Study on high-temperature spectra of asymptotic asymmetric-top radical SiO_2*

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Total internal partition sums are calculated in the product approximation at temperatures up to 6000 K for the asymptotic asymmetric-top SiO_2 molecule. The rotational partition function and the vibrational partition function are calculated with the rigid-top model and in the harmonic oscillator approximation, respectively. Our values of the total internal partition sums are consistent with the calculated value in the Gaussian program within −0.137% at 296 K. Using the calculated partition functions and the rotationless transition dipole moment squared as a constant, we calculate the line intensities of 001–000 band of SiO_2 at normal, medium and high temperatures. Simulated spectra of the 001–000 band of the asymptotic asymmetric-top SiO_2 molecule at 2000, 5000 and 6000 K are also obtained.

Keywords: asymptotic asymmetric-top molecule, line intensities, partition functions, high temperature spectra

PACC: 3310, 3320E

1. Introduction

Molecular spectroscopy is one of the most important methods of studying molecular structure, and it is also of importance in astrophysics. Using this technique we can not only detect the presence of various molecules on fixed stars, planets, and comets, in the upper atmosphere, and in interstellar space based on their spectra, but also draw definite conclusions concerning the physical conditions in these objects from a more detailed analysis.[1] In recent years, with the development of astrophysics and atmospheric sciences, molecular spectra have been widely used in remote sensing measurements, the identification of objective characteristics, environmental pollution and atmospheric radiation and transfers.[2,3] For SiO_2 with angular structure, up to now, there have been scarcely any spectral measurements in experiment and theoretical calculations at either normal temperature or higher temperatures. In the HITRAN database, we can obtain only the line intensities at temperatures up to 3000 K by the extrapolating method.[4] With the rapid development of aeronautics, the study of molecular spectra at higher temperatures is becoming very necessary. Recently, our work has focused on the high-temperature molecular spectrum. We obtained line intensities of the vibration–rotation transition at temperatures up to 6000 K on the basis of our calculated partition function. With these methods, the high-temperature spectra of asymptotic asymmetric-top molecules were investigated in Refs. [5]–[7]. Here, we concentrate on the calculation of the transition line intensities of the asymptotic asymmetric-top molecule SiO_2 at normal, medium and high temperatures. Firstly, we calculate the partition sums of the 001–000 band of SiO_2 by directly calculating total internal partition sums (TIPS) at normal temperature. Secondly, we calculate them at 5000 K and 6000 K. Finally, we calculate the line intensities at different temperatures by using the foregoing TIPS, and present the simulated spectra of 001- 000 band of SiO_2 at different temperatures. The results are of significance for the study of molecular spectra in both experiment and theory.

2. Theoretical details

2.1. Partition functions

The total internal partition sums were calculated in the product approximation to be[8]

$$Q(T) = Q_{\rm vib} \times Q_{\rm rot}. \quad (1)$$

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The vibrational partition functions $Q_{\rm vib}$ were calculated in the harmonic oscillator approximation to be[9]

$$Q_{\rm vib}(T) = \prod_{\nu_i} \frac{1}{1-\exp(hc\nu_i/k_{\rm B}T)}, \tag{2}$$

where h is Planck's constant, c is the velocity of light in vacuum, ν_i is the fundamental vibrational frequency, $k_{\rm B}$ is the Boltzmann constant, and T is the temperature. The high-temperature asymptotic expansion of the rotational partition function of a rigid asymmetric-top molecule can be written in the form as follows:[10]

$$Q = \bar{g}Q' + \sum_{\xi=a,b,c} g_\xi Q'_\xi, \tag{3}$$

where $\bar{g}$ is the mean nuclear statistical weight given by

$$\bar{g} = \frac{1}{\sigma} \Pi(2I+1). \tag{4}$$

Here $\Pi(2I+1)$ is the total number of nuclear spin functions; σ is the symmetry number, the order of the rotational subgroup of the molecular point group; g_ξ is a nuclear statistical weight factor associated with the principal axis ξ. If this axis is not a proper axis of asymmetry of the molecular point group, the coefficient vanishes. If the a-axis is a twofold axis of symmetry, we have

