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Theoretical studies of partition functions of flue gas SO_2 isotope

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Abstract. The geometrical structure of flue gas $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$ molecule have been optimized at B3P86/cc-PV5Z level using Gaussian03 program, we gain theirs equilibrium geometry, resonance frequency and rotational constants *et al.*. The total internal partition functions are calculated at the temperatures from 70 K to 6000 K for $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$ with the product approximation. Thereinto, the rotational partition sums $Q_{\rm rot}$ adopt the WATSON rigid rotator model, which take into account centrifugal distortion corrections. The vibrational partition sums $Q_{\rm vib}$ use the harmonic oscillator approximation model. It is found that the calculated total internal partition functions are consistent with those offered by HITRAN database from 70 K to 3000 K, and the errors shows linear correlation approximately. By fitting the errors, the total internal partition functions values at high temperature range of 3000 K to 6000 K were corrected. The corrected total internal partition functions are fitted to a four-order polynomial expression in T, and the coefficients are gained at high temperature. This allows a rapid and accurate calculation of the total internal partition functions at the temperature from 3000 K to 6000 K.

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Key words: flue gas, SO_2, isotope, partition functions

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1 Introduction

Energy structure in China is a country dominated by coal, occupies the coal output 75% raw coal to use in burning directly, the burning of fossil fuels is released into the atmosphere, which is the major source of sulfur and NO_x. Thereinto, SO_2 can enter the trachea through the breath, it will stimulate and corrode partial organization, then induce one of the causes of diseases such as bronchitis, especially when it coexists with dust and other aerosols, it can increase the damage to respiratory mucosa. SO_2 and other gases will be the role of acid rain, which will endanger the health of terrestrial biology and human. When the SO_2 content

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achieves $0.1/1000000 \sim 1$ in the air, plants and structure of the building materials will be seriously damaged, achieves $1/1000000 \sim 10$, human respiratory tract can cause cramps, tears, coughing and even death, to one ten thousandth time, all life will end [1]. Recent years, atmospheric and environmental scientists have paid special attention to this kinds of gases, but most concentrated in the monitoring and measurement content [1–5]. A majority of monitors adopt differential absorption spectroscopy at home and abroad, which measurement and calibration standard to the flue gas. It will lead to nonlinear and other factors when absorption for the flue gas with high temperature and concentration, which result in the monitoring results have large errors. In HITRAN04 database of the molecular spectra mainly focus on 70–3000 K [6], therefore, it is necessary to calculate the high temperature spectral intensity of flue gas through theoretical simulation, which will be beneficial to more accurately monitor air pollution.

When studying systems that are not isothermal, the intensity of a spectral line at a given temperature can be calculated from the linear density at a reference temperature and the total internal partition sum (TIPS) at both temperatures. Therefore, the accurate calculation the TIPS is importance to calculate the spectral intensity of flue gas SO_2. The model has been constructed using the product approximation in this work [7], in which rotational partition functions adopt the non-rigid rotor model WATSON and vibrational partition functions use harmonic oscillator approximation. The TIPS of flue gas SO_2 isotope molecules in the 70–6000 K temperature range have been computed in this paper. Compared the computed values from 70 K to 3000 K with HITRAN04 datum, we find that the two datum are good agreement, the deviation value less than 4%, but the relative deviation will increase gradually along with temperature increment, which can be approximated as a straight line from the chart. By linear fitting to the relative deviation, the calculated datum in high temperature (3000–6000 K) are revised further. The corrected TIPS are fitted to a four-order polynomial expression in T, and the coefficients are gained at high temperature. This allows a rapid and accurate calculation of TIPS at the temperature from 3000 K to 6000 K, which gives more accurate total partition function at high temperatures. It will provide theoretical reference for studying high temperature spectra and monitoring environmental pollution.

2 Theoretical method

2.1 Quantum mechanics method

Using Gaussian03 program with density functional B3P86 method and uniting Dunning, which related consistent five heavy (cc-pV5Z) base groups [8–10], the geometrical structure, resonance frequency and rotational constant of flue gas $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$ molecule have been optimized. The results are: the ground state configuration and electronic state of $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$ all are C_{2V} and X^1A_1, respectively. The results are presented in Table 1, where R is the S-O bond long, Alpha is bond angle O-S-O, A, B, C are the rotational constants, v_1, v_2 and v_3 for resonance frequency. It is shown that, the calculated results are accordant well with the experimental values [11].

