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Ab initio calculations of the ionization spectrum of SO_2*

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The ionization spectrum of sulfur dioxide has been successfully studied by using the symmetry-adapted-cluster configuration-interaction (SAC-CI) general-R and SD-R methods and the basis set correlation-consistent polarized valence triple-zeta (cc-pVTZ). The SAC-CI general-R method reproduces the experimental spectrum well for both the main peaks and the satellite peaks of ionization spectrum of SO_2. The sequence of ionic states corresponding to main peaks of SO_2 has been re-determined according to the SAC-CI conclusions and it is reordered as $\tilde{X}^2A_1$, $\tilde{A}^2B_2$, $\tilde{B}^2A_2$, $\tilde{C}^2B_1$, $\tilde{D}^2A_1$, $\tilde{E}^2B_2$ and $\tilde{F}^2A_1$. Besides, the equilibrium structures and adiabatic ionization potentials (AIPs) of ionic states of main peaks of SO_2 are calculated by using the SAC-CI SD-R method.

Keywords: ionization spectrum, satellite state, equilibrium structure, ionization potential
PACC: 3110, 3450E

1. Introduction

The sulfur dioxide (SO_2) and the ion (SO_2^+) play important roles in atmospheric chemistry, environmental pollution, and industry, such as in the overall chemistry of the dry etching process.[1,2] A great many of experimental studies have been devoted to the SO_2^+, such as photoelectron spectroscopy,[3−5] electron impact ionization,[6,7] photoionization,[8,9] photodissociation,[10] and photofragment excitation spectrum.[11] The common ground of the above-mentioned contents is to excite the neutral molecule SO_2 by using the high-energy photons or electrons. In their studies,[3−5,8], three bands were observed in the photoelectron spectrum of SO_2: the ionic $\tilde{X}$ state of SO_2^+ that was in the first band, the ionic $\tilde{A}$ and $\tilde{B}$ states of SO_2^+ that were in the second band, and the ionic $\tilde{C}$, $\tilde{D}$ and $\tilde{E}$ states of SO_2^+ that were in the third band.

The symmetries for the electronic states $\tilde{X}$-to-$\tilde{E}$ of SO_2^+ are suggested in different assignments according to different experimental and theoretical studies. In the early experimental and theoretical papers,[4,10,12,13] the assignments of $\tilde{A}$ and $\tilde{B}$ states were uniform, assigned as $\tilde{A}^2A_2$ and $\tilde{B}^2B_2$. Recently, the theoretical assignments[14−16] of $\tilde{A}$ and $\tilde{B}$ states were given as $\tilde{A}^2B_2$ and $\tilde{B}^2A_2$ based on CASPT2, MRD-CI and CCSD (T) calculations. In the experimental papers,[4,5,8] the $\tilde{C}$, $\tilde{D}$ and $\tilde{E}$ states were assigned as $\tilde{C}^2B_2$, $\tilde{D}^2A_1$ and $\tilde{E}^2B_1$ states, respectively. However, the theoretical studies[12,14−16] showed the assignments $\tilde{C}^2B_1$, $\tilde{D}^2A_1$ and $\tilde{E}^2B_2$ for $\tilde{C}$, $\tilde{D}$ and $\tilde{E}$ states, respectively. Thomas *et al*[10] questioned the assignment of $\tilde{D}^2A_1$ and proposed the assignments of $\tilde{C}^2B_1$ and $\tilde{D}^2B_2$. Zhang *et al*[11] suggested an assignment of $\tilde{D}^2B_1$ and possible assignments of $\tilde{C}^2A_1$ and $\tilde{E}^2B_2$ based on their photofragment excitation spectrum experiment.

The satellite peaks of ionization spectrum of SO_2 have been investigated experimentally[4,5] and theoretically.[15,16] Two weak bands occurring at about 14.6 and 17.5 eV were interpreted by Wang *et al*,[4] and they indicated that the band at 14.6 eV was the $He_I\beta$ line spectrum of the third band and the band at 17.5 eV was a satellite band, which might be two components of a spin–orbit split state. Since the shake-up states to satellite peaks are numerous and congested, their assignments are difficult. In an energy region from 16 to 21 eV, many states with shake-up characters were discussed by Li and Huang[15] and Palmer *et al*.[16] The results of Holland *et al*[5] showed that some states of SO_2^+ were the admixtures of two-hole-one-particle (2h1p) configurations above 15 eV. The SAC-CI general-R method is considered as a powerful tool for studying the properties of molecules, such as analytic potential energy functions[17−21] and molecular spectroscopic problems including ionization spectroscopy.[22−26] In particular,

