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The $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states of the SO_2^+ ion studied using multiconfiguration second-order perturbation theory

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The $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ electronic states of the SO_2^+ ion have been studied using multiconfiguration second-order perturbation theory (CASPT2) and two contracted atomic natural orbital basis sets, S[$6s4p3d1f$]/O[$5s3p2d1f$] (ANO-L) and S[$4s3p2d$]/O[$3s2p1d$] (ANO-S), and the three states were considered to correspond to the observed $\tilde{X}$, $\tilde{B}$, and $\tilde{A}$ states, respectively, in the previous experimental and theoretical studies. Based on the CASPT2/ANO-L adiabatic excitation energy calculations, the $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ states of SO_2^+ are assigned to $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$, respectively, and our assignments of the $\tilde{A}$ and $\tilde{B}$ states are contrary to the previous assignments ($\tilde{A}$ to $^2A_2$ and $\tilde{B}$ to $^2B_2$). The CASPT2/ANO-L energetic calculations also indicate that the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states are, respectively, the ground, first excited, and second excited states at the ground-state ($1\,^2A_1$) geometry of the ion and at the geometry of the ground-state SO_2 molecule. Based on the CASPT2/ANO-L results for the geometries, we realize that the experimental geometries (determined by assuming the bond lengths to be the same as the neutral ground state of SO_2) were not accurate. The CASPT2/ANO-S calculations for the potential energy curves as functions of the OSO angle confirm that the $1\,^2B_2$ and $1\,^2A_2$ states are the results of the Renner–Teller effect in the degenerate $^2\Pi_g$ state at the linear geometry, and it is clearly shown that the $1\,^2B_2$ curve, as the lower component of the Renner splitting, lies below the $1\,^2A_2$ curve. The UB3LYP/cc-pVTZ adiabatic excitation energy calculations support the assignments ($\tilde{A}$ to $^2B_2$ and $\tilde{B}$ to $^2A_2$) based on the CASPT2/ANO-L calculations. © *2004 American Institute of Physics.*
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I. INTRODUCTION

The sulfur dioxide ion (SO_2^+) plays an important role in atmospheric chemistry.[1] Numerous experimental studies have been devoted to the SO_2^+ ion, including photoelectron spectroscopy,[2,3] electron impact ionization,[4] photoionization,[5,6] photodissociation spectrum,[7] and photofragment excitation spectrum.[8] Based on the resolutions of the photoelectron spectra (see Ref. 2, and references therein), the $\tilde{X}$ state of SO_2^+ is in the first band and the $\tilde{A}$ and $\tilde{B}$ states are in the second band. The first and second bands are close in energy and the third band is at least 2.5 eV higher in energy than the second band. In the present theoretical work we have studied the three lowest-lying electronic states ($\tilde{X}$, $\tilde{A}$, and $\tilde{B}$) of the SO_2^+ ion.

The experimental adiabatic ionization potential (AIP) values for the $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ states of SO_2^+ were reported to be 12.35, 12.99, and 13.34 eV by Wang *et al.*,[2] and similar values were reported by Holland *et al.*[3] The adiabatic excitation energy (T_0) values for the SO_2^+ ion are considered to be equal to the differences between the AIP values for excited states and the AIP value for the ground state, and therefore the (experimental) T_0 values for the $\tilde{A}$ and $\tilde{B}$ states of SO_2^+ are 0.64 and 0.99 eV, respectively, evaluated using the AIP values of Wang *et al.*[2] The observed vibrational frequencies[7] for the ν_1 and ν_2 modes were reported to be around 1151 and 454 cm^{-1} in the $\tilde{X}$ state and to be around 953 and 499 cm^{-1} in the $\tilde{A}$ state, respectively (frequencies for the ν_3 mode were not reported). Experimental geometries for the $\tilde{X}$ and $\tilde{A}$ states were found in the literature and the S–O bond length and the OSO bond angle were reported to be 1.432 Å and 136.5° for the $\tilde{X}$ state and to be 1.432 Å and 102.5° for the $\tilde{A}$ state, respectively.[9] We note in Ref. 9 that in determination of the geometries for the $\tilde{X}$ and $\tilde{A}$ states the bond lengths were assumed to be the same (1.432 Å) as the neutral ground state of SO_2. Experimental geometric parameters and frequencies for the $\tilde{B}$ state are not available. In all the experimental papers,[2–9] the $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ states of the SO_2^+ ion were assigned to $1\,^2A_1$, $1\,^2A_2$, and $1\,^2B_2$, respectively. These assignments were based on the energy ordering of the three highest occupied molecular orbitals ($\ldots 5b_2^2 1a_2^2 8a_1^2$) in the electronic structure of the ground-state SO_2 molecule.