$$g_a = \chi_{ev}(C_{2a}) \prod_i^{a-\rm axis} (2I_i+1) \times \prod_j^{C_{2a}-\rm pairs} (-1)^{2I_j}(2I_j+1), \tag{5}$$

where the first factor is the character of the vibronic wavefunction under the symmetry operation C_{2a}, the I product is over all nuclei on the a-axis, and the j product has one factor for each pair of equivalent nuclei related by the C_{2a} operation. Similar formulae are applicable to g_b and g_c. The asymptotic expansion of Q' is expressed in the formulation of McDowell as

$$Q' = \left(\frac{\pi}{\alpha\beta\gamma}\right)^{1/2} {\rm e}^{f_1}(1+f'_2+f'_3+\ldots), \tag{6}$$

where

$$f_1 = \frac{1}{12}\left[2\sum\alpha - \sum\frac{\alpha\beta}{\gamma}\right], \tag{7}$$

$$f'_2 = \frac{1}{90}\sum\frac{\alpha\beta(\gamma-\alpha)(\gamma-\beta)}{\gamma^2}, \tag{8}$$

$$f'_3 = \frac{1}{2835}\sum\frac{(\gamma-\alpha)(\gamma-\beta)}{\gamma^3}\{(\alpha-\beta)^2\gamma^2 + 4(\alpha+\beta)\alpha\beta\gamma - 8\alpha^2\beta^2\}. \tag{9}$$

Here, α, β and γ are the dimensionless temperature reduced rotational constants $hcA/k_{\rm B}T$, $hcB/k_{\rm B}T$ and $hcC/k_{\rm B}T$, and each sum is taken over the three cyclic permutations of (α, β, γ).

For Q'_ξ, the principal asymptotic approximations are

$$Q'_{a0} = \left(\frac{\pi}{\alpha}\right)^{3/2} \exp\left(-\pi^2/4\alpha\right) \times \sec\left\{\frac{\pi\sqrt{(\alpha-\beta)(\alpha-\gamma)}}{2\alpha}\right\}, \tag{10}$$

$$Q'_{b0} = \left(\frac{\pi}{\beta}\right)^{3/2} \exp\left(-\pi^2/4\beta\right) \times \sec\left\{\frac{\pi\sqrt{(\alpha-\beta)(\beta-\gamma)}}{2\beta}\right\}, \tag{11}$$

$$Q'_{c0} = \left(\frac{\pi}{\gamma}\right)^{3/2} \exp\left(-\pi^2/4\gamma\right) \times \sec\left\{\frac{\pi\sqrt{(\alpha-\gamma)(\beta-\gamma)}}{2\gamma}\right\}. \tag{12}$$

2.2. Line intensities

Line intensities were computed with the conventional formula to be[11]

$$S_{b\leftarrow a}(T) = \frac{8\pi^3 I_x}{3hc} v_{b\leftarrow a} \frac{g_a {\rm e}^{-hcE_a/k_{\rm B}T}}{Q(T)} \times [1-\exp(-hcv_{b\leftarrow a}/k_{\rm B}T)] \times R_{\rm V}^2 F(m) L(J) \times 10^{-36}, \tag{13}$$

where I_x is the isotopic abundance of the corresponding molecule in the sample; $\nu_{b\leftarrow a}$ is the wavenumber of the transition ($\rm cm^{-1}$); g_a is the nuclear-spin degeneracy factor; E_a is the energy of lower state ($\rm cm^{-1}$); $R_{\rm V}^2$ is the square of the rotationless transition dipole moment (Debye^2); $F(m) = (1+A_1 m)^2$ is the Herman–Wallis factor; $m = -J$ and $m = J+1$ are for P and R branches, respectively; $L(J)$ is the Honl–London factor; for Σ–Σ transition, $L(J) = J$ and $L(J) = J+1$ are for P and R branches, respectively; $Q(T)$ is the total internal partition sum of molecules; the value of I_x is obtained from Ref. [12]; $\nu_{b\leftarrow a}$ and the ground vibrational state rotational energies E_a are the calculated values from our program; the nuclear-spin degeneracy factor g_a for SiO_2 is equal to 1.[12] We obtained the value of $R_{\rm V}^2$ at 296 K in the Gaussian program. Then we further calculate the line intensities of the 001–000 transition of SiO_2 at 500 K and several higher temperatures.