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the SAC-CI general-R method is effective for studying a large number of states appearing in the ionization spectra including the multiple electron processes in a high accuracy.[25,26] Although the SAC-CI SD-R method is insufficient to describe the orbital reorganizations, which is caused by the ionizations and excitations of the inner-shell electrons, it can be used to calculate the main peaks caused by valence orbitals quite well. In our studies, we apply the SAC-CI general-R method and the SAC-CI SD-R method to the calculation of the ionization spectrum of SO_2 and assign the main states of SO_2^+ for the main peaks and the satellite states of SO_2^+ for satellite peaks in a region below 23.3 eV. Based on the assignments of the main states of SO_2^+ for the main peaks, the SAC-CI SD-R method is applied to optimizing the geometries for ionic states. We also calculate the AIPs of these ionic states at their equilibrium geometries.

2. Calculation details

Vertical ionization spectrum of SO_2 is studied and the experimental geometry of ground state[3] is used for the calculation, namely, $R_{SO} = 0.1432$ nm and $\angle OSO = 119.5°$ for SO_2 in C_{2v}. The basis set is selected to be as flexible as possible to describe the electron correlations of shake-up states, namely, correlation-consistent polarized valence triple-zeta (cc-pVTZ) basis set. The basis set for O is the (4s, 3p, 2d, 1f) contraction of a (10s, 5p, 2d, 1f) primitive set,[27] and for S it is the (5s, 4p, 2d, 1f) contraction of a (15s, 9p, 2d, 1f) primitive set.[28]

Hartree–Fock (HF) molecular orbitals (MOs) are used as the reference orbitals in the SAC/SAC-CI calculations. For the active space, 9 higher occupied MOs and 78 lower unoccupied MOs are used, and only the 1s orbitals of O and 1s, 2s, 2p orbitals of S are separately frozen as a core. The ionization spectrum of SO_2 is calculated by using the SAC-CI general-R method and the SAC-CI SD-R method in an energy region below 23.3 eV. From the preliminary calculations, most of the shake-up states are shown to be described dominantly by two-electron processes, and therefore the R-operators are included up to triples. The ionization cross-sections are calculated in the monopole approximation[25] to estimate the relative intensities of the peaks. For the calculations of monopole intensities, the correlated SAC/SAC-CI wavefunctions are used for the ground state and the ionized states to include both initial- and the final-state correlation effects.

The geometries for the main states of SO_2^+ corresponding to the main peaks are optimized by performing the SAC-CI SD-R calculation. The adiabatic ionization potential of the ionic state is considered to be equal to the difference in energy between the ionic state and the ground state of molecule at their equilibrium geometries. Based on the energies of the main states of SO_2^+ and ground state of SO_2 at their equilibrium structures, the AIPs of excited states are calculated.

Calculation of SAC/SAC-CI is carried out by using the SAC/SAC-CI program system,[29] which has been incorporated into the version of the Gaussian03 suite of programs.[30]

3. Results and discussion

Photoelectron spectroscopy[8] shows that the ionic states of SO_2 are created by vacuum ultraviolet photo-excitation. In the ground state $\tilde{X}^1A_1$, SO_2 molecule is a bent triatomic molecule, whose electronic configuration (C_{2v} point group symmetry, $C_2(z)$, y axis in plane as a defined axis) is considered to be as follows on a single configuration basis:

$$(\text{Core})^{14}\ 5a_1^2 3b_2^2 6a_1^2 4b_2^2 7a_1^2 2b_1^2 5b_2^2 1a_2^2 8a_1^2 3b_1^0 9a_1^0 6b_2^0 \ldots \tilde{X}^1A_1$$

where the number in the superscript shows the occupation number. The outer three occupied molecular orbitals and the three virtual molecular orbitals of SO_2 are shown in Fig.1. The $8a_1$ and $3b_1$ orbitals are the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of SO_2 molecule, respectively. The natures of $6a_1$, $4b_2$, $7a_1$, $2b_1$, $5b_2$, $1a_2$, $8a_1$ and $3b_1$ MOs are sulphur '3s' non-bonding, weakly S–O bonding, S–O σ bonding, S–O π bonding, O–O σ anti-bonding, S–O dπ-pπ bonding, sulphur 'lone pair' and S–O π anti-bonding, O–O π bonding, respectively.