Theoretical studies should be able to assign the observed electronic states of the SO_2^+ ion and accurate calculations should be able to reproduce the experimental data (for example, geometric and energetic data for the ground and excited states). To our knowledge, there are only two theoretical (*ab initio*) papers on electronic states of the SO_2^+ ion[10,11] in the literature, and both were published in 1970s. Hillier and Saunders[10] performed *ab initio* restricted Hartree–Fock

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(RHF) calculations for electronic states of SO_2^+. Their calculated AIP values for the $(1)\,^2A_1$, $(1)\,^2A_2$, and $(1)\,^2B_2$ states of SO_2^+ were 11.84, 11.94, and 12.88 eV, respectively, which indicated that the $1\,^2A_1$, $1\,^2A_2$, and $1\,^2B_2$ states corresponded to the $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ states, respectively, and the calculated equilibrium geometries were also reported.[10] Cederbaum *et al.*[11] performed Green's function calculations for the vertical ionization potentials for the three lowest-lying states of SO_2^+. Their "final" calculation results indicated that at the geometry of the ground-state SO_2 molecule the three lowest-lying states of SO_2^+ were $^2A_1$, $^2A_2$, and $^2B_2$, in an increasing order of energy. These two theoretical papers supported the assignments ($\tilde{X}$ to $1\,^2A_1$, $\tilde{A}$ to $1\,^2A_2$, and $\tilde{B}$ to $1\,^2B_2$) presented in the experimental papers.[2–9]

It is known that the CASSCF (complete active space self-consistent field)[12] and CASPT2 (multiconfiguration second-order perturbation theory)[13,14] methods are effective for theoretical studies of excited electronic states of molecules. We have studied the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states of the SO_2^+ ion by using the CASPT2 method, and in the present article we will present our assignments of the $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ states of the SO_2^+ ion based on our CASPT2 calculations. We will report the CASPT2 results for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states, which include equilibrium geometries, adiabatic excitation energies, vertical excitation energies, and potential energy curves, and we will compare the results with available experimental data for the $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ states. We also performed the CASSCF and density functional theory (DFT) UB3LYP calculations for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states.

II. CALCULATION DETAILS

We performed the CASPT2, CASSCF, and UB3LYP calculations for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states of the SO_2^+ ion, though the main conclusions of the present study will be drawn on the basis of the CASPT2 calculation results. For confirming that the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states are the three lowest-lying states of the ion, we also performed CASPT2 energetic calculations for some higher-lying states (see Sec. III).

The CASSCF and CASPT2 calculations were carried out using the MOLCAS 5.2 quantum-chemistry software.[15] With a CASSCF wave function constituting the reference function the CASPT2 calculations were performed to compute the first-order wave function and the second-order energy in the full-CI space. In the CAS calculations we used two contracted atomic natural orbital (ANO) basis sets,[16–18] S[6*s*4*p*3*d*1*f*]/O[5*s*3*p*2*d*1*f*] and S[4*s*3*p*2*d*]/O[3*s*2*p*1*d*], denoted as ANO-L and ANO-S, respectively.

The equilibrium geometries of the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states were predicted by performing the CASSCF/ANO-L geometry optimization calculations and by the CASPT2/ANO-L stepwise geometry optimization calculations. The vibrational frequencies in the three states were calculated only at the CASSCF/ANO-L level. Based on the CASPT2/ANO-L energies of the three states calculated at the respective geometries optimized at the CASSCF/ANO-L, CASPT2/ANO-L, and UB3LYP/cc-pVTZ (see the following) levels, we obtained the CASPT2/ANO-L//CASSCF/ANO-L, CASPT2/ANO-L//CASPT2/ANO-L, and CASPT2/ANO-L//UB3LYP/cc-pVTZ (abbreviated to "CASPT2//CASSCF," "CASPT2//CASPT2," and "CASPT2//UB3LYP," respectively) adiabatic excitation energy (T_0) values for the three states. Based on the CASPT2/ANO-L energies of the three states calculated at the CASSCF/ANO-L, CASPT2/ANO-L, and UB3LYP/cc-pVTZ optimized geometries of the $1\,^2A_1$ ($\tilde{X}\,^2A_1$) state, we obtained the CASPT2//CASSCF, CASPT2//CASPT2, and CASPT2//UB3LYP vertical excitation energy (T_v) values for the three states. The potential energy curves of the three states as functions of the OSO bond angle were calculated at the CASPT2/ANO-S level. In the CASPT2/ANO-S curve calculations, the OSO angle ranged from 60° to 180° and the S–O bond length value was fixed at 1.4489 Å, which is the bond length value in the CASSCF/ANO-S optimized geometry for the $1\,^2A_1$ ($\tilde{X}\,^2A_1$) state. In all the CASPT2 calculations performed in the present work the weight values of the CASSCF reference functions in the first-order wave functions were larger than 0.87 (for the three states).