3. Results and discussion

In Table 1, we list the correlation parameters for calculating partition function, rotational energy level and wavenumber of the transition. The rotational constants A, B, C and fundamental vibrational frequencies are cited from the work of calculated values in the Gaussian program. In Refs. [13]–[15], the expression used is a four-order one in temperature and requires five storage coefficients for a given temperature range

$$Q(T) = a + bT + cT^2 + dT^3 + eT^4.$$

For accuracy, a temperature range from 20 K to 6000 K is divided into five separate ranges, which are listed in Table 2. The fitted coefficients are presented in Table 3, and the fitted plot in 3000–4500 K is shown in Fig. 1.

Table 1. Correlation parameters for SiO_2 with angular structure.

σ	$\bar{g}$	g_a	g_b	g_c	A/cm^{-1}	B/cm^{-1}	C/cm^{-1}	ν_i/cm^{-1} $(i=3)$		
2	0	1	0	0	0.8760556	0.5212611	0.3268076	1031.4	712.2	708.4

Table 2. Five temperature ranges, grid spacings of fits and ranges of application.

range	temperatures used in fit/K	temperature grid/K	application range/K
1	20–510	10	20–500
2	500–1520	20	500–1500
3	1490–3020	30	1500–3000
4	2990–4520	30	3000–4500
5	4490–6020	30	4500–6000

Table 3. Fitted polynomial coefficients for five temperature ranges.

range	a	b	c	d	e
1	6.61791	1.27226	7.56229×10^{-4}	1.1423×10^{-5}	1.93397×10^{-9}
2	1667.60066	–8.49218	0.02402	-1.66509×10^{-5}	1.67498×10^{-8}
3	115556.74233	–269.51671	0.25307	-1.08413×10^{-4}	3.0985×10^{-8}
4	1.61545×10^{6}	–2192.33134	1.18886	-3.1352×10^{-4}	4.80773×10^{-8}
5	8.8837×10^{6}	–8537.58499	3.27832	-6.21173×10^{-4}	6.51691×10^{-8}

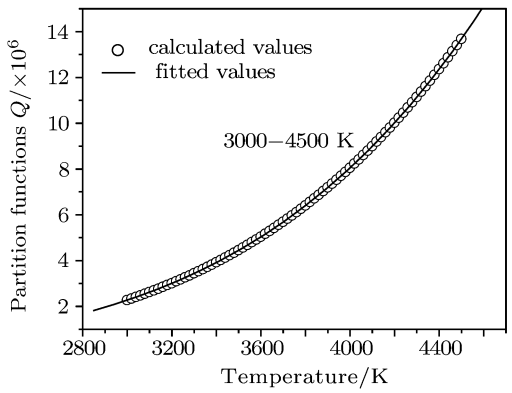


Fig. 1. Fitted plot with 3000–4500 K for SiO_2.

The calculated values for Q_{vib}, Q_{rot} and $Q(T)$ are 1.073, 6776.354 and 7271.028 at 296 K, respectively. The value of the total internal partition function $Q(T)$, 7271.028, is comparable to that of the calculated value in the Gaussian program, 7280.970, with a deviation of −0.137% at 296 K, which shows that our method is dependable. From Table 2 and Fig. 1, we find that the calculation values are in good agreement with the fitted values.

In Table 4, we list the calculated values of line intensities for the 001–000 band of SiO_2 at temperatures 500 K and 3000 K. Furthermore, we further calculate the line intensities at temperatures up to 4000, 5000 and 6000 K. The calculated simulated spectra of the 001–000 transition band of SiO_2 at 296 K and 2000 K are shown in Fig. 2. The spectral simulations at 4000 K and 6000 K are shown in Fig. 3.

Table 4. Line intensity data in the 001–000 band at 500 K and 3000 K for SiO_2.

