The analytical potential energy function of flue gas $SO_2(X^1A_1)$*

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The equilibrium structure of flue gas SO_2 is optimized using the density functional theory (DFT)/ B3P86 method and CC-PV5Z basis. The result shows that it has a bent (C_{2V}, X^1A_1) ground state structure with an angle of 119.1184°. The vibronic frequencies and the force constants are also calculated. Based on the principles of atomic and molecular reaction statics (AMRS), the possible electronic states and reasonable dissociation limits for the ground state of SO_2 molecule are determined. The potential functions of SO and O_2 are fitted by the modified Murrell–Sorbie+$c6$ (M-S+$c6$) potential function and the fitted parameters, the force constants and the spectroscopic constants are obtained, which are all close to the experimental values. The analytic potential energy function of the SO_2 (X^1A_1) molecule is derived using the many-body expansion theory. The contour lines are constructed, which show the static properties of SO_2 (X^1A_1), such as the equilibrium structure, the lowest energies, the most possible reaction channel, etc.

Keywords: flue gas SO_2, analytical potential energy function, many-body expansion theory

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1. Introduction

Energy structure in China is dominated by coal, which amounts to 75% total raw coal output and is directly burnt as fuel. The burning of fossil fuels can release sulfur, NOx and others into the atmosphere. Therein, SO_2 can enter the trachea through the breath, thereby stimulating and corroding partial organization, then inducing diseases such as bronchitis; especially when it co-exists with dust and other aerosols, it can increase the damage to the respiratory mucosa. SO_2 and other gases will lead to acid rain, which will endanger the health of terrestrial biology and humans.[1] In recent years, atmospheric and environmental scientists have paid special attention to these kinds of gases, but most of them concentrated in the monitoring and measurement content.[1−5] The molecular spectrum and the dynamic reaction can greatly affect the monitoring of flue gas SO_2, therein the reasonable potential energy surface is the most important. To this day, the potential function and the spectrum intensity of the SO_2 molecule in many-body expansion form has not been reported.

The molecular potential energy function is the expression of the eigen-energy of an electron for a given electronic state in the fixed-nuclei and Born–Oppenheimer approximation. The molecular potential energy function is the complete description of molecular electronic energy and the potential function of nuclei motion, and it is also the base of studying the atom and molecule collision and molecular reaction dynamics.[6−8] In this work, we report on the fitted parameters of SO and O_2 by the modified M-S+$c6$ potential function and many-body expansion potential energy function of SO_2 based on *ab initio* calculation with the many-body expansion theory.[9−13] All calculations are carried out with DFT (B3P86)/CC-PV5Z method[14] and are performed by Gaussian 03 program. The analytical potential energy function of SO_2 is conducive to its dynamic study and spectrum intensity computation directly.

2. Theoretical details

2.1. Electronic states and dissociation limits

For the calculation and the description of the full space potential function for SO_2, we must determine

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the possible electronic states and their reasonable dissociation limits. Based on atomic and molecular reaction statics (AMRS)[15] and quantum mechanical calculation, the ground electronic states of SO_2 are obtained.

Firstly, we derive the electronic states using the separated atomic method.[15] The ground electronic states for S, O and O are all ^3P_g, and they belong to the $SU(n)$ group,[9] while the SO_2 molecule belongs to the C_{2V} group. Due to the fact that the irreducible representation of the $SU(n)$ group can be decomposed into those of the C_{2V} group to obtain the possible electronic states, then $S(^3P_g)$ and $O(^3P_g)$ are decomposed into the direct summation of irreducible representations of the C_{2V} group as follows:

$$^3P_g \to {}^3A_2 \oplus {}^3B_1 \oplus {}^3B_2,$$
$$^3P_g \to {}^3A_2 \oplus {}^3B_1 \oplus {}^3B_2.$$

When SO is in the ground state $X^3\Sigma^-$, it can be decomposed into the direct summation of irreducible representations of C_{2V} $(\sigma_h \to \sigma)$ group for $^3A_2$, their direct product and reduction of the ground state of SO with $O(^3P_g)$ are

$$^3A_2 \otimes (^3A_2 \oplus {}^3B_1 \oplus {}^3B_2) \to {}^{1,3,5}A_1 \oplus^{1,3,5} B_2 \oplus^{1,3,5} B_1. \quad (1)$$