The states in an energy region up to 23.3 eV are studied by using the SAC-CI general-R method and the SAC-CI SD-R method. With the SAC-CI SD-R method, 9 electronic states are calculated, while about 20 ones are solved with the general-R method. In Table 1 in Subsection 3.1 of this paper, the vertical ionization potentials (VIPs), monopole intensities and the configurations of the main states of SO_2^+ are

summarized. The experimental photoelectron spectrum and the present theoretical spectrum are shown in Fig.2. The optimized geometrical parameters for the ground state of SO_2 and the main states of SO_2^+ are included in Table 2 in Subsection 3.2, together with the experimental values and previous theoretical estimates. The theoretically estimated AIPs of ground and exited states of SO_2^+ are included in Table 3 in Subsection 3.3, together with the experimental AIPs.

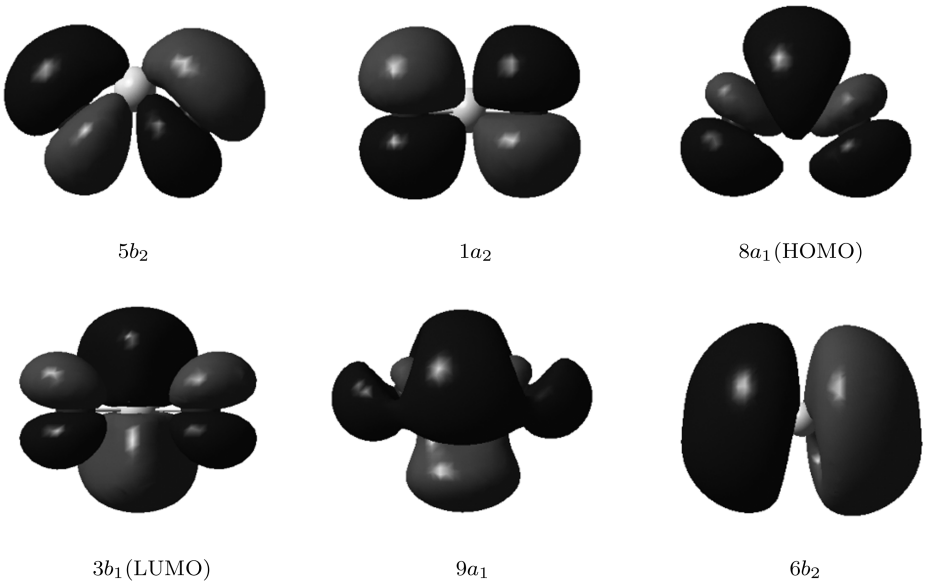


Fig.1. The three outer valence molecular orbitals and the three virtual molecular orbitals of SO_2.

3.1. The ionization spectra, vertical ionization potentials and monopole

In Fig.2, for the experimental spectrum, we adopt the spectra measured by Wang *et al.*[4] For the main peaks of ionization spectra of SO_2 below 17 eV, the spectra measured by using both SAC-CI general-R method and the SAC-CI SD-R method are shown to be almost the same, which accord with the experimental spectra. The energy range above 17 eV contains broad bands due to many shake-up states. There are remarkable differences between the spectra obtained by using the SAC-CI general-R method and the SAC-CI SD-R method in this energy region. The SAC-CI general-R method reproduces the positions and the shapes of the satellite bands, while the SAC-CI SD-R method does not produce acceptable results in this region. It implies the importance of including higher excitation operators in the linked excitation operators of the SAC-CI calculation to describing the shake-up spectrum, which is consistent with the previous results.[23,24]

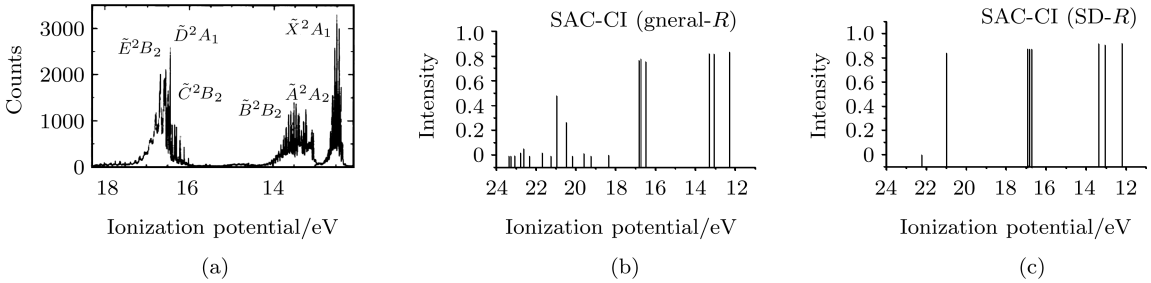


Fig.2. The experimental photoelectron spectra (a) and the ionization spectra of SO_2 calculated by using the SAC-CI general-R method (b) and the SAC-CI SD-R method (c).

