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Theoretical calculations of $C_{2\nu}$ excited states of SO_2^+

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ARTICLE INFO	ABSTRACT
Article history: Received 15 September 2009 In final form 29 December 2009 Available online 4 January 2010	The ${}^{2}B_{2}$, ${}^{2}A_{2}$ and ${}^{2}B_{1}$ ionic excited states of sulfur dioxide were studied by quantum calculations with the density functional theory (B3LYP functional) and the coupled cluster singles and doubles with perturbative triples [CCSD(T)] methods. The optimized structure of the ${}^{2}B_{2}$ state was of a transition state correlating to an equilibrium geometry of the C_{s} point group, contrary to previous studies. The ${}^{2}B_{1}$ state has two equilibrium structures of a bent and a cyclic geometry. By the computation of Franck–Condon factors, the photoelectron spectrum of the ${}^{2}A_{2}$ state was simulated and was found to be in agreement with the experiment, but with different assignments.

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1. Introduction

In a series of studies [1-4], we developed a method for calculating Franck-Condon factors (FCFs) of harmonic oscillators taking into account the Duschinsky effect [5], from which vibronic spectra of polyatomic molecules can be simulated. In the study of the photoelectron spectroscopy (PES) of $H_2O^+(\tilde{B}^2B_2)$ [3], it was found that the first peak did not correspond to the adiabatic transition, in conflict with the assignment of experimentalists [6]. In another study of the PES of the ground-state $SO_2^+(\tilde{X}^2A_1)$ [4], some splitting peaks, which had been regarded as an evidence of a potential barrier by previous researchers [7,8], were identified as signals contributing from combination and hot bands, in addition to the progressions of a single mode. It seems that even for small polyatomic molecules, earlier assignments of vibronic or photoelectron spectroscopy without theoretical interpretation of intensity distribution deserve reexamination, needless to say large molecules. The best marriage of quantum theory and experimental spectroscopy should be that both of the calculated energy and intensity distribution is closely matched with experiments.

In this work, the PES of $C_{2\nu}$ excited states of SO_2^+ was investigated by theoretical calculations. Sulfur dioxide is of interest due to its importance in astrophysics and atmospheric chemistry. For example, it plays a role in the chemistry of Venus' atmosphere [9] and exists in the interstellar medium [10]. It is also well known that combustion of sulfur-containing coals produces gaseous SO_2 which is a source of acid rain.

The SO_2^+ ion has been investigated by various experimental techniques, e.g., photoelectron [7,8,11,12], photoionization [13–16], photodissociation [17,18], electron impact [19], spectroscopy,

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etc. Conversely, theoretical studies of SO₂⁺ were rare. Hillier and Saunders performed Hartree–Fock calculations of electronic states of SO₂⁺ in 1971 [20]. They found that the first four electronic states, with energy in increasing order, were ${}^{2}A_{1}$, ${}^{2}A_{2}$, ${}^{2}B_{2}$, and ${}^{2}B_{1}$. Lauer et al., in 1975, reported the same order of ionic states by adopting a semiempirical configuration interaction approach to calculate the vertical ionization potentials of SO₂ [21]. Cederbaum et al. computed the ionization potentials and the vibrational structure of SO_2^+ by using the Green's function method in 1977 [22]. They obtained that the first three ionic states were ²A₁, ²A₂, and ²B₂, in accord with Hillier and Saunders's calculations [20]. In the 1980s and 1990s, the experimental spectroscopy of SO₂⁺ was usually interpreted based on the above theoretical works. However, Li et al. argued that the electronic states of SO_2^+ need be reassigned according to their calculations in 2004 by using the complete active-space self-consistent field (CASSCF) and multiconfiguration second-order perturbation theory (CASPT 2) [23,24]. For example, the \tilde{A} and \tilde{B} states of SO_2^+ should be 2B_2 and 2A_2 [23], respectively, contrary to the previous assignments (\tilde{A}^2A_2 and \tilde{B}^2B_2) [7,8]. The CASSCF and CASPT 2 methods are, of course, anticipated to give more accurate energies than the calculations in the 1970s [20-22]. Nonetheless, Li et al. reassigned the electronic states of SO_2^+ from the viewpoint of ionization energy [23,24], whereas the intensity distribution of the PES was not accounted for. Meanwhile, Li et al. computed the vibrational frequencies only for v_1 and v_2 , but not v_3 . Therefore, the geometries optimized by them might correspond to either equilibrium or transition structures, albeit they presumed that those were equilibrium geometries [23,24].