We find that equation (1) includes $^1A_1$, there are nine states in the combination of the $SO_2(C_{2V})$ molecule by the ground state $SO(X^3\Sigma^-)$ with $O(^3P_g)$, it can be described as follows:

$$O + SO \to SO_2,$$
$$^3P_g\,{}^3\Sigma^{-1,3,5}A_1 \oplus^{1,3,5} B_2 \oplus^{1,3,5} B_1.$$

When O_2 is in the ground state $X^3\Sigma_g^-$ and S atom is in the ground state ^3P_g, under the same condition as mentioned above, it also contains $^1A_1$, so

$$^3A_2 \otimes (^3A_2 \oplus {}^3B_1 \oplus {}^3B_2) \to {}^{1,3,5}A_1 \oplus^{1,3,5} B_2 \oplus^{1,3,5} B_1,$$
$$S + O_2 \to SO_2,$$
$$^3P_g\,{}^3\Sigma_g^{-1,3,5}A_1 \oplus^{1,3,5} B_2 \oplus^{1,3,5} B_1. \quad (2)$$

Similarly, when S and 2O atoms are all in the ground state ^3P_g, their direct product and reduction are as follows:

$$(^3A_2 \oplus {}^3B_1 \oplus {}^3B_2) \otimes 2(^3A_2 \oplus {}^3B_1 \oplus {}^3B_2) \to 6^{1,3,5}A_1 \oplus 7^{1,3,5}A_2 \oplus 7^{1,3,5}B_2 \oplus 7^{1,3,5}B_1. \quad (3)$$

Equation (3) also contains $^1A_1$. So it can be described as

$$S + 2O \to SO_2,$$
$$^2S_g\,{}^3P_g 6^{1,3,5}A_1 \oplus 7^{1,3,5}A_2 \oplus 7^{1,3,5}B_2 \oplus 7^{1,3,5}B_1.$$

Therefore, according to the principle of microscopic reversibility,[15] the possible dissociation processes for the SO_2 molecule can be expressed as

$$SO_2(X^1A_1) \to \begin{cases} SO(X^3\Sigma^-) + O(^3P_g), \\ S(^3P_g) + O_2(X^3\Sigma_g^-), \\ S(^3P_g) + 2O(^3P_g). \end{cases} \quad (4)$$

2.2. Equilibrium geometry and vibronic frequency of the $SO_2(X^1A_1)$ molecule

The singlet, triplet, and five heavy condition states of the ground state SO_2 molecule with angular structure are optimized with DFT/B3P86, CCSD, QCISD, MP2 methods, and 6-311++G**, CC-PVTZ, and CC-PV5Z bases, and we find that the singlet state energy of the ground state SO_2 molecule with angular structure is lowest, obtained with B3P86/CC-PV5Z method, and the bond length, and bond angle are both close to the experimental values. It belongs to the C_{2V} group. The equilibrium geometry, the force constants, and the vibronic frequencies of the ground state SO_2 molecule are calculated too, and it takes on $^1A_1$ electronic state. The results show that $\angle$OSO=119.1184°, R_{S-O} = 0.1430 nm, E = −549.3254 a.u. (atomic unit), and vibronic frequencies that are as follows: the symmetrical stretching vibronic frequency is 527.2 cm^{-1}, the bent vibronic frequency is 1199.8 cm^{-1}, and the dissymmetry stretching vibronic frequency is 1401.1 cm^{-1}.

To calculate the dissociation energy of $SO_2(X^1A_1)$ corresponding to the dissociation limit $S(^3P_g)+2O(^3P_g)$ at the B3P86/CC-PV5Z level, firstly, we calculate the energy for $SO_2(X^1A_1)$, which is 549.3254 a.u., then those for $S(^3P_g)$ and $O(^3P_g)$, which are −398.3797 a.u. and −75.1258 a.u., respectively, so the dissociation energy of $SO_2(X^1A_1)$ is $D_e = E(S)+2E(O)–E(SO_2)$=18.88 eV. The results are all listed in Table 1 and the experimental values are given in the brackets.[16]

Table 1. Equilibrium structural parameters and force constants for $SO_2(X^1A_1)$.