In our CASSCF calculations, eleven electrons were active and the active space included thirteen orbitals [CASSCF(11,13)]. The choice of this active space stemmed from the molecular orbital (MO) sequence in the ground-state SO_2 molecule. Based on the HF/6-31+G(*d*) calculations for the SO_2 molecule, the twelve valence molecular orbitals (MOs) are listed in the following sequence: $5a_1 3b_2 6a_1 4b_2 7a_1 2b_1 5b_2 1a_2 8a_1 3b_1 9a_1 10a_1$. The MOs in the sequence are given in an increasing order of the MO energy and the last three are unoccupied. Our active space was formed from the full-valence active space (see the sequence) by deleting the $5a_1$, $3b_2$, and $6a_1$ MOs (the energy gap between $6a_1$ and $4b_2$ being larger than 5 eV) and by adding four virtual MOs ($6b_2$, $4b_1$, $11a_1$, and $7b_2$) lying above $10a_1$. Labeling the orbitals within the C_{2v} point group in the order of a_1, a_2, b_2, and b_1, this active space is named (5143).

We also calculated the six lowest-lying electronic states of SO_2^+ at the linear geometry at the CASPT2/ANO-S level. The calculations were carried out in the D_{2h} group, and the calculation details will be given in Sec. III C.

We also performed DFT (density functional theory[19,20]) B3LYP (Becke's three-parameter hybrid function[21] with the nonlocal correlation of Lee–Yang–Parr[22]) and *ab initio* MP2 (second-order Møller–Plesset perturbation theory[23,24]) calculations for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states. In these calculations we used the GAUSSIAN 98W suite of programs[25] and the cc-pVTZ basis set.[26] The UB3LYP/cc-pVTZ calculation results for $1\,^2A_2$ are probably not so reliable since the spin contamination was relatively large ($\langle S^2\rangle = 0.832$). In the UMP2/cc-pVTZ calculations the $\langle S^2\rangle$ value for $1\,^2A_2$ was as large as 1.210 and the $\langle S^2\rangle$ value for $1\,^2B_2$ was also quite large. We will not report the UMP2/cc-pVTZ results. The UMP method and other *ab initio* methods based on spin-unrestricted theory are not appropriate for a theoretical study of these states.

TABLE I. CASPT2/ANO-L optimized geometries for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states of SO_2^+, together with the CASSCF/ANO-L and UB3LYP/cc-pVTZ optimized geometries (bond lengths are in angstroms and angles in degrees).

	CASSCF		UB3LYP[a]		CASPT2			Experimental[b]	
State	R(S–O)	∠OSO	R(S–O)	∠OSO	R(S–O)	∠OSO		R(S–O)	∠OSO
$1\,^2A_1$	1.439	127.7	1.446	131.0	1.439	132.0	$\tilde{X}$:	1.432	136.5
$1\,^2B_2$	1.492	100.1	1.490	100.0	1.491	99.9	$\tilde{A}$:	1.432	102.5
$1\,^2A_2$	1.507	109.3	1.516	108.5	1.504	109.3			

[a]Spin contamination was relatively large for the $1\,^2A_2$ state ($\langle S^2\rangle = 0.832$).
[b]Reference 9, in which the bond lengths were assumed to be the same as the neutral ground state of SO_2.

III. RESULTS AND DISCUSSION

In Table I are given the CASSCF/ANO-L, UB3LYP/cc-pVTZ, and CASPT2/ANO-L optimized geometries for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states of the SO_2^+ ion. In Table II are given the CASSCF/ANO-L frequency values for the ν_1 and ν_2 modes in the three states. In Table III are given the CASPT2//CASSCF (CASPT2/ANO-L//CASSCF/ANO-L), CASPT2//UB3LYP (CASPT2/ANO-L//UB3LYP/cc-pVTZ), and CASPT2//CASPT2 (CASPT2/ANO-L//CASPT2/ANO-L) adiabatic excitation energies (T_0) and vertical excitation energies (T_v) for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states of the SO_2^+ ion. These CASPT2 energetic results indicate that $1\,^2A_1$ is the ground state ($\tilde{X}\,^2A_1$) of the SO_2^+ ion (see Sec. III B).