Table 1. Main configurations, VIPs (eV), and monopole intensities for the ionized state of SO_2, calculated by using the SAC-CI general-R method and the SAC-CI SD-R method.

state	SAC-CI (general-R)			Exp[4]	SAC-CI(SD-R)	TDA[16]	MRD-CI[16]
	main configuration($\|C\| >= 0.3$)	VIPs	intensity	I.P	VIP	VIP	VIP
$\tilde{X}^2A_1$	$-0.93(8a_1)^{-1}$	12.278	0.844	12.346(3)	12.208	12.403	12.012
$\tilde{A}^2B_2$	$-0.92\ (5b_2)^{-1}$	13.052	0.828	12.988(5)	13.036	13.248	12.749
$\tilde{B}^2A_2$	$-0.93(1a_2)^{-1}$	13.356	0.830	13.338(4)	13.399	12.689	13.145
$\tilde{C}^2B_1$	$-0.88(2b_1)^{-1}$	16.603	0.754	15.903(3)	16.788	15.587	16.130
$\tilde{D}^2A_1$	$0.89(7a_1)^{-1}$	16.787	0.789	16.339(3)	16.825	16.773	16.249
$\tilde{E}^2B_2$	$0.89(4b_2)^{-1}+0.31(8a_1)^{-1}\ (1a_2)^{-1}\ (3b_1)^1$	16.830	0.776	16.507(3)	16.877	17.382	16.346
$\tilde{F}^2A_1$	$0.71(6a_1)^{-1}-0.55(1a_2)^{-1}\ (5b_2)^{-1}\ (3b_1)^1$	20.964	0.489		25.524	21.665	20.703
Shake-up states							
$2\ ^2B_1$	$-0.89(8a_1)^{-2}(3b_1)^1$	18.412	0.008			16.246	16.809
$2\ ^2A_2$	$-0.95(8a_1)^{-1}(5b_2)^{-1}\ (3b_1)^1$	19.222	0.000			16.913	17.340
$3\ ^2B_2$	$-1.01(1a_2)^{-1}(8a_1)^{-1}(3b_1)^1-0.61(8a_1)^{-1}(1a_2)^{-1}(3b_1)^1$	19.548	0.022		22.170	16.258	17.769
$3\ ^2A_2$	$1.01\ (5b_2)^{-1}\ (8a_1)^{-1}\ (3b_1)^1+0.39(8a_1)^{-1}(5b_2)^{-1}\ (3b_1)^1$	20.163	0.000			17.742	18.144
$3\ ^2A_1$	$0.53(6a_1)^{-1}+0.65(1a_2)^{-1}(5b_2)^{-1}(3b_1)^1+0.54(2b_1)^{-1}(8a_1)^{-1}(3b_1)^1$ $+0.42(8a_1)^{-1}(2b_1)^{-1}(3b_1)^1+0.36(5b_2)^{-1}\ (1a_2)^{-1}\ (3b_1)^1$	20.469	0.274		21.013	17.239	18.453
$3\ ^2B_1$	$-0.73(5b_2)^{-2}(3b_1)^1-0.47(8a_1)^{-1}(7a_1)^{-1}(3b_1)^1-0.47(7a_1)^{-1}\ (8a_1)^{-1}\ (3b_1)^1$	21.265	0.001				
$4\ ^2B_2$	$-0.72(8a_1)^{-1}\ (1a_2)^{-1}\ (3b_1)^1$	21.664	0.028				
$5\ ^2B_2$	$0.75(2b_1)^{-1}(5b_2)^{-1}(3b_1)^1-0.71(1a_2)^{-1}(7a_1)^{-1}(3b_1)^1$ $+0.48(5b_2)^{-1}(2b_1)^{-1}(3b_1)^1-0.43(7a_1)^{-1}(1a_2)^{-1}\ (3b_1)^1$	22.335	0.000				
$4\ ^2B_1$	$-0.26\ (2b_1)^{-1}-0.75(1a_1)^{-2}(3b_1)^1+0.36(2b_1)^{-2}(3b_1)^1$	22.633	0.061				
$5\ ^2A_1$	$0.64(2b_1)^{-1}(8a_1)^{-1}(3b_1)^1\ +\ 0.55(8a_1)^{-1}\ (2b_1)^{-1}\ (3b_1)^1\ +\ 0.45(1a_2)^{-1}$ $(4b_2)^{-1}(3b_1)^1\ -0.44(1a_2)^{-1}(5b_2)^{-1}(3b_1)^1+0.36(4b_2)^{-1}\ (1a_2)^{-1}\ (3b_1)^1$	22.719	0.027				
$5\ ^2B_1$	$-0.60(8a_1)^{-1}(7a_1)^{-1}(3b_1)^1+0.38(7a_1)^{-1}\ (8a_1)^{-1}\ (3b_1)^1$	22.985	0.002				
$4\ ^2A_2$	$-0.67(8a_1)^{-1}(4b_2)^{-1}(3b_1)^1$	23.271	0.000				
$6\ ^2A_1$	$0.68(5b_2)^{-1}(1a_2)^{-1}(3a_1)^1-0.33(2b_1)^{-1}(8a_1)^{-1}(3b_1)^1$	23.288	0.018				