Bond length/nm	$R = R_{S-O} = 0.1430$ (0.143)
Bond angle/(°)	$\theta = \angle$OSO=119.1184 (121±5)
Dissociation energy[a]/eV	18.88
Force constants[b]	f_{11}=0.68713, f_{22}=0.68713, f_{12}=0.00687, $f_{1\theta} = 0.02943$, $f_{2\theta} = 0.02943$, $f_{\theta\theta} = 0.38732$

[a]Relative to the dissociation limit $S(^3P_g)+2O(^3P_g)$.

[b]The units are in atomic units.

2.3. Many-body expansion analytical potential energy function of the $SO_2(X^1A_1)$ molecule

The analytical potential energy function[17,18] and the potential energy surface of triatomic molecules are the basis of studying the molecular reaction dynamics, and the latter is a hypersurface in the three-dimensional space.[9] If we choose the energy of ground state to be zero that satisfies Eq. (4), the many-body expansion analytical potential energy function[9] of the ground state $SO_2(X^1A_1)$ molecule is

$$V = V_{OS}^{(2)}(R_1) + V_{SO}^{(2)}(R_2) + V_{OO}^{(2)}(R_3) + V_{OSO}^{(3)}(R_1, R_2, R_3). \quad (5)$$

In Eq. (5), $R_1 = R_{O-S}$, $R_2 = R_{S-O}$, $R_3 = R_{O-O}$, $V_{OS}^{(2)}(R_1)$, $V_{SO}^{(2)}(R_2)$, and $V_{OO}^{(2)}(R_3)$ are the two-body terms represented by the potential functions of SO $(X^3\Sigma^-)$ and $O_2(X^3\Sigma_g^-)$, respectively, and $V_{OSO}^{(3)}(R_1, R_2, R_3)$ is the three-body term, which will be zero if any of the atoms are removed to infinity. We will impose the modified M-S+c_6 potential function on the two-body terms[19–21]

$$V = -D_e(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho) - c_6/R^6,$$

where $\rho = R - R_e$, R and R_e are the diatomic distance and its equilibrium value respectively, D_e is dissociation energy and a_1, a_2, a_3, and c_6 are the two-body terms fitting parameters of M-S+c_6 potential energy function. The potential energy values of $SO(X^3\Sigma^-)$ and $O_2(X^3\Sigma_g^-)$ are calculated by the same *ab initio* method. Force constants and spectroscopic constants of the M-S+c_6 function are calculated by the following formulas:[20]

$$f_2 = D_e(a_1^2 - 2a_2) - 42c6/R_e^8,$$

$$f_3 = -6D_e\left(a_3 - a_1a_2 + \frac{1}{3}a_1^3\right) + 336c6/R_e^9,$$

$$f_4 = D_e(3a_1^4 - 12a_1^2a_2 + 24a_1a_3) - 3024c6/R_e^{10},$$

$$B_e = \frac{h}{8\pi c\mu R_e^2}, \quad \omega_e = \sqrt{\frac{f_2}{4\pi^2\mu c^2}},$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(1 + \frac{f_3R_e}{3f_2}\right),$$

and

$$\omega_e\chi_e = \frac{B_e}{8}\left[-\frac{f_4R_e^2}{f_2} + 15\left(1 + \frac{\omega_e\alpha_e}{6B_e^2}\right)^2\right].$$

The two-body term parameters of potential energy function of SO and O_2 molecules are all listed in Table 2, the force constants and spectroscopic constants are presented in Table 3 and the experimental values are also listed there.[22] Here, we mainly derive the three-body terms.

To obtain the many-body expansion potential energy function, it is required to choose appropriate reference coordinates. In this paper, we choose C_{2v} symmetry ($R_1^0 = R_{O-S} = R_2^0 = R_{S-O} = 0.1430$ nm, $R_3^0 = R_{O-O} = 0.2466$ nm) as the reference structure, then the symmetrical internal coordinates S_1, S_2, and S_3 are given by the following transformation:[9]

$$\begin{pmatrix} S_1 \\ S_2 \\ S_3 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1/\sqrt{2} & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix} \begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \end{pmatrix}, \quad (6)$$

where the internal coordinates ρ_i are given by $\rho_i = R_i - R_i^0$ $(i = 1, 2, 3)$.