The purpose of this study was to investigate the $C_{2\nu}$ excited states of SO₂⁺ by using the density functional theory (B3LYP functional) and the coupled cluster singles doubles and perturbative triples [CCSD(T)] method. The lowest-energy states of each symmetry species (i.e., ²B₂, ²A₂ and ²B₁) were considered. It was found

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Table 1 Optimized stationary points in $C_{2\nu}$ symmetry for excited states of SO₂⁺.

Method	² B ₂		² A ₂	² A ₂		² B ₁ (bent)		² B ₁ (cyclic)	
	R ^a	A (°)	R	A (°)	R	A (°)	R	A (°)	
B3LYP/6-311+G(2d)	148.13	100.0	150.40	108.8	152.54	117.5	160.61	57.8	
B3LYP/6-311+G(3d)	147.57	100.5	149.84	109.1	151.69	117.9	160.10	58.1	
B3LYP/6-311+G(3df)	147.13	100.3	149.30	109.3	151.05	117.7	158.97	58.3	
B3LYP/aug-cc-pVTZ	148.42	99.5	150.72	108.5	152.83	116.5	160.13	61.1	
CCSD(T)/6-311+G(2d)	149.42	99.6	151.04	108.8	160.88	110.7	161.78	59.5	
CCSD(T)/6-311+G(3d)	148.91	99.8	150.61	108.7	159.57	111.2	161.28	59.7	
CCSD(T)/6-311+G(3df)	147.88	100.0	149.44	109.3	156.42	113.0	159.30	59.6	
CCSD(T)/aug-cc-pVTZ	149.40	99.2	150.98	108.5	159.10	111.1	160.62	59.2	
CASSCF/cc-pVTZ	149.70	100.1							
CASSCF/ANO-L ^b	149.2	100.1	150.7	109.3	159.3	109.2	160.0	60.8	

^a *R* and *A* stand for the SO bond length (in pm) and the OSO bond angle, respectively.

^b Refs. [23,24].

that the results of the B3LYP and CCSD(T) calculations were consistent with those of the CASSCF and CASPT 2 calculations by Li et al. [23,24]. However, the optimized geometry of the ²B₂ state is identified as a transition structure in the present study. Moreover, the ²B₂ state correlates to an equilibrium structure of the C_s point group as shown by our CASSCF computations. Meanwhile, both the calculated adiabatic ionization energy (AIE) and the simulated PES of the ²A₂ state are in agreement with the experiment, showing that the \tilde{B} state of SO₂⁺ is of the ²A₂ symmetry as proposed by Li et al. [23].

2. Computational methods

The equilibrium geometries and harmonic vibrational frequencies of SO_2^+ were calculated by using the unrestricted B3LYP and CCSD(T) methods with four basis sets up to 6-311+G(3df) and aug-cc-pVTZ. Corresponding computations for the ground-state of SO₂ have been published elsewhere [4]. For the ²B₂ state, which was inferred to have a *C_s* equilibrium structure, we also performed the CASSCF calculations. The PES of the ²A₂ state was simulated by computing FCFs with the method developed by our group [3,4], in which harmonic oscillators with the Duschinsky effect were taken into account. The AIE was obtained by extrapolating CCSD(T) energies to the complete basis set (CBS) limit [25] with aug-cc-pVXZ (X = D, T, Q, 5). While the B3LYP and CCSD(T) calculations were performed by using the GAUSSIAN 03 package [26], the CASSCF by using the MOLPRO 2008.1 programs [27].