	500 K	3000 K
wavenumber/cm^{-1}	$S_{\rm cal}$/cm·molecule^{-1}	$S_{\rm cal}$/cm·molecule^{-1}
1035.23	1.96594×10^{-20}	6.27199×10^{-23}
1037.88	6.53415×10^{-21}	2.19923×10^{-23}
1039.55	6.25915×10^{-21}	2.22868×10^{-23}
1041.21	5.81883×10^{-21}	2.22804×10^{-23}
1043.18	3.96462×10^{-20}	1.32168×10^{-22}
1045.75	4.53409×10^{-20}	1.57292×10^{-22}
1047.46	1.51527×10^{-19}	5.42056×10^{-22}
1049.16	5.49484×10^{-20}	2.03526×10^{-22}
1051.74	6.30719×10^{-20}	2.48719×10^{-22}
1053.45	1.96822×10^{-19}	8.11925×10^{-22}
1055.15	6.75297×10^{-20}	$2.9.2603\times10^{-22}$
1057.57	7.06042×10^{-20}	3.33324×10^{-22}
1059.43	2.25468×10^{-19}	1.12926×10^{-21}
1060.55	7.23950×10^{-20}	3.76149×10^{-22}
1062.90	7.54371×10^{-20}	1.30458×10^{-21}
1065.40	5.91538×10^{-20}	3.02887×10^{-22}
1068.27	1.88145×10^{-20}	9.97229×10^{-23}
1070.13	6.66395×10^{-20}	3.60390×10^{-22}
1071.98	6.88087×10^{-20}	3.80570×10^{-22}

In the line intensity calculation formula (13), the square of the rotationless transition dipole moment, $R_{\rm V}^2$, can be expressed as

$$R_{\rm V}^2 = \left| \int \Psi_v' \boldsymbol{d} \Psi_v'' {\rm d}\tau \right|^2 . \tag{14}$$

In Eq. (14), the wavefunctions Ψ_v' and Ψ_v'' and electronic dipole moment d are functions of nuclear displacement coordinates. That is to say, the square of the rotationless transition dipole moment, $R_{\rm V}^2$, is dependent on the molecular structure. The theoretical calculation based on an equation of state for detonation products (CO_2, O_2, H_2O, etc.) of CHNO explosives shows that the molecular structures of CO_2, O_2, H_2O, etc. almost do not change at temperatures up to 5000 K. Therefore, $R_{\rm V}^2$ can be regarded as a constant in calculation.

Besides $R_{\rm V}^2$, the Herman–Wallis factor $F(m)$ and the Honl–London factor $L(J)$ are independent of temperature T in Eq. (13), and only the partition function $Q(T)$ is dependent on T. Therefore, as long as the partition function $Q(T)$ is calculated within a sufficient accuracy, the line intensities at high temperatures should be credible within the same accuracy. Of course, as a result of product approximation, TIPS at high temperatures would have a certain error, which in turn will produce an error of line intensities at high temperatures. The value of error should be verified experimentally.

In the absence of experimental values or other reference data of SiO_2, we think that the line intensities of SiO_2 should be reliable, because the total internal partition function $Q(T)$ that we calculated is relatively accurate. From Figs. 2 and 3, we command a view of the line intensities of SiO_2 that will reduce with increasing temperature. Up to 2000 K, the distribution of spectral simulations of SiO_2 will be hardly changed.