For confirming that the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states are the three lowest-lying electronic states of SO_2^+, we calculated the CASPT2/ANO-L T_v values for the $2\,^2A_1$, $2\,^2B_2$, $2\,^2A_2$, and $1\,^2B_1$ states at the CASPT2/ANO-L optimized geometry of the $1\,^2A_1$ ($\tilde{X}\,^2A_1$) state. The calculated (CASPT2//CASPT2) T_v values for these four states were all larger than 4.4 eV and they are much higher in energy than the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states (see the CASPT2//CASPT2 T_v values for $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ in Table III).

A. Equilibrium geometries

In the CASPT2/ANO-L optimized geometry for the $1\,^2A_1$ ($X\,^2A_1$) state the S–O bond length [R(S–O)] and the OSO bond angle (∠OSO) are 1.439 Å and 132.0°, respectively (see Table I). The bond angle value in the CASSCF/ANO-L geometry is 4.3° smaller than that in the CASPT2/ANO-L geometry. The UB3LYP/cc-pVTZ geometry [R(S–O) = 1.446 Å and ∠OSO = 131.0°; $\langle S^2\rangle = 0.757$] is similar to the CASPT2/ANO-L geometry. We believe that the UB3LYP/cc-pVTZ calculations predict reliable geometries when spin contaminations are small (for example, $\langle S^2\rangle < 0.77$ for doublet species).

TABLE II. CASSCF/ANO-L frequency values (in cm^{-1}) for the ν_1 and ν_2 modes in the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states of SO_2^+.

State	ν_1	ν_2		Experimental[a]
$1\,^2A_1$	1049.6	424.0	$\tilde{X}$:	$\nu_1(\sim 1151)$, $\nu_2(\sim 454)$
$1\,^2B_2$	1084.6	443.9	$\tilde{A}$:	$\nu_1(953)$, $\nu_2(499)$
$1\,^2A_2$	1032.2	467.8		

[a]Reference 7.

In the CASPT2/ANO-L optimized geometry for the $1\,^2B_2$ state the S–O bond length and the OSO bond angle are 1.491 Å and 99.9°, respectively (see Table I). The CASSCF/ANO-L geometry [R(S–O) = 1.492 Å and ∠OSO = 100.1°] and the UB3LYP/cc-pVTZ geometry [R(S–O) = 1.490 Å and ∠OSO = 100.0°; $\langle S^2\rangle = 0.761$] are almost identical to the CASPT2/ANO-L geometry. In the CASPT2/ANO-L optimized geometry for the $1\,^2A_2$ state the S–O bond length and the OSO bond angle are 1.504 Å and 109.3°, respectively (see Table I). The CASSCF/ANO-L geometry [R(S–O) = 1.507 Å and ∠OSO = 109.3°] is almost identical to the CASPT2/ANO-L geometry. The UB3LYP/cc-pVTZ geometry [R(S–O) = 1.516 Å and ∠OSO = 108.5°; $\langle S^2\rangle = 0.832$] is quite close to the CASPT2/ANO-L geometry though the spin contamination was relatively large.

It is noted that the CASPT2/ANO-L geometry for the $1\,^2A_1$ ($X\,^2A_1$) state is significantly different from the experimental geometry for the $\tilde{X}$ state and the CASPT2/ANO-L geometries for the $1\,^2B_2$ and $1\,^2A_2$ states are both far from the experimental geometry for the $\tilde{A}$ state. We realize that those experimental geometries[9] for the $\tilde{X}$ and $\tilde{A}$ states of SO_2^+ were not accurately determined, and it is not possible to assign the $\tilde{A}$ state of SO_2^+ (to $1\,^2B_2$ or $1\,^2A_2$) based on the calculation results for geometries. The previous RHF calculations[10] predicted a S–O bond length value of 1.501 Å for the $1\,^2A_1$ state, which is much larger than the CASPT2/ANO-L value. The RHF geometries[10] for the $1\,^2B_2$ [R(S–O) = 1.553 Å and ∠OSO = 104.7°] and $1\,^2A_2$ [R(S–O) = 1.571 Å and ∠OSO = 108.8°] states are significantly different from the CASPT2/ANO-L geometries for the respective states (the RHF bond lengths were too long).