Table 2. The M-S function parameters, force constants for SO and O_2.

Molecule	D_e/eV	R_e/nm	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}	c_6/eV·nm^6
SO($X^3\Sigma^-$)	5.339	0.1500	48.059	663.03	5265.7	-0.1376×10^{-5}
Expt.	5.430	0.1481	47.480	650.40	5228.0	
O_2($X^3\Sigma_g^-$)	5.228	0.1200	61.091	1149.5	10956.0	-0.9212×10^{-6}
Expt.	5.213	0.1208	60.800	1147.7	11003.0	

Table 3. Force constants and spectroscopic constants for SO and O_2.

Molecule	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	f_2/aJ·nm^{-2}	f_3/aJ·nm^{-3}	f_4/aJ·nm^{-4}
SO($X^3\Sigma^-$)	1145.31	5.81	0.7026	0.0056	877.515	–55310.75	3281212.6
Expt.	1149.22	5.63	0.7208	0.0057	883.524	–45005.12	3294600.3
O_2($X^3\Sigma_g^-$)	1645.83	9.547	1.4634	0.0140	1359.336	–94732.62	6121031.5
Expt.	1580.19	11.981	1.4456	0.0159	1253.067	–93476.66	5232779.1

The three-body term of Eq. (5) can be written in symmetric internal coordinates as

$$V_{\mathrm{OSO}}^{(3)}(R_1, R_2, R_3) = PT. \tag{7}$$

Here P is a polynomial

$$P = C_1 + C_2S_1 + C_3S_2^2 + C_4S_3 + C_5S_3^2 + C_6S_1S_3 + C_7S_1^2, \tag{8}$$

and T is a range function

$$T = [1 - \tanh(\gamma_1 S_1/2)][1 - \tanh(\gamma_2 S_2/2)]. \tag{9}$$

To gain $V_{\mathrm{OSO}}^{(3)}(R_1, R_2, R_3)$, we need to determine seven linear parameters C_1–C_7 in polynomial P and two nonlinear parameters γ_1 and γ_2 in range function T. The nonlinear parameters can be determined by optimizing the potential energy surface and the linear parameters by using the equilibrium structure, dissociation energy and force constants (in Table 1). The parameters are listed in Table 4. Finally, we can plot the contours of the potential according to analytical potential energy function Eq. (5), which are shown in Figs. 1–3.

Table 4. Three-body term parameters of analytical potential energy function for SO_2.

C_1	C_2	C_3	C_4	C_5	C_6	C_7	γ_1	γ_2
0.202997	–14.359945	–15.138925	–12.039650	–17.874103	13.563107	–6.017785	2.0	3.1

3. Results and discussion

Figures 1–3 are for the contours of potential for the $SO_2(X^1A_1)$ molecule. They clearly reproduce the character of the ground state $SO_2(X^1A_1)$ molecule in equilibrium structure. Figure 1 shows the S–O bond stretching contours for a fixed angle ∠OSO=119.1184°, which represents the stretching and vibronic conditions of S–O bonds. From this figure, we can see that there is a potential well (−18.8 eV) at $R_{\mathrm{S-O}} = 0.1430$ nm, which accords with the dissociation energy (−18.88 eV) of equilibrium structure. Moreover, the evident potential barrier does not exist during the reaction. Consequently, this could be a non-threshold energy reaction, and it can easily occur.

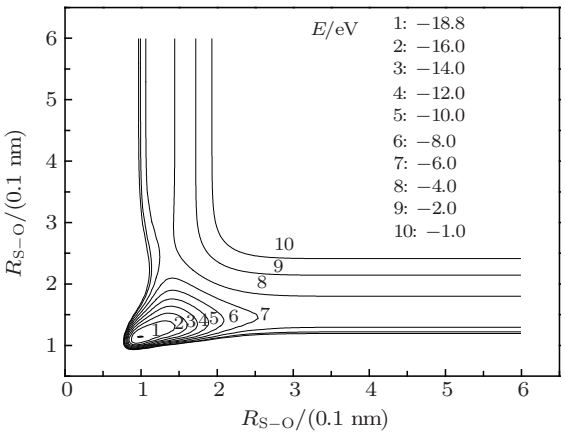


Fig. 1. S–O bonds stretching contours for $SO_2(X^1A_1)$.