Table 1: The optimization results of the ground state for the $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$ molecules.

	R/nm	α/°	ν_1/cm^{-1}	ν_2/cm^{-1}	ν_3/cm^{-1}	A/cm^{-1}	B/cm^{-1}	C/cm^{-1}
$^{32}S^{16}O_2$	1.4304	119.1184	1199.7673	527.1933	1401.0869	1.989877	0.346480	0.295475
exp.	1.43	121 ± 5	1150.5	524.5	1336.0	–	–	–
$^{34}S^{16}O_2$	1.4452	118.2901	1178.0274	516.5932	1358.4054	2.030000	0.342338	0.290510

2.2 Total partition functions

The total molecular partition function is defined as the factor e^{-E_s/k_BT} sum of all states s, its expression may simplify as equation below [12]

$$Q(\text{elec, vib, rot, tors,}\cdots)=d_i\sum_{\text{all states } s}d_s e^{-E_s/k_BT}, \tag{1}$$

where d_s is the state degeneration factor, d_i is the independent degeneration factor, E_s is the total energy of s state, including electronic, vibration, rotation and any other quantum movement total energy (unit: cm^{-1}), T is the temperature (unit: K). Until now, it had many kinds of methods for computation molecular partition function [13, 14], generally speaking, to all condition summation should be most accurate, but it is very difficult to accurately calculate the partition function through getting high vibrational energy level of a certain molecular, therefore, reasonable approximation can be used to dispose. Assumption of a molecular electronic, vibration and rotational energy can be separated, then the molecular total energy may regard as three sum totals, namely $E_{tot}=E_{elec}+E_{vib}+E_{rot}$. Ignoring the interaction between them, the TIPS can be written as

$$Q(\text{elec, vib, rot})=Q_{\text{elec}}\times Q_{\text{vib}}\times Q_{\text{rot}}.$$

When all molecules are in their ground electronic state, thus $Q_{\text{elec}}=1$, then

$$Q(T)=Q_{\text{vib}}\times Q_{\text{rot}}. \tag{2}$$

The expression is called the product approximation of the partition function. For high temperature applications it appears that direct summation over complete energy sets by Eq. (1) with a very high cut off is need for accurate results. However, when such a set of energies is not available, the product approximation is more accurate. Therefore, in this paper, the TIPS are calculated with the product approximation.

2.2.1 Vibration partition function

The vibration partition functions adopt here is the harmonic oscillator approximation [11]

$$Q_{\text{vib}}(T)=\prod_{\nu_i}\frac{1}{1-\exp(hc\nu_i/k_BT)}. \tag{3}$$

In this formula, h is the Planck constant, c is in the vacuum speed of light, v_i is the molecular ith vibration base frequency (the unit: cm^{-1}), k_B is the Boltzmann constant, T is temperature. The molecular vibration base frequency constants are from the optimized calculated value of this paper.

2.2.2 Rotation partition function

Rotation partition functions Q_{rot} use the results of WATSON [15]

$$Q = \bar{g}Q' + \sum_{\xi=a,b,c} g_\xi Q'_\xi, \tag{4}$$

where $\bar{g}$ is the average nuclear spin statistical weight

$$\bar{g} = \frac{1}{\sigma}\Pi(2I+1). \tag{5}$$

In above equation, $\Pi(2I+1)$ is the nuclear spin total, σ is the molecular symmetry number. g_ξ is corresponds to main axle ξ nuclear spin statistical weight factor in the Eq. (4), if this axis is not the appropriate symmetry axis of molecular group, then this factor is zero, if main axle a is a symmetrical double axis, then has

$$g_a = \chi_{ev}(C_{2a}) \prod_{i}^{a\text{-axis}} (2I_i+1) \prod_{j}^{C_{\text{2a-pairs}}} (-1)^{2I_j}(2I_j+1). \tag{6}$$