The main peaks of ionization spectra of SO_2 observed at 12.349, 12.988, 13.338, 15.903, 16.339, 16.507 and 20.06 eV are assigned to $\tilde{X}^2A_1$, $\tilde{A}^2A_2$, $\tilde{B}^2B_2$, $\tilde{C}^2B_2$, $\tilde{D}^2A_1$, $\tilde{E}^2B_1$ and $\tilde{F}^2A_1$ states of SO_2^+[4] respectively. In the present work, the 1^2A_1, 1^2B_2, 1^2A_2, 1^2B_1, 2^2A_1, 2^2B_2 states are described dominantly by one-electron process, namely, $(8a_1)^{-1}$, $(5b_2)^{-1}$, $(1a_2)^{-1}$, $(2b_1)^{-1}$, $(7a_1)^{-1}$, $(4b_2)^{-1}$ respectively. Their VIPs calculated by the general-R method are 12.278, 13.052, 13.356, 16.603, 16.787, 16.830 eV, respectively, which have considerable monopole intensities. Distinguishingly, the main configurations of the 3^2A_1 and 4^2A_1 states are $0.53(6a_1)^{-1}$ $+0.65(1a_2)^{-1}(5b_2)^{-1}(3b_1)^1$ + $0.54(2b_1)^{-1}(8a_1)^{-1}(3b_1)^1 + 0.42(8a_1)^{-1}(2b_1)^{-1}(3b_1)^1$, and $0.71(6a_1)^{-1}$ – $0.55(1a_2)^{-1}(5b_2)^{-1}(3b_1)^1$. From the coefficients of configurations, we can find that the $(6a_1)^{-1}$ plays an important role in the configurations of 3^2A_1 and 4^2A_1 states. However, the monopole intensity of the 4^2A_1 state is remarkably larger than that of 3^2A_1. Through the above analysis, we assign the 1^2A_1, 1^2B_2, 1^2A_2, 1^2B_1, 2^2A_1, 2^2B_2 and 4^2A_1 states as the $\tilde{X}$, $\tilde{A}$, $\tilde{B}$, $\tilde{C}$, $\tilde{D}$, $\tilde{E}$ and $\tilde{F}$ states of SO_2^+.