3. Results and discussion

3.1. Optimized geometries and vibrational frequencies

Table 1 lists the optimized geometries of the $C_{2\nu}$ excited states of SO₂⁺ and Table 2 depicts their harmonic vibrational frequencies. The results of the CASSCF calculations by us and by Li et al. [23,24] are also given for comparison. The frequency calculations for the ²B₂ and the ²B₁(bent) states were unsuccessful. The structures optimized by the B3LYP, CCSD(T) and CASSCF methods are generally in agreement with each other (Table 1), except the ²B₁(bent) state in which the bond length (*R*) and bond angle (*A*) obtained by B3LYP deviate from those of CASSCF [24] by about 7 pm and 8°, respectively. This indicates that the effect of configuration interaction is not vital for the structures of these $C_{2\nu}$ excited states.

The vibrational frequencies computed by us and by Li et al. [23,24] are also in harmony with each other, except the ${}^{2}B_{1}(\text{bent})$ state. However, the v_{3} mode of the ${}^{2}B_{2}$ state possesses an imaginary frequency according to our calculation (Table 2), although the values of B3LYP differ from that of CASSCF by about 1000*i*

and need more investigation. It means that the optimized structure is not an equilibrium one, rather, it should be a transition state connecting two potential minima along the Q_3 (antisymmetric stretch) coordinate. The equilibrium geometry of this excited state is anticipated to have unequal bond lengths and belong to the C_s point group. Our CASSCF calculations, with 17 electrons distributed in 12 orbitals, are consistent with this argument (Table 3). This state is the $\tilde{A}(2^2A')$ excited state which has the same symmetry with the ground-state of SO_2^+ under the C_s point group. Accordingly, this state was computed by the multiconfigurational CASSCF method instead of the single-determinant B3LYP and CCSD(T) approaches. On the other hand, the optimized geometries of the 2A_2 state and the two conformers (one bent and one cyclic) of the 2B_1 state are equilibrium structures of the $C_{2\nu}$ point group, since all of them have three positive vibrational frequencies (Table 2).

3.2. Photoelectron spectrum

Fig. 1 shows the simulated PES of the ${}^{2}A_{2}$ state of SO₂⁺. Since the structure of the ${}^{2}B_{1}$ (bent) state obtained by the B3LYP method was uncertain to be reliable, its photoelectron spectrum was not computed. The PES of the $\tilde{A}(2^{2}A')$ state was also not simulated in the present study, because its potential energy surface was not harmonic but had double wells, corresponding to two C_{s} equilibrium structures, along the Q_{3} coordinate. We did calculate FCFs of the ${}^{2}B_{1}$ (cyclic) state, however, it was found that the total FCF was very



Fig. 1. Photoelectron spectra of SO_2^+ (1²A₂) simulated by (a) B3LYP and (b) CCSD(T) methods with the 6-311+G(3df) basis set (FWHM = 50 cm⁻¹), showing that both methods give similar results.

Table 2

Calculated harmonic vibrational frequencies (in cm⁻¹) of excited states of SO₂⁺.

Method	² B ₂			² A ₂			² B ₁ (ben	t)		² B ₁ (cycli	c)	
	<i>v</i> ₁	<i>v</i> ₂	<i>V</i> ₃	<i>v</i> ₁	<i>v</i> ₂	<i>v</i> ₃	<i>v</i> ₁	<i>v</i> ₂	<i>v</i> ₃	<i>v</i> ₁	<i>v</i> ₂	<i>v</i> ₃
B3LYP/6-311+G(2d)	1132	447	464 <i>i</i>	1022	451	439	944	438	1319	1036	643	683
B3LYP/6-311+G(3d)	1144	452	464 <i>i</i>	1033	457	436	959	441	1370	1037	645	694
B3LYP/6-311+G(3df)	1162	454	405 <i>i</i>	1053	462	479	982	453	1401	1068	660	733
B3LYP/aug-cc-pVTZ	1146	448	465 <i>i</i>	1035	458	475	961	445	1310	1066	663	719
CCSD(T)/6-311+G(2d)				1008	443	367				958	558	684
CCSD(T)/6-311+G(3d)				1017	452	349				958	547	690
CCSD(T)/6-311+G(3df)				1059	458	437				1019	591	751
CCSD(T)/aug-cc-pVTZ				1040	453	441				1013	595	738
CASSCF/cc-pVTZ	1060	432	1469i									
CASSCF/ANO-L ^a	1085	444		1032	468		788	370				

^a Refs. [23,24].