The first factor $\chi_{ev}(C_{2a})$ is the characteristic table of vibrates the wave function under the symmetry operation C_{2a}, the second item is quadrature to all nuclear i in a-axis, the third item is quadrature to each pair of same nuclear when carries on C_{2a} operation to molecule. Likewise, g_b and g_c may solve. Q' with McDowell result [16]

$$Q' = \left(\frac{\pi}{\alpha\beta\gamma}\right)^{1/2} e^{f_1}(1+f'_2+f'_3+\cdots), \tag{7}$$

$$f_1 = \frac{1}{12}\left(2\sum\alpha - \sum\frac{\alpha\beta}{\gamma}\right), \tag{8}$$

$$f'_2 = \frac{1}{90}\sum\frac{\alpha\beta(\gamma-\alpha)(\gamma-\beta)}{\gamma^2}, \tag{9}$$

$$f'_3 = \frac{1}{2835}\sum\frac{(\gamma-\alpha)(\gamma-\beta)}{\gamma^3}\left((\alpha-\beta)^2\gamma^2 + 4(\alpha+\beta)\alpha\beta\gamma - 8\alpha^2\beta^2\right), \tag{10}$$

where α, β and γ is the dimensionless temperature reduction of the rotational constants hcA/k_BT, hcB/k_BT and hcC/k_BT, each sum is for (α,β,γ) of the three loop replacement.

But the evolution expression of Q'_ξ is as follows

$$Q'_{a0}=\left(\frac{\pi}{\alpha}\right)^{3/2}\exp\left(-\frac{\pi^2}{4\alpha}\right)\times\sec\left(\frac{\pi\sqrt{(\alpha-\beta)(\alpha-\gamma)}}{2\alpha}\right), \tag{11}$$

$$Q'_{b0}=\left(\frac{\pi}{\beta}\right)^{3/2}\exp\left(-\frac{\pi^2}{4\beta}\right)\times\sec\left(\frac{\pi\sqrt{(\alpha-\beta)(\beta-\gamma)}}{2\beta}\right), \tag{12}$$

$$Q'_{c0}=\left(\frac{\pi}{\gamma}\right)^{3/2}\exp\left(-\frac{\pi^2}{4\alpha}\right)\times\sec\left(\frac{\pi\sqrt{(\alpha-\gamma)(\beta-\gamma)}}{2\gamma}\right), \tag{13}$$

I_1 and I_2 all are the nuclear spin of ^{16}O, I_3 is corresponding to the nuclear spin of ^{32}S and ^{34}S, σ is the molecular symmetry number, for the molecular group is C_{2V} in this paper, therefore σ is 2, The rotational constant A, B and C are also from the optimized calculated values. g_a, g_b and g_c are the nuclear spin statistical weight factor, which correspond to ^{32}S, ^{16}O, ^{16}O and ^{34}S, ^{16}O, ^{16}O, respectively.

3 Results and discussion

In Table 2, the TIPS of calculated values and HITRAN04 database for flue dusty gas $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$ at the temperature from 70 K to 3000 K are listed [6], the relative deviation are also listed in the table. The relative deviation of computed results and database datum along with the temperature change diagram of curves is drawn in Fig. 1. See from Table 2 and Fig. 1, the computed values and database datum are good agreement, the error less than 4%. It explained the computation model that we have constructed is reliable, which may use

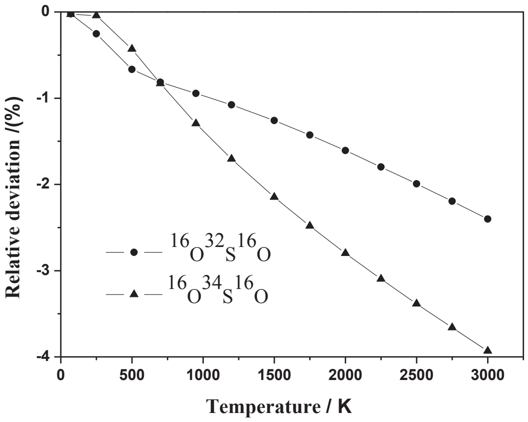

Figure 1: The relative deviation of TIPS between this work and HITRAN database vary with temperature.