The experimental frequency values for the ν_1 and ν_2 vibrational modes in the $\tilde{X}$ and $\tilde{A}$ states of SO_2^+ were reported in several papers (see Ref. 7, and references therein). We calculated the ν_1 and ν_2 frequency values in the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states of SO_2^+ at the CASSCF/ANO-L level using the MCLR program of the MOLCAS software. The calculated ν_1 (1049 cm^{-1}) and ν_2 (424 cm^{-1}) values in the $1\,^2A_1$ state are slightly smaller than the experimental ν_1 (1151 cm^{-1}) and ν_2 (454 cm^{-1}) values in the $\tilde{X}$ state,[7] respectively. The calculated ν_1 values in the $1\,^2B_2$ and $1\,^2A_2$ states are similar and they are slightly larger than the experimental ν_1 value in the $\tilde{A}$ state; and the calculated ν_2 values in the $1\,^2B_2$ and $1\,^2A_2$ states are also similar and they are slightly smaller than the experimental ν_2 value in the $\tilde{A}$ state

TABLE III. CASPT2 adiabatic (T_0) and vertical (T_v) excitation energies (in eV) for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states of SO_2^+ calculated using the CASSCF, UB3LYP, and CASPT2 optimized geometries, together with the CASSCF and UB3LYP adiabatic excitation energies.[a]

		CASSCF	UB3LYP[b]	CASPT2				
	State			//CASSCF	//UB3LYP	//CASPT2	Experimental[c]	
T_0	$1\,^2A_1$	0.00	0.00	0.00	0.00	0.00		0.00
	$1\,^2B_2$	−0.06	0.34	0.54	0.56	0.56	$\tilde{A}$:	0.64
	$1\,^2A_2$	0.03	0.84[b]	1.20	1.21	1.21	$\tilde{B}$:	0.99
T_v	$1\,^2A_1$			0.00	0.00	0.00		
	$1\,^2B_2$			1.52	1.69	1.79		
	$1\,^2A_2$			1.82	1.95	2.04		

[a]The ANO-L basis was used in the CASSCF and CASPT2 calculations and the cc-pVTZ basis was used in the UB3LYP calculations.
[b]Spin contamination was relatively large for the $1\,^2A_2$ state ($\langle S^2\rangle = 0.832$).
[c]Evaluated using the experimental adiabatic ionization potential data reported in Ref. 2.

(see Table II). It is not possible to assign the $\tilde{A}$ state of SO_2^+ (to $1\,^2B_2$ or $1\,^2A_2$) based on the calculation results for frequencies.

B. Adiabatic and vertical excitation energies

The CASPT2//CASSCF, CASPT2//UB3LYP, and CASPT2//CASPT2 adiabatic excitation energy (T_0) values for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states of the SO_2^+ ion (see Table III) indicate that the $1\,^2A_1$ state is the ground state ($\tilde{X}\,^2A_1$) of SO_2^+ and that $1\,^2B_2$ and $1\,^2A_2$ are the first and second excited states, respectively. At the CASPT2//CASPT2 level the T_0 values for the $1\,^2B_2$ and $1\,^2A_2$ states are predicted to be 0.56 and 1.21 eV, respectively. The CASPT2//CASSCF and CASPT2//UB3LYP T_0 values for the $1\,^2B_2$ and $1\,^2A_2$ states are very close to the CASPT2//CASPT2 values for the respective states. The experimental T_0 values for the $\tilde{A}$ and $\tilde{B}$ states of the SO_2^+ ion are evaluated to be 0.64 and 0.99 eV, respectively, based on the experimental AIP data.[2] The CASPT2//CASPT2 T_0 value of 0.56 eV for $1\,^2B_2$ is 0.06 eV smaller than the experimental T_0 value for the $\tilde{A}$ state and the CASPT2//CASPT2 T_0 value of 1.21 eV for $1\,^2A_2$ is 0.22 eV larger than the experimental T_0 value for the $\tilde{B}$ state. We assign the $\tilde{A}$ state of SO_2^+ to $1\,^2B_2$ and the $\tilde{B}$ state to $1\,^2A_2$. These assignments based on the CASPT2//CASPT2 T_0 values are unambiguous, since the smaller one of the two calculated T_0 values is smaller than the smaller one of the two experimental T_0 values and the larger one of the two calculated T_0 values is larger than the larger one of the two experimental T_0 values. We consider that the deviation of 0.06 eV is small and the deviation of 0.22 eV is not large. Our assignments of the $\tilde{A}$ and $\tilde{B}$ states of SO_2^+ ($\tilde{A}$ to $^2B_2$ and $\tilde{B}$ to $^2A_2$) are contrary to the assignments ($\tilde{A}$ to $^2A_2$ and $\tilde{B}$ to $^2B_2$) presented in the previous experimental papers[2–7] based on the energy ordering of the three highest occupied molecular orbitals in the electronic structure of the ground-state SO_2 molecule and in the previous theoretical paper[10] based on the RHF calculations.