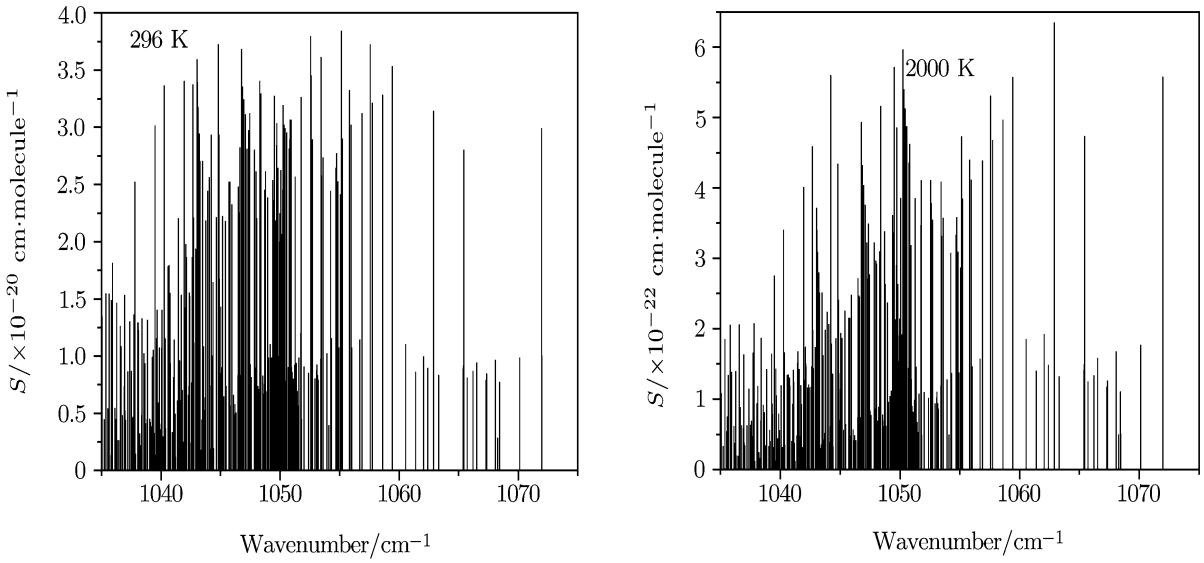


Fig. 2. Simulated spectra of the 001–000 band of SiO_2 at 296 K and 2000 K.

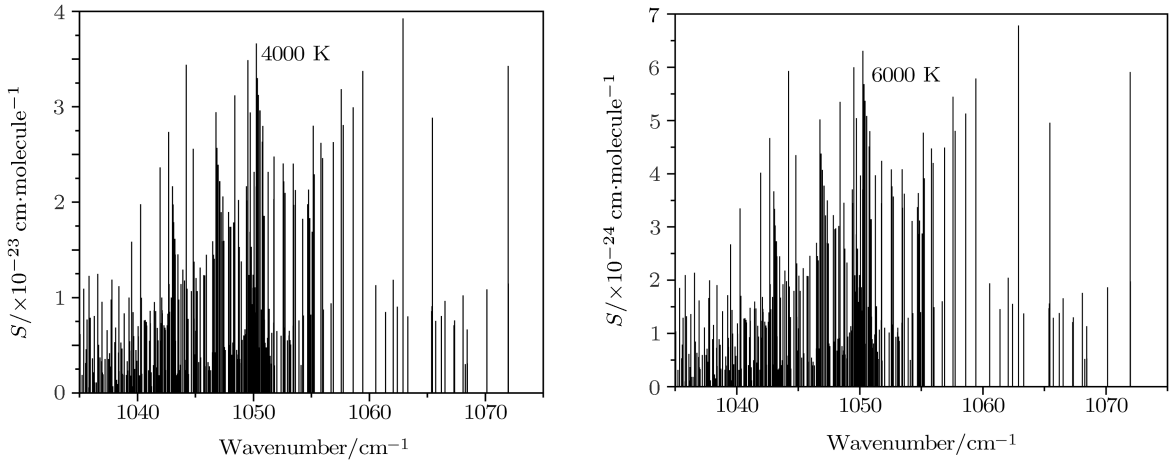


Fig. 3. Simulated spectra of the 001–000 band of SiO_2 at 4000 K and 6000 K.

4. Conclusion

The total internal partition functions are calculated for temperatures up to 6000 K for the asymptotic asymmetric-top molecule SiO_2 in the product approximation. The rotational partition functions are obtained by using the analytical expression of Watson and the vibrational partition functions in the harmonic oscillator approximation. Using the calculated partition functions, the rotationless transition dipole moment squared, and the Herman–Wallis factor, we computed the line intensities of the 001–000 band of the asymptotic asymmetric-top SiO_2 molecule at temperatures of 296, 500, 3000, 4000, 5000 and 6000 K. The high-temperature spectra of the asymptotic asymmetric-top molecule obtained by using these methods are reported in the literature, and the results are in good agreement with those in the HITRAN database for temperatures at 500 K and 3000 K. We believe that the simulated spectra of the 001–000 band of the SiO_2 radical at different temperatures (500 K, 3000 K and even higher temperatures 5000 K and 6000 K) should be reliable. This is of importance for asymptotic asymmetric-top SiO_2 molecule spectra in experiment or theory at normal or high temperatures.

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