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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_{rot} adopt the WATSON rigid rotator model, which take into account centrifugal distortion corrections. The vibrational partition sums Q_{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

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, ν_1, ν_2 and ν_3 for resonance frequency. It is shown that, the calculated results are accordant well with the experimental values [11].