Table 2: The total internal partition functions and the difference with HITRAN database for $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$ molecules.

T	$^{32}S^{16}O_2$			$^{34}S^{16}O_2$		
	Calculation	HITRAN	S%*	Calculation	HITRAN	S%
70	6.663E+02	6.665E+02	-0.023	6.693E+02	6.695E+02	-0.027
250	4.737E+03	4.749E+03	-0.253	4.768E+03	4.770E+03	-0.042
500	1.732E+04	1.743E+04	-0.666	1.744E+04	1.751E+04	-0.431
700	3.767E+04	3.797E+04	-0.814	3.782E+04	3.814E+04	-0.83
950	8.489E+04	8.570E+04	-0.944	8.496E+04	8.608E+04	-1.295
1200	1.696E+05	1.714E+05	-1.077	1.692E+05	1.721E+05	-1.707
1500	3.463E+05	3.507E+05	-1.259	3.446E+05	3.522E+05	-2.148
1750	5.831E+05	5.915E+05	-1.427	5.793E+05	5.941E+05	-2.483
2000	9.313E+05	9.465E+05	-1.608	9.239E+05	9.505E+05	-2.798
2250	1.424E+06	1.450E+06	-1.797	1.411E+06	1.456E+06	-3.097
2500	2.101E+06	2.144E+06	-1.993	2.080E+06	2.153E+06	-3.384
2750	3.006E+06	3.073E+06	-2.195	2.973E+06	3.086E+06	-3.662
3000	4.189E+06	4.292E+06	-2.401	4.141E+06	4.310E+06	-3.932

for further calculation the high temperature partition function. At the same time can be seen from the chart, the relative deviation is getting bigger and bigger along with temperature, but the relative deviation and temperature nearly becomes a straight line in the high temperature area, carries on the linear fitting to it and estimates the relative deviation of high temperature to correct the results of our calculations, which makes the results closer to the true values. For the flue dusty gas $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$, the relative deviation approximate straight line expression respectively is:

$$^{32}S^{16}O_2:\ S=-7.45\times10^{-6}T-0.001529, \tag{14}$$

$$^{34}S^{16}O_2:\ S=-1.41\times10^{-5}T+0.0011625. \tag{15}$$

By the relative deviation approximate straight line expression Eqs. (14) and (15) in (70–3000 K) temperature range, we have forecast the relative deviation of high temperature partition function for flue dusty gas $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$, which are listed in Table 3. At the same time, the calculated values at high temperature area (3000–6000 K) partition function are revised through the deviation, also included in the table. See from Table 3, the relative deviation is also bigger and bigger along with the temperature getting higher and higher, but the deviation amount is quite small, the error also below 10% even if in 6000 K, this further shows the computation model is reliable. Comparing with the literatures [17–20], we carry on the revision of molecular partition function for high temperature area and obtain closer real values. For obtaining the partition function of high temperature area random temperature, accurately and fast, we fit the revised partition function with polynomial expression in T, which may reproduce TIPS with high accuracy. This paper uses the fourth-order polynomial in T

$$Q(T)=a+bT+cT^2+dT^3+eT^4. \tag{16}$$

It will obtain five fitting coefficients through the above fitting equation, which are listed in Table 4. The fitting chart is drawn in Fig. 2, from which the correctional partition function and fitting value is good agreement.