The CASPT2//CASSCF, CASPT2//UB3LYP, and CASPT2//CASPT2 vertical excitation energy (T_v) values for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states of the SO_2^+ ion (see Table III) indicate that the $1\,^2B_2$ and $1\,^2A_2$ states are the first and second excited states, respectively, at the ground-state ($1\,^2A_1$) geometry of the SO_2^+ ion. At the CASPT2//CASPT2 level the T_v values for the $1\,^2B_2$ and $1\,^2A_2$ states are predicted to be 1.79 and 2.04 eV, respectively. The CASPT2//CASSCF and CASPT2//UB3LYP T_v values for the $1\,^2B_2$ and $1\,^2A_2$ states are smaller than the CASPT2//CASPT2 values for the respective states (see Table III). Experimental data for the vertical excitation energies are not available. We also performed the CASPT2/ANO-L energetic calculations for the three states of SO_2^+ at the experimental geometry[27] [R(S–O) = 1.432 Å and ∠OSO = 119.5°] of the ground-state SO_2 molecule, and the relative energies for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states are 0.00, 1.01, and 1.45 eV, respectively. These values indicate that the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states are the ground state, the first excited state, and the second excited states of SO_2^+, respectively, at the geometry of the ground-state SO_2 molecule. It is noted that the energy ordering ($1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$) for the three states at the geometry of the ground-state SO_2 molecule indicated by the CASPT2/ANO-L calculations is not the same as the ordering ($^2A_1$, $^2A_2$, and $^2B_2$) indicated by the Green's function calculations.[11]

The CASSCF (CASSCF/ANO-L//CASSCF/ANO-L) and UB3LYP (UB3LYP/cc-pVTZ//UB3LYP/cc-pVTZ) adiabatic excitation energy values for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states are also given in Table III. The CASSCF T_0 values (−0.06 and 0.03 eV for $1\,^2B_2$ and $1\,^2A_2$, respectively) are very small and they are far from the CASPT2//CASSCF (and CASPT2//CASPT2) values and from the experimental values, which indicates that dynamic electron correlation effects are important in these states. Though the UB3LYP T_0 values (0.34 and 0.84 eV for $1\,^2B_2$ and $1\,^2A_2$, respectively) are not in very good agreement with the experimental values and there was relatively large spin contamination for the $1\,^2A_2$ state, the UB3LYP/cc-pVTZ adiabatic excitation energy calculations support the assignments ($\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ states to $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$, respectively) based on the CASPT2/ANO-L calculations.

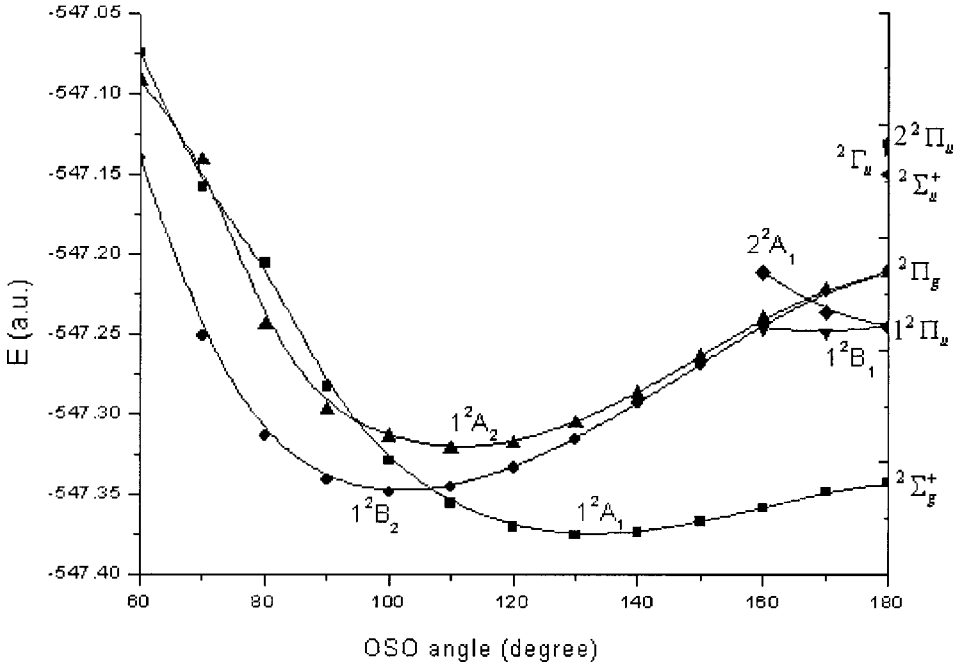

FIG. 1. CASPT2/ANO-S potential energy curves for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states of SO_2^+, as functions of the OSO bond angle.