From the main configurations of these shake-up states in Table 1, we can find that the HOMO and LUMO orbitals of SO_2 molecule play important roles in the shake-up states of SO_2^+. All of the configurations of these shake-up states have a composition of $(8a_1)^{-1}(3b_1)^1$. Among the shake-up states in our work, the 2^2B_1 state has a 2h1p configuration with a primary configuration of $-0.89(8a_1)^{-2}(3b_1)^1$. The main configuration of 3^2B_1 is the 2h1p state, $(5b_2)^{-2}(3b_1)^1$, with which $(8a_1)^{-1}(7a_1)^{-1}(3b_1)^1$ and $(7a_1)^{-1}$ $(8a_1)^{-1}$ $(3b_1)^1$ are strongly mixed. The main configuration of 4^2B_1 is an admixture of 2h1p configurations, $(1a_1)^{-2}(3b_1)^1$ and $(2b_1)^{-2}(3b_1)^1$. From the configurations of $\tilde{F}^2A_1$ and 3^2A_1 states, we can find that $(6a_1)^{-1}$ is important because of the coefficients 0.71 and 0.53 for these two states. So they may be two spin–orbit split states of $6a_1$ orbital. The main configurations of 2^2A_2, 4^2B_2, 4^2A_2 are $-0.95(8a_1)^{-1}(5b_2)^{-1}$ $(3b_1)^1$, $-0.72(8a_1)^{-1}$ $(1a_2)^{-1}$ $(3b_1)^1$, and $-0.67(8a_1)^{-1}(4b_2)^{-1}(3b_1)^1$, respectively, which are shown to be described dominantly by two-electron processes.

3.2. Equilibrium geometries

In Table 2, the S–O bond length (R_{SO}) and the OSO bond angle ($\angle OSO$) of the ground state ($\tilde{X}^1A_1$) of SO_2 are 0.1430 nm and 119.1°, respectively. Compared with the experimental values[3] R_{SO} = 0.1432 nm and $\angle OSO$ = 119.5°, the results are in good agreement with the measurements within the differences of 0.0002 nm and 0.4°. For the ground state and the exited states of SO_2^+, the bond angles of O–S–O range from 102.7 to 134.9°, and the S–O bond lengths from 0.1427 to 0.1533 nm. In the geometry of the ground state SO_2^+ ion, the S–O bond length is close to that of the ground state SO_2 molecule, while the OSO bond angle is 15.8°, larger than that of the ground state SO_2 molecule. The S–O bond lengths of exited states of SO_2^+ are longer than that of the ground state SO_2 molecule. The OSO bond angles of the three exited states ($\tilde{A}^2B_2$, $\tilde{B}^2A_2$ and $\tilde{E}^2B_2$) are smaller than the angle of the ground state SO_2 molecule, while the OSO bond angles of the other two exited states ($\tilde{C}^2B_1$ and $\tilde{D}^2A_1$) are close to the angle of the ground state SO_2 molecule. Comparing the geometry parameters of excited states of SO_2^+ ion with that of the ground state SO_2^+ ion, all of the bond lengths of excited states are longer than that of the ground state SO_2^+, while the bond angles of excited states are smaller than that of the ground state SO_2^+.

Table 2. Optimized geometry parameters for the ground state of SO_2 and ground and excited states of SO_2^+.

symmetry	SAC-CI/cc-pVTZ		CASPT2/ANO-L[14,15]		SCFMO[12]		Exp[3]	
	R_{SO}/nm	$\angle OSO$/(°)	R_{SO}/nm	$\angle OSO$/(°)	R_{SO}/nm	$\angle OSO$/(°)	R_{SO}/nm	$\angle OSO$/(°)
$\tilde{X}^1A_1$	0.1430	119.1			0.1504	121.0	0.1432	119.5
$\tilde{X}^2A_1$	0.1427	134.9	0.1439	132.0	0.1501	131.6	0.1432*	136.5
$\tilde{A}^2B_2$	0.1487	102.7	0.1491	99.9	0.1571	108.8	0.1432*	102.5
$\tilde{B}^2A_2$	0.1506	108.1	0.1504	109.3	0.1553	104.7		
$\tilde{C}^2B_1$	0.1533	118.2	0.1593	109.2	0.1605	118.4	0.1561	119.5*
$\tilde{D}^2A_1$	0.1504	119.3	0.1533	118.4	0.1581	123.8	0.1514	119.5*
$\tilde{E}^2B_2$	0.1485	110.6	0.1557	101.0	0.1560	110.3		

*assumed to be the same as that of the ground state of neutral SO_2.[3]

Applying the Franck–Condon principle[3] and compared with the angle of the ground state of SO_2, the increased band angle for the $\tilde{X}$ state was estimated to be 17° and the decreased band angle for the $\tilde{A}$ state 17°. From Table 2, the increased angle of the $\tilde{X}^2A_1$ state is 15.8° and the decreased angle of $\tilde{A}^2B_2$ state is 16.4°, which are in reasonable accord with the early measurements.[3] From the above analysis, the two states of SO_2^+ are caused by the excitation of strong bending vibration of SO_2. The bond lengths of $\tilde{C}^2B_1$ and $\tilde{D}^2A_1$ states in their equilibrium geometries are smaller than the experimental values, and the discrepancies between experiment and theory are 0.0028 nm and 0.001 nm, respectively. For the $\tilde{B}^2A_2$ state, the equilibrium geometry is similar to the CASPT2/ANO-L result, while the equilibrium geometry of $\tilde{E}^2B_2$ state is distinctly different from the geometry of CASPT2/ANO-L.