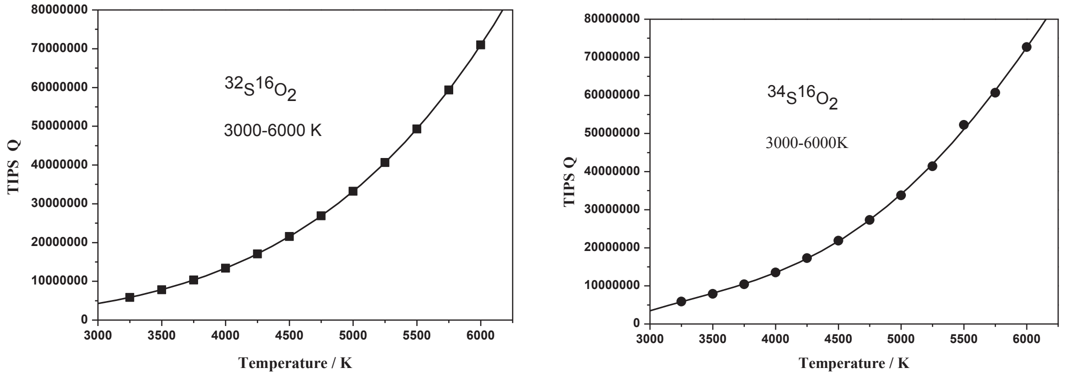

Figure 2: The fitted charts for $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$ molecule at high temperature.

Table 3: The total partition functions of $^{32}S^{16}O_2$, and $^{34}S^{16}O_2$ and the corrected results at high temperature.

T	$^{32}S^{16}O_2$			$^{34}S^{16}O_2$		
	Calculated	Corrected	S%	Calculated	Corrected	S%
3250	5.708E+06	5.841E+06	-2.27	5.639E+06	5.903E+06	-4.47
3500	7.626E+06	7.818E+06	-2.45	7.530E+06	7.912E+06	-4.83
3750	1.001E+07	1.032E+07	-2.95	9.881E+06	1.042E+07	-5.17
4000	1.294E+07	1.336E+07	-3.13	1.277E+07	1.352E+07	-5.52
4250	1.651E+07	1.707E+07	-3.32	1.628E+07	1.729E+07	-5.88
4500	2.079E+07	2.154E+07	-3.51	2.049E+07	2.185E+07	-6.23
4750	2.589E+07	2.688E+07	-3.69	2.551E+07	2.731E+07	-6.58
5000	3.192E+07	3.320E+07	-3.88	3.144E+07	3.378E+07	-6.93
5250	3.898E+07	4.063E+07	-4.06	3.839E+07	4.141E+07	-7.29
5500	4.721E+07	4.931E+07	-4.25	4.826E+07	5.225E+07	-7.64
5750	5.673E+07	5.937E+07	-4.44	5.585E+07	6.070E+07	-7.99
6000	6.769E+07	7.097E+07	-4.62	6.662E+07	7.269E+07	-8.34

In summary, the high temperature molecular partition function are revised through the relative deviation approximate straight line expression of this article, then fitted the correctional high temperature partition function with polynomial expression in T, this will accurately and fast obtain the partition function at high temperature area random temperature, thus gives the more accurate total partition function in high temperature, it is helpful to us further study the high temperature intensity of spectral line of flue gas SO_2.

Table 4: The fitted polynomial coefficients for $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$ molecules at high temperature.

Molecule	*a*	*b*	*c*	*d*	*e*
$^{32}S^{16}O_2$	3.168E+06	-4.150 E+03	2.117	-4.846E-04	9.349E-08
$^{34}S^{16}O_2$	-2.103E+08	1.957 E+05	-6.689 E+01	9.920E-03	-4.833E-07

4 Conclusions

The balanced geometry structure, resonance frequency and rotational constant and so on physical parameters of flue gas SO_2 isotope molecule have optimization calculated through the quantum mechanics *ab inito* calculation. This article has constructed the reasonable partition function computation model with product approximate method, the rotation partition function adopts the WATSON rigid rotor model and vibration partition function uses the harmonic oscillator to be approximate. The TIPS of $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$ in the temperature from 70 K to 6000 K have calculated through the reasonable model. The calculated values and database datum are good agreement in the 70–3000 K scope, the relative deviation less than 4%, furthermore, the relative deviation may become a straight line approximately along with temperature increment. Carries on the linear fitting to the relative deviation and revises the partition function values in high temperature area 3000–6000 K, which will obtain more accurate partition function values. Fitting the correctional high temperature partition function with polynomial expression in T, it will accurately and fast obtain the partition function at high temperature area random temperature, thus gives the more accurate TIPS under high temperature. It is helpful to us further study the high temperature intensity of spectral line for flue dusty gas SO_2 isotope molecule and provide the theory reference for monitoring environmental pollution.

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