Table 3

Equilibrium geometries and vibrational frequencies (in cm⁻¹) of the $\bar{A}(2^2A')$ state of SO₂⁺ calculated by the CASSCF (17,12) method.

Basis set	R ₁ ^a	R_2^a	A (°) ^a	v ₁	<i>v</i> ₂	<i>v</i> ₃
6-311+G(2d)	143.28	155.83	112.3	748	259	1246
6-311+G(3d)	142.80	155.00	112.3	768	277	1266
cc-pVTZ	143.51	155.09	113.3	785	216	1271

^a *R* and *A* stand for the SO bond length (in pm) and the OSO bond angle, respectively.

small (less than 10^{-18}) even when this state was highly excited ($v_{1,2} = 0-40$; $v_3 = 0-14$). Accordingly, we infer that it is difficult to produce this cyclic state ($A \approx 60^\circ$, Table 2) by ionizing the ground-state ($A = 119.5^\circ$, [28]) of SO₂ due to the drastic geometry change. Ionization from cyclic excited states of SO₂ [29] is a possible route to prepare the ²B₁(cyclic) state of SO₂⁺.

The spectral patterns are similar for both of the B3LYP and CCSD(T) simulations (Fig. 1). The spectrum is composed mainly of the progressions of v_2 and the combination bands of v_1 and v_2 . The simulated PES is compared with the high-resolution molecular beam experiment of Wang et al. [7] in Fig. 2, where the full width at half maximum (FWHM) of the peaks were adjusted to fit the experiment in the simulation. A nice agreement between these



Fig. 2. Comparison of (a) experimental (taken from Ref. [7]) and (b) simulated (B3LYP/6-311+G(3df); FWHM = 150 cm⁻¹) photoelectron spectra of SO₂⁺ (1²A₂), where the agreement depicts that the \bar{B} state of SO₂⁺ is of the ²A₂ symmetry.

two spectra is evident (Fig. 2), although the simulated peaks shift to the right of the experiment as the excitation energy gets higher, a consequence of the harmonic model adopted in the present study.

The simulation demonstrates that the peak at 13.338 eV corresponds to the adiabatic transition from the ground-state of SO₂ to the ${}^{2}A_{2}$ state of SO₂⁺ (Fig. 2). Yet, there are still signals present below 13.338 eV, meaning that the ${}^{2}A_{2}$ state is the \tilde{B} state of SO₂⁺, while the peaks of the lower ionization energies are those of the \tilde{A} state (Fig. 2). Moreover, the apparent simple structure and nearly regular peak spacing (Fig. 2a), which led previous researchers [7,8] to assign them as the v_2 progressions, is in fact due to overlap of the peaks detailed in Fig. 1. For instance, the strongest peak in Fig. 2a was assigned as 2_0^3 by Wang et al. [7], but the present study indicated that it contained the signals of $1_0^1 2_0^1$ and 2_0^3 , and the former took about 82% of the intensity. This also accounts for why the vibrational intervals do not decrease linearly as a function of v_2 by the assignments of Wang et al. [7]. In addition, the v_3 transitions were found to have small FCFs and were unlikely to be observed experimentally. Therefore, the weak v_3 transitions assigned by Wang et al. [7] are probably the small peaks of the \tilde{B}^2A_2 state (Fig. 1) or those of the \tilde{A} sate (Fig. 2). In short, Wang et al. correctly assigned the peak at 13.338 eV as the band origin of the \tilde{B} state [7], but its symmetry species should be ²A₂ instead of ²B₂.

3.3. Adiabatic ionization energy

We computed accurate energies by the CBS limit method developed by Peterson et al. [25] for the ${}^{2}B_{2}$, ${}^{2}A_{2}$ and ${}^{2}B_{1}$ (cyclic) states. Both the equilibrium geometry and zero-point energy (ZPE) correction were taken from the CCSD(T)/aug-cc-pVTZ results, except that the ZPE of the ${}^{2}B_{2}$ transition state was taken from the CASSCF/ cc-pVTZ computation. Table 4 lists the energies computed by four basis sets in conjunction with their CBS limit.