3.3. Adiabatic ionization potentials

In Table 3, the AIPs of six electronic states of SO_2^+ are listed and compared with the previous measurements or the *ab initio* calculated results. The calculated AIPs of SO_2^+ in our work are shown in the second column, the errors between the calculated values and the experiment values are shown in the third column. The results obtained by using the SCFMO[12] method are given in the fourth and fifth columns. The experimental results from the references (Ref.[4] and reference therein) are listed in the sixth, seventh, and eighth columns, respectively. It can be seen from Table 3 that the errors between the calculated values for SAC-CI/cc-pVTZ and the experimental values are 0.2%–4.5%. However, the errors between the calculated values for SCFMO calculation and the experimental values are 1.5%–15.9%. The AIPs of $\tilde{X}^2A_1$ and $\tilde{A}^2B_2$ are lower than the experimental AIPs, but the AIPs of $\tilde{C}^2B_1$, $\tilde{D}^2A_1$ and $\tilde{E}^2B_2$ are higher than the experimental AIPs. The adiabatic ionization potential of $\tilde{B}^2A_2$ state is 13.26 eV, which is close to the experimental value 13.24 eV, though a little lower than the 13.34 eV. Generally speaking, the SAC-CI/cc-pVTZ AIPs are close to the experimental values, better than those obtained by using the SCFMO.

Table 3. The AIPs of ground and exited states of SO_2^+.

symmetry	SAC-CI/cc-pVTZ		SCFMO[12]		Exp[4]		
	AIPs/eV	%	AIPs/eV	%	AIPs/eV	AIPs/eV	AIPs/ eV
$\tilde{X}^2A_1$	12.11	1.6–1.9	11.84	3.8–4.1	12.31		12.35
$\tilde{A}^2B_2$	12.74	2.1–1.9	11.94	8.2–8.1	13.01		12.99
$\tilde{B}^2A_2$	13.26	0.2–0.6	12.88	2.7–3.4	13.24		13.34
$\tilde{C}^2B_1$	16.41	2.7–2.7–3.2	16.23	1.5–1.5–2.1	15.99	15.99	15.90
$\tilde{D}^2A_1$	16.73	2.5–2.5–2.4	17.28	5.8–5.6–5.8	16.33	16.32	16.34
$\tilde{E}^2B_2$	17.01	3.1–3.1	17.21	4.3–4.3		16.50	16.51

4. Conclusions

The SAC-CI general-R method and the SAC-CI SD-R method are applied to studying the ionization spectrum of SO_2. The main peaks of ionization spectra of SO_2 are well obtained by using the SAC-CI general-R method and the SAC-CI SD-R method. According to the VIPs, configurations, and monopole intensities, we assign the electronic states of SO_2^+ as $\tilde{X}^2A_1$, $\tilde{A}^2B_2$, $\tilde{B}^2A_2$, $\tilde{C}^2B_1$, $\tilde{D}^2A_1$, $\tilde{E}^2B_2$ and $\tilde{F}^2A_1$ for the main peaks of ionization spectra of SO_2, which are described dominantly by one-electron process. For the satellite peaks of SO_2, the SAC-CI general-R method reproduces well the structures of the satellite peaks observed by experimental photoelectron spectrum. In the satellite bands, most of the shake-up states are shown to be described dominantly by two-electron processes, and the 2^2B_1, 3^2B_1 and 4^2B_1 states have a considerable number of 2h1p characters. The equilibrium structures and the AIPs for the states of $\tilde{X}^2A_1$-to-$\tilde{E}^2B_2$, calculated by using the SAC-CI SD-R method, are in accord with the experimental results.

