-1} , and 1.81×10^{-1} .¹⁵

The transition probability from excited state ($A^2\Pi_u$) to the ground state is equal to the Einstein coefficient $A_{v'v''}$. The Einstein coefficient $A_{v'v''}$ for spontaneous emission between vibrational levels v' and v'' is defined by

$$A_{v'v''} = 2.026 \times 10^{-6} \tilde{\nu}^3 (TDM)^2 q_{v'v''} \quad (1)$$

where $\tilde{\nu}$ is the transition energy in unit of cm^{-1} , TDM is the average electronic transition dipole moment in Franck-

Table 5. Franck-Condon factors of the $A^2\Pi_u-X^2\Pi_g$ transition of S_2^+

	$v'' = 0$	$v'' = 1$	$v'' = 2$	$v'' = 3$	$v'' = 4$	$v'' = 5$	$v'' = 6$
This work							
$v' = 0$	3.30×10^{-4}	3.18×10^{-3}	1.46×10^{-2}	4.26×10^{-2}	8.86×10^{-2}	1.40×10^{-1}	1.74×10^{-1}
$v' = 1$	2.10×10^{-3}	1.60×10^{-2}	5.22×10^{-2}	1.02×10^{-1}	1.26×10^{-1}	9.12×10^{-2}	2.82×10^{-2}
$v' = 2$	7.08×10^{-3}	3.97×10^{-2}	9.21×10^{-2}	1.07×10^{-1}	5.36×10^{-2}	1.75×10^{-3}	2.56×10^{-2}
$v' = 3$	1.67×10^{-2}	6.87×10^{-2}	1.02×10^{-1}	5.34×10^{-2}	5.38×10^{-4}	3.47×10^{-2}	7.19×10^{-2}
$v' = 4$	3.12×10^{-2}	9.02×10^{-2}	7.48×10^{-2}	6.00×10^{-3}	2.47×10^{-2}	6.43×10^{-2}	2.01×10^{-2}
$v' = 5$	4.88×10^{-2}	9.45×10^{-2}	3.26×10^{-2}	5.87×10^{-3}	5.73×10^{-2}	2.70×10^{-2}	4.26×10^{-3}
$v' = 6$	6.67×10^{-2}	8.02×10^{-2}	4.23×10^{-3}	3.47×10^{-2}	4.52×10^{-2}	5.38×10^{-6}	4.04×10^{-2}
Expt. ^a							
$v' = 0$	4.22×10^{-4}	3.97×10^{-3}	1.77×10^{-2}	4.98×10^{-2}	9.96×10^{-2}	1.51×10^{-1}	1.81×10^{-1}
$v' = 1$	2.61×10^{-3}	1.87×10^{-2}	6.01×10^{-2}	1.11×10^{-1}	1.25×10^{-1}	8.06×10^{-2}	1.78×10^{-2}
$v' = 2$	8.54×10^{-3}	4.58×10^{-2}	9.83×10^{-2}	1.05×10^{-1}	4.23×10^{-2}	3.19×10^{-6}	3.81×10^{-2}
$v' = 3$	1.96×10^{-2}	7.59×10^{-2}	1.02×10^{-1}	4.32×10^{-2}	2.28×10^{-4}	4.62×10^{-2}	7.01×10^{-2}
$v' = 4$	3.55×10^{-2}	9.53×10^{-2}	6.76×10^{-2}	1.84×10^{-3}	3.48×10^{-2}	6.25×10^{-2}	1.07×10^{-2}
$v' = 5$	5.42×10^{-2}	9.53×10^{-2}	2.42×10^{-2}	1.22×10^{-2}	6.04×10^{-2}	1.74×10^{-2}	1.15×10^{-2}
$v' = 6$	7.24×10^{-2}	7.66×10^{-2}	1.14×10^{-3}	4.35×10^{-2}	3.75×10^{-2}	1.59×10^{-3}	4.73×10^{-2}

^aReference 15.

Condon region in atomic unit, and $q_{v'v''}$ is the FCF between vibrational levels v' and v'' . The radiative lifetime of vibrational level v' is defined as the inverse of the total transition probability

$$\tau = \left(\sum_{v''} A_{v'v''} \right)^{-1} \quad (2)$$

On the basis of Eq. (2), FCFs, and TDM of A-X, the radiative lifetime of $v'=0$ vibrational level of $A^2\Pi_u$ is calculated to be 887 ns, which agrees well with the previous experimental value of 805 ± 10 ns measured in a solid argon matrix.