C. Potential energy curves

The CASPT2/ANO-S potential energy curves for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states of SO_2^+, as functions of the OSO bond angle, are given in Fig. 1. The minima along the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ curves were located at the OSO bond angle values of 133°, 102°, and 112°, which are quite close to the bond angle values in the CASPT2/ANO-L geometries (see Table I) of the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states, respectively. The relative values (0.00, 0.76, and 1.51 eV) for the CASPT2/ANO-S energies at these minima are in the order of $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$, and at the OSO angle values of 133° (see above) and 119.5° (the experimental bond angle value for the ground-state SO_2 molecule[27]) the $1\,^2A_1$ state is the lowest-lying state and the $1\,^2B_2$ state lies below $1\,^2A_2$. These facts are in line with the CASPT2/ANO-L energetic results reported in Sec. III B. It is noted that the $1\,^2B_2$ state is lower in energy than $1\,^2A_1$ when the OSO angle is smaller than 106°.

Low-lying electronic states of the SO_2^+ ion at the linear geometry with the S–O bond length of 1.4489 Å (see Sec. II) were calculated at the CASPT2/ANO-S level. The calculations were carried out in the D_{2h} subgroup of $D_{\infty h}$, where Σ_g^+ corresponds to the A_g irreducible representation, Σ_u^+ to B_{1u}, Π_g to $B_{2g}+B_{3g}$, Π_u to $B_{2u}+B_{3u}$, and Γ_u to A_u+B_{1u}. The CASPT2 calculations in the D_{2h} point group were still based on the CASSCF(11,13) calculations (eleven electrons were active and the active space included thirteen orbitals, see Sec. II). Labeling the orbitals within the D_{2h} point group in the order of a_g, b_{3u}, b_{2u}, b_{1g}, b_{1u}, b_{2g}, b_{3g}, and a_u, an active space named (23302210) was used. It is equivalent to the (5143) active space (labeling the orbitals within the C_{2v} point group, see Sec. II). In the CASSCF calculation steps of our CASPT2/ANO-S calculations for the electronic states at the linear geometry, the state-averaging technique was used. The averaging includes all the states of interest for a given symmetry of the D_{2h} group.

Our CASPT2/ANO-S calculations predict that the $^2\Sigma_g^+$, $(1)^2\Pi_u$, $^2\Pi_g$, $^2\Sigma_u^+$, $^2\Gamma_u$, and $(2)\,^2\Pi_u$ states (see Fig. 1) are the six lowest-lying states of the SO_2^+ ion at the linear geometry, and the CASPT2/ANO-S relative energies for these states are 0.0, 2.66, 3.59, 5.24, 5.65, and 5.73 eV, respectively. In Fig. 1 the following state-correlations are shown: the $1\,^2A_1(\tilde{X}\,^2A_1)$ curve converges to the $(\tilde{X})^2\Sigma_g^+$ state at the linear geometry; both the $1\,^2B_2$ and $1\,^2A_2$ curves converge to the degenerate $^2\Pi_g$ state, which is the third lowest-lying state at the linear geometry; and the second lowest-lying state $[(1)\,^2\Pi_u]$ is correlated to $1\,^2B_1$ and $2\,^2A_1$, which are high-lying states at the ground-state $(\tilde{X}\,^2A_1)$ geometry of the SO_2^+ ion (see the beginning of Sec. III).

The $1\,^2B_2$ and $1\,^2A_2$ states are considered as the results of the Renner–Teller effect[28] in the degenerate $^2\Pi_g$ state. Since each of the $1\,^2B_2$ and $1\,^2A_2$ states has one minimum at an OSO angle value not equal to 180°, the Renner-splitting pattern for the $^2\Pi_g$ state is pattern (c) of Pople and Longuet-Higgin's scheme.[29] The most important fact shown in Fig. 1 is that the curve for the $1\,^2B_2$ state (the lower component of the Renner splitting) lies below the curve for the $1\,^2A_2$ state (the upper component). The $1\,^2B_1$ and $2\,^2A_1$ states are the results of the Renner–Teller effect in the $(1)\,^2\Pi_u$ state, and we will not discuss them in the present paper.