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References

[1] Forney D, Kellogg C B, Thompson W E and Jacox M E 2000 *J. Chem. Phys.* **113** 86

[2] Khokhar M F, Frankenberg C, Beirle S, Kühl S, van Roozendael M, Richter A, Platt U and Wagner T 2005 *J. Adv. in Space Res.* **36** 879

[3] Eland J H D and Danby C J 1968 *Int. J. Mass Spectrom. Ion Phys.* **1** 111

[4] Wang L, Lee Y T and Shirley D A 1987 *J. Chem. Phys.* **87** 2489

[5] Holland D M P, MacDonald M A, Hayes M A, Baltzer P, Karlsson L, Lundqvist M, Wannberg B and Niessen W 1994 *Chem. Phys.* **188** 317

[6] Basner R, Schmidi M, Deutsch H, Tarnovsky V, Levin A and Becker K 1995 *J. Chem. Phys.* **103** 211

[7] Vuskovic L and Trajmar S 1982 *J. Chem. Phys.* **77** 5436

[8] Dujardin G and Leach S 1981 *J. Chem. Phys.* **75** 2521

[9] Han X F and Zhang L 2005 *Spectral Analysis of Valance Electronic States and Rydberg States of SO_2 Molecule* Master Dissertation, College of Physical Science and Technology, Heibei University, p36 (in Chinese)

[10] Thomas T F, Dale F and Paulson J F 1986 *J. Chem. Phys.* **84** 1215

[11] Zhang L, Wang Z, Li J, Wang F, Liu S, Yu S and Ma X 2003 *J. Chem. Phys.* **118** 9185

[12] Hillier I H and Saunders V R 1971 *Mol. Phys.* **22** 193

[13] Cederbaum L S, Domcke W, Niessen W V and Kraemer W P 1977 *Mol. Phys.* **34** 381

[14] Li W Z, Huang M B and Chen B Z 2004 *J. Chem. Phys.* **120** 4677

[15] Li W Z and Huang M B 2004 *J. Phys. Chem.* A **108** 6901

[16] Palmer M H, Shaw D A and Guest M F 2005 *Mol. Phys.* **103** 1183

[17] Shi D H, Sun J F, Yang X D, Zhu Z L and Liu Y F 2005 *Chin. Phys.* **14** 1566

[18] Shi D H, Liu Y F, Sun J F, Zhu Z L and Yang X D 2006 *Chin. Phys.* **15** 2928

[19] Liu Y F, Sun J F, Ma H and Zhu Z L 2007 *Chin. Phys.* **16** 680

[20] Yu B H, Shi D H, Sun J F, Zhu Z L, Liu Y F and Ma H 2007 *Chin. Phys.* **16** 2371

[21] Shi D H, Sun J F, Zhu Z L and Liu Y F 2007 *Chin. Phys.* **16** 2701

[22] Hasegawa J, Ehara M and Nakatsuji H 1998 *Chem. Phys.* **230** 23

[23] Ehara M and Nakatsuji H 1999 *Spectrochimica Acta* Part A **55** 487

[24] Ehara M, Ishida M and Nakatsuji H 2002 *J. Chem. Phys.* 117 3248

[25] Ehara M, Yasuda S and Nakatsuji H 2003 *Z. Phys. Chem.* **217** 161

[26] Sankari R, Ehara M, Nakatsuji H, De Fanis A, Aksela H, Sorensen S L, Piancastelli M N, Kukk E and Ueda K 2006 *Chem. Phys. Lett.* **422** 51

[27] Dunning T H 1989 *J. Chem. Phys.* **90** 1007

[28] Woon D E and Dunning T H 1993 *J. Chem. Phys.* **98** 1358

[29] Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, and Nakai H 2005 *SAC/SAC-CI Program Combined with Gaussian for Calculating Ground, Excited, Ionized, and Electron-Attached States and Singlet, Doublet, Triplet, Quartet, Quintet, Sextet, and Septet Spin States and Their Analytical Energy Gradients* (Kyoto: Kyoto University) p7, p38, p52, p150

[30] Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Jr Montgomery J A, Vreven T, Kudin K N, Burant J C, Millam J M, Iyengar S S, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson G A, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox J E, Hratchian H P, Cross J B, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Ayala P Y, Morokuma K, Voth G A, Salvador P, Dannenberg J J, Zakrzewski V G, Dapprich S, Daniels A D, Strain M C, Farkas O, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Ortiz J V, Cui Q, Baboul A G, Clifford S, Cioslowski J, Stefanov B B, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin R L, Fox D J, Keith T, Al-Laham M A, Peng C Y, Nanayakkara A, Challacombe M, Gill P M W, Johnson B, Chen W, Wong M W, Gonzalez C and Pople J A 2003 *Gaussian 03* Revision A.1 (Pittsburgh, PA: Gaussian Inc.)