Figure 2 shows the contours for S atom moving around the fixed O–O bond, the lowest energy at point 1 (−19.5 eV), and the contour reproducing the C_{2V} symmetrical structure of $SO_2(X^1A_1)$. The SO_2 molecule could form easily if the S atom attacks the O–O bond from perpendicular bisector. Angle ∠OSO is about 119.1184°, which is also accordant with the optimum structure and in agreement with the result of Fig. 1, where no potential barrier exists. Figure 3 shows the contour for O atom moving around the fixed S–O bond, and the contour reproducing the C_{2V} symmetrical structure. In Fig. 3, there is no evident potential barrier, but an extremum (−27.5 eV) exists, which also illuminates that the reaction will occur more easily if the O atom attacks the S–O bond from the perpendicular bisector than from other directions. From Figs. 2 and 3 it follows that the lowest energy in Fig. 2 is higher than that in Fig. 3. The above-mentioned analysis explains that the S + O_2 →SO_2 reaction will occur more than O+SO→SO_2, which accords with Fig. 3.

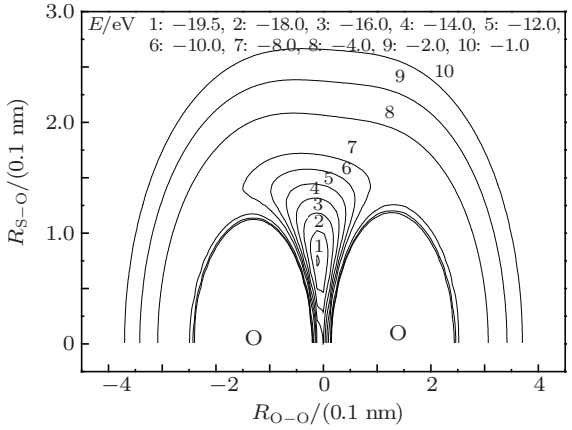


Fig. 2. Contour lines of $SO_2(X^1A_1)$ for S atom moving around the O–O bond.

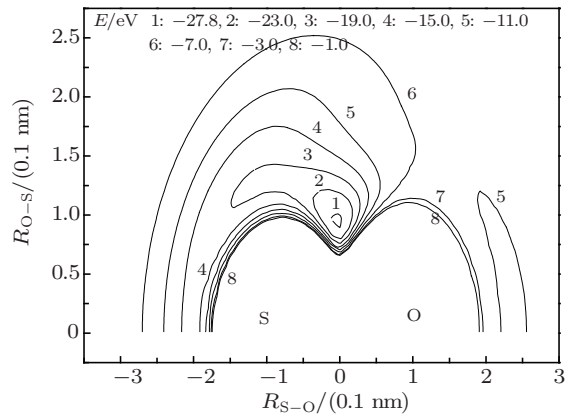


Fig. 3. Contour lines of $SO_2(X^1A_1)$ for O atom moving around the S–O bond.

4. Conclusions

The equilibrium geometry, the force constants, and the vibronic frequencies of flue gas $SO_2(X^1A_1)$ are calculated with the B3P86/CC-PV5Z method. Afterward, we further scan the whole potential curves for the ground states of SO and O_2 molecules using the same method, and employ a least square method to fit the potential by a modified M-S+c_6 function and obtain the fitted potential parameters and the corresponding force constants and spectroscopic constants, which are all close to the experimental values. Based on the principles of atomic and molecular reaction statics, the dissociation limits of $SO_2(X^1A_1)$ are determined. For the first time, we report on the potential parameters of SO and O_2 in M-S+c_6 and potential function of SO_2 in many-body expansion form. The contours of the potential clearly reproduce the character of the ground state SO_2 molecule in equilibrium structure, at the same time, they show that S + O_2 → SO_2 is a non-threshold energy reaction, and it occurs more easily than other dissociation reactions. The above results are conducive to the dynamic and spectrum studies of SO_2.

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