IV. CONCLUSIONS

The three lowest-lying electronic states of the SO_2^+ ion, $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$, were studied using the CASPT2 method and two contracted ANO basis sets, S[6*s*4*p*3*d*1*f*]/O[5*s*3*p*2*d*1*f*] (ANO-L) and S[4*s*3*p*2*d*]/O[3*s*2*p*1*d*] (ANO-S).

The CASPT2/ANO-L geometries for the $1\,^2A_1$ [R(S–O)=1.439 Å and ∠OSO=132.0°], $1\,^2B_2$ [R(S–O)=1.491 Å and ∠OSO=99.9°), and $1\,^2A_2$ [R(S–O)

$=1.504$ Å and $\angle$OSO$=109.3°$] states are compared with the experimental geometries for the $\tilde{X}$ [R(S–O)$=1.432$ Å and $\angle$OSO$=136.5°$] and $\tilde{A}$ [R(S–O)$=1.432$ Å and $\angle$OSO $=102.5°$] states. We realize that the experimental geometries (reported in Ref. 9) for the $\tilde{X}$ and $\tilde{A}$ states of the SO_2^+ ion were not accurately determined since the bond length values were assumed to be 1.432 Å. The CASSCF/ANO-L frequency calculations predict similar ν_1 values and similar ν_2 values for the $1\,^2B_2$ and $1\,^2A_2$ states. It is not possible to assign the $\tilde{A}$ state of SO_2^+ (to $1\,^2B_2$ or $1\,^2A_2$) based on the calculation results for geometries and vibrational frequencies.

Based on the CASPT2/ANO-L T_0 calculations, the observed $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ states of the SO_2^+ ion are assigned to $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$, respectively. The CASPT2// CASPT2 T_0 values of 0.56 and 1.21 eV for $1\,^2B_2$ and $1\,^2A_2$ are in reasonable agreement with the experimental values of 0.64 and 0.99 eV (based on the experimental AIP data) for the $\tilde{A}$ and $\tilde{B}$ states, respectively. Our assignments of the $\tilde{A}$ and $\tilde{B}$ states ($\tilde{A}$ to $^2B_2$ and $\tilde{B}$ to $^2A_2$) are contrary to the assignments ($\tilde{A}$ to $^2A_2$ and $\tilde{B}$ to $^2B_2$) presented in the previous experimental papers based on the energy ordering of the three highest occupied molecular orbitals in the electronic structure of the ground-state SO_2 molecule and in the previous theoretical paper based on the RHF calculations. The CASPT2/ANO-L energetic calculations also indicate that the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states are, respectively, the ground, first excited, and second excited states of SO_2^+ at the ground-state ($1\,^2A_1$) geometry of the ion and at the geometry of the ground-state SO_2 molecule.

The potential energy curves for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states of SO_2^+ were calculated as functions of the OSO angle (ranging from 60° to 180°) at the CASPT2/ANO-S level, and the six lowest-lying states of SO_2^+ at the linear geometry were also calculated at the same level. These CASPT2/ANO-S calculations confirm that the $1\,^2B_2$ and $1\,^2A_2$ states are the results of the Renner–Teller effect in the degenerate $^2\Pi_g$ state at the linear geometry, and it is clearly shown that the curve for the $1\,^2B_2$ state (the lower component of the Renner splitting) lies below the curve for the $1\,^2A_2$ state (the upper component).

The UB3LYP/cc-pVTZ calculations were performed for the $1\,^2A_1$, $1\,^2B_2$, and $1\,^2A_2$ states of SO_2^+ (spin contamination for $1\,^2A_2$ was relatively large). The UB3LYP/cc-pVTZ geometries for the three states are similar to the CASPT2/ANO-L geometries for the respective states. The UB3LYP/cc-pVTZ adiabatic excitation energy calculations support the assignments ($\tilde{X}$ to $1\,^2A_1$, $\tilde{A}$ to $1\,^2B_2$, and $\tilde{B}$ to $1\,^2A_2$) based on the CASPT2/ANO-L calculations. The UMP2 method is not appropriate for a theoretical study of these states due to large spin contaminations for $1\,^2A_2$ and $1\,^2B_2$. The CASSCF calculations predict no good results for the T_0 values, which indicates that dynamic electron correlation effects are important in these states.

Theoretical study for higher-lying states in the third band ($\tilde{C}$, $\tilde{D}$, and $\tilde{E}$) of the photoelectron spectrum of SO_2^+ is in progress. Preliminary CAS calculations indicate that in that energy region there may be more states including shake-up ionized states.

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