Conclusion

In the present paper, the PECs of the low-lying electronic states ($X^2\Pi_g$, $a^4\Pi_u$, $A^2\Pi_u$, $b^4\Sigma^-_g$, and $B^2\Sigma^-_g$) for the S_2^+ cation were investigated by the MRCI method with the correlation-consistent basis sets (aug-cc-pV($n+d$)Z, $n=Q, 5, 6$). The Davidson and the core-valence correlation corrections were also taken into account in calculations. Subsequently, on the basis of PECs obtained by the CASSCF and MRCI+Q method with different correlation-consistent basis sets, we obtained the PECs of $X^2\Pi_g$, $a^4\Pi_u$, $A^2\Pi_u$, $b^4\Sigma^-_g$, and $B^2\Sigma^-_g$ states, which have been extrapolated to the CBS limit. Based on the computed PECs, the spectroscopic constants of the corresponding states were evaluated, which agree well with the existing experimental results. The spin-orbit coupling of $X^2\Pi_g$ and $A^2\Pi_u$ states was taken into account *via* state interaction method with the full Breit-Pauli Hamiltonian. The spin-orbit splittings of $X^2\Pi_g$ and $A^2\Pi_u$ states were found to be consistent with the experimental data. Utilizing the PECs determined by the MRCI+Q/CBS+CV+DK+SOC calculations, vibrational levels $G(v)$, vibration-dependent rotational constants B_v for each vibrational state of $X^2\Pi_g$, and $A^2\Pi_u$ states were evaluated by solving nuclear Schrödinger equations. The transition dipole moment function of spin-allowed transition $A^2\Pi_u-X^2\Pi_g$ was investigated, and the radiative lifetime of $A^2\Pi_u$ ($v'=0$) vibrational level was evaluated. Our studies indicate that core-valence correlation, and relativistic corrections have great influence to the spectroscopic parameters of S_2^+ . The present theoretical investigation should help to understand the transition and spectroscopic properties of the low-lying electronic states of the S_2^+ cation.

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References

- Ahearn, M. F.; Feldman, P. D.; Schleicher, D. G. *Astrophys. J.* **1983**, *274*, 99.
- Grim, R. J.; Greenberg, J. M. *Astron. Astrophys.* **1987**, *181*, 155.
- Maurellis, A. N.; Cravens, T. E. *Icarus* **2001**, *154*, 350.
- Frederix, P. W.; Yang, C. H.; Groenenboom, G. C.; Parker, D. H.; Alnama, K.; Western, C. M.; Orr-Ewing, A. J. *J. Phys. Chem. A* **2009**, *113*, 14995.
- Tsuji, M.; Murakami, I.; Nishimura, Y. *Chem. Phys. Lett.* **1980**, *75*, 536.
- Capel, A. J.; Eland, J. H.; Barrow, R. F. *Chem. Phys. Lett.* **1981**, *82*, 496.
- Zen, C. C.; Lee, Y. P.; Ogilvie, J. F. *Spectrochim. Acta Part A* **1996**, *52*, 1727.
- Khriachtchev, L.; Pettersson, M.; Isoniemi, E.; Lundell, J.; Räsänen, M. *Chem. Phys. Lett.* **1999**, *302*, 324.
- Peterson, K. A.; Lyons, J. R.; Francisco, J. S. *J. Chem. Phys.* **2006**, *125*, 084314.
- Balaban, A. T.; Demaré, G. R.; Poirier, R. A. *J. Mol. Struct. THEOCHEM* **1989**, *183*, 103.
- Grant, D. J.; Dixon, D. A.; Francisco, J. S. *J. Chem. Phys.* **2007**, *126*, 144308.
- Yan, B.; Pan, S. F.; Yu, J. H. *Chin. Phys.* **2007**, *16*, 1956.
- Berkowitz, J. *J. Chem. Phys.* **1975**, *62*, 4074.
- Dyke, J. M.; Golob, L.; Jonathan, N.; Morris, A. *J. Chem. Soc. Faraday Trans.* **1975**, *71*, 1026.
- Brabaharan, K.; Coxon, J. *J. Mol. Spectrosc.* **1988**, *128*, 540.
- Werner, H. J.; Knowles, P. J.; Lindh, R. et al. MOLPRO: a package of *ab initio* programs 2010, <<http://www.molpro.net>>.
- Knowles, P. J.; Werner, H. J. *Chem. Phys. Lett.* **1985**, *115*, 259.
- Werner, H. J.; Knowles, P. J. *J. Chem. Phys.* **1985**, *82*, 5053.
- Knowles, P. J.; Werner, H. J. *Chem. Phys. Lett.* **1988**, *145*, 514.
- Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61.
- Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548.
- Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.
- Dunning, T. H.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244.
- Bytautas, L.; Nagata, T.; Gordon, M. S.; Ruedenberg, K. *J. Chem. Phys.* **2007**, *127*, 164317.
- Polyansky, O. L.; Császár, A. G.; Shirin, S. V.; Zobov, N. F.; Barletta, P.; Tennyson, J.; Schwenke, D. W.; Knowles, P. J. *Science* **2003**, *299*, 539.
- Helgaker, T.; Klopper, W.; Tew, D. P. *Mol. Phys.* **2008**, *106*, 2107.
- Bytautas, L.; Ruedenberg, K.; *J. Chem. Phys.* **2010**, *132*, 074109.
- Berning, A.; Schweizer, M.; Werner, H.-J.; Knowles, P. J.; Palmieri, P. *Mol. Phys.* **2000**, *98*, 1823.
- Le Roy, R. J. LEVEL 7.5: a Computer Program for Solving the Radial Schrödinger Equation for Bound and Quasibound Levels, University of Waterloo, Chemical Physics Research Report CP-655, 2002.