The AIE of the ${}^{2}B_{2}$ state was obtained as follows. The ionization energy of the $C_{2\nu}$ transition state was first computed by the CCSD(T) CBS limit approach. The energy barrier between the $C_{2\nu}$ transition and the C_{s} equilibrium structures calculated by the CASSCF method was then taken into account. Table 4 depicts that the ionization energy of the ${}^{2}B_{2}$ transition state is lower than that of the $\tilde{B}^{2}A_{2}$ state, indicating that it correlates with the \tilde{A} state of SO₂⁺. The energy difference is about 1040 cm⁻¹ between the $C_{2\nu}$ transition and the C_{s} equilibrium structures calculated by the CASSCF method without ZPE correction. For such a small energy difference, only one vibrational level of ν_{3} can exist below the barrier maximum along the Q_{3} coordinate. The barrier height is estimated to be about 650 cm⁻¹ by taking the ZPE into account, three times larger than but of the same order of magnitude with

Table 4

Calculated CCSD(T) energies (in hartree) and adiabatic ionization energies (AIE) of excited states of SO₂⁺.

п	Basis set	² B ₂	² A ₂	² B ₁ (cyclic)
2	aug-cc- pVDZ	-547.33748	-547.31830	-547.28186
3	aug-cc- pVTZ	-547.52877	-547.50812	-547.46643
4	aug-cc- pVDZ	-547.58611	-547.56509	-547.52018
5	aug-cc- pV5Z	-547.60848	-547.58705	-547.53980
∞	CBS limit ^a	-547.61997(117)	-547.59851(100)	-547.55069(39)
	AIE (eV) ^b Experiment ^c	12.492 12.988	13.369 13.338	14.695

Values in parentheses are errors in the last digit.

^b The energy of the ground-state SO₂ was taken from Ref. [4].

^c Ref. [7].

that (202 cm⁻¹) inferred by Wang et al. from experimental PES of SO₂ [7].

The calculated AIE of the ${}^{2}A_{2}$ state is in agreement with the experiment [7] within 0.031 eV (Table 3). Accordingly, the result of quantum calculations on this state matches with the experiment very well, both in energy and intensity distribution. This is a strong evidence to assign the \tilde{B} state of SO₂⁺ as ²A₂. For the ²B₁(cyclic) state, its AIE is predicted to lie around 14.695 eV (Table 3), yet it is not expected to appear, unless very weak, in the PES of SO₂ as mentioned above. Experimental results supported such viewpoints, where the PES of SO₂ was scarce in the energy range between 14.1 and 15.8 eV [7,8].

4. Conclusion

We calculated the equilibrium geometries and harmonic vibrational frequencies for the ${}^{2}B_{2}$, ${}^{2}A_{2}$ and ${}^{2}B_{1}$ ionic excited states of SO₂ by using the B3LYP, CCSD(T) and CASSCF methods. The B3LYP and CCSD(T) results are similar to those of CASSCF computations [23,24], indicating that the structures of these states are not seriously altered by the effect of configuration interaction. Interestingly, the B3LYP method performed equally well with CCSD(T), except in one case.

The optimized structure of the ²B₂ state is identified as corresponding to a transition state. It correlates with the $\tilde{A}(2^2A')$ state of SO_2^+ whose equilibrium structure is of the C_s point group, as shown by the CASSCF calculations. By computing FCFs, the PES of the ²A₂ state was simulated and was found to be consistent with the experiment, but with assignments different from previous experimental reports [7,8]. The calculated AIE of this state is in agreement with the experimental value [7] within 0.031 eV. Accordingly, the ${}^{2}A_{2}$ state is inferred to be the \hat{B} state of SO₂⁺. The ²B₁ state has both bent and cyclic equilibrium structures, in which the cyclic form can hardly be prepared from ionization of the ground-state of SO₂ due to small FCFs arising from large geometry change.

Following the present study, we will calculate the equilibrium geometries of some other higher excited states of SO₂⁺. Their PES will be simulated and compared with the experiment. It should be interesting and important to test how well modern quantum calculations can do in interpreting and predicting experimental spectroscopy.

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