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ABSORPTION AND RADIATION PROPERTIES OF THE SULFUR-CONTAINING GASEOUS COMPOUNDS¹

We report the scheme of calculating spectral line parameters (PSL) for hydrogen sulfide (H₂S) and sulfur dioxide (SO₂) gases based on the algorithm of calculating PSL for the asymmetric type molecules. The peculiarity of the procedure is the need to calculate the large volumes of PSL as the investigation temperature range 300-1200 (K) imposes the certain demands on the maximum values of the quantum numbers of vibration – rotation (VR) states. With the temperature growth the populations of the “hot” transition levels are increased and, accordingly, the all higher VR states must be included in calculation process. Derived by calculation the intensities and the wavenumber of absorption lines of SO₂ and H₂S were used for finding the absorption coefficient and emissivity of these gases with parallel analysis of the contributions of every vibrational band in the total band intensity.

Keywords: hydrogen sulfur, sulfur dioxide, absorption coefficient, emissivity.

The data of PSL of the hydrogen sulfur and sulfur dioxide molecules are an important for solving the problems of controlling the concentration these gases in the Earth’s atmosphere and in astrophysical applications. The traditional approach of describing the spectrum of asymmetric type molecules based on the effective VR Hamiltonian. Generally the corresponding VR Hamiltonian has the form of block diagonal matrix [1]:

$$H = \sum_{v, v' \in P} H_{vv'} |v\rangle \langle v'|,$$

which consists of the polyad of interacting vibrational states, selected by the following rules: $2v_1 + v_2 + 2v_3 = P = 1, 2, 3, \dots$, where v_1, v_2 , and v_3 – vibrational quantum numbers.

According to the formalism proposed in the work [2] the computer program for obtaining the energy of VR levels with an accounting of non-diagonal operators has been created and the calculations of the spectra of investigation gases have been made.

The Fig. 1a presents the absorption coefficient of SO₂ in the terahertz range ($1\text{--}250\text{ cm}^{-1}$) at different temperatures with the wavenumber spectral intervals of $\Delta\nu = 10\text{ cm}^{-1}$. It can be seen that with the growth of the temperature the number of the “hot” transitions increase which leads to decreasing the absorption coefficient in the center of band and to its shifting to the more high wavenumbers. At normal conditions ($T = 300\text{ K}$, $P = 1\text{ atm}$) the strongest absorption transitions belong to (000-000) band but at high temperature the total value depends on transitions within the other bands. Particularly the contribution of (010-010) band enlarges from 7.7 % at $T = 300\text{ K}$ to 20.8 % at $T = 900\text{ K}$ (table 1).

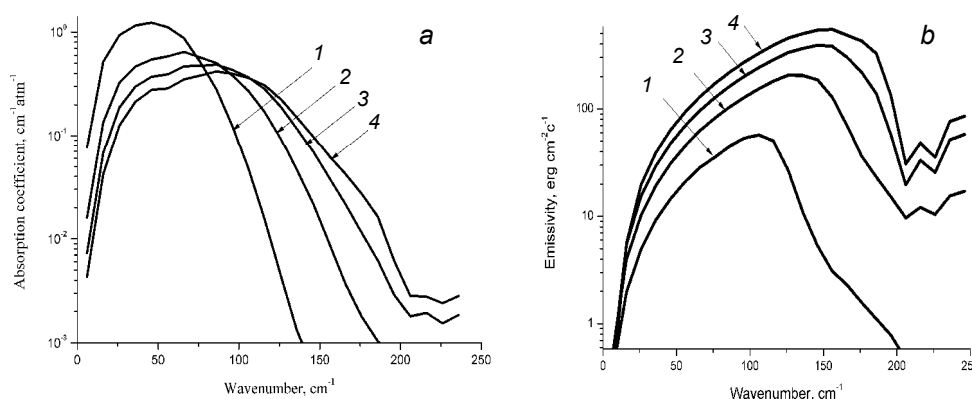


Fig. 1. Temperature dependence of the absorption coefficient (a) and emissivity (b) of SO₂ molecule in the range $1\text{--}250\text{ cm}^{-1}$: 1 – 300 K; 2 – 600 K; 3 – 900 K; 4 – 1200 K.

The line intensity for the pure rotational transition was determined by the method, described in detail in [3] but in the formula (1) we used the VR partition sum instead of rotational and as HITEMP [4] the

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temperature coefficient T/T_0 didn't take into account. The constant of permanent dipole moment (μ_0) was equal 1.6331 D [5].

The emissivity (Fig.1b) was got according to [6] with the partial pressure (ρ) equal 1 atm and the length of a trace (L) –1 m.

The Fig.2 demonstrates the absorption coefficient (a) and emissivity (b) of H_2S molecule corresponding to the fundamental transitions (000-000) at $T = 300$ K, $\rho=1$ atm⁻¹ and $L=1$ m. The calculation were carried out with $\mu_0 = 0.974$ D [7] and the set of parameters of the Hamiltonian from [8].

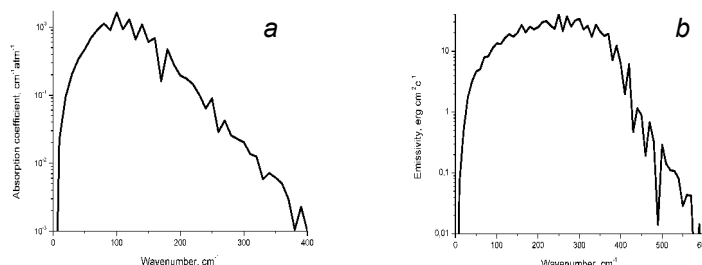


Fig.2. Absorption coefficient (a) and emissivity (b) of H_2S molecule corresponding to the fundamental transitions (000-000) at $T = 300$ K.

Table 1

The estimation of contribution of the fundamental bands to the total absorption coefficient of the SO_2 molecule

Band, $\nu_1\nu_2\nu_3-\nu_1\nu_2\nu_3$	000-000	010-010	001-001	100-100	020-020	011-011	110-110	030-030	
	[9]	[9]	[10]	[10]	[10]	[11]	[11]	[11]	
Relative contribution*, %	300 K ^o	90.9	7.7	0.13	0.36	0.66	$1.13 \cdot 10^{-2}$	$3.12 \cdot 10^{-2}$	$5.59 \cdot 10^{-2}$
	600 K ^o	64.6	19	2.36	3.95	5.42	0.68	1.14	1.56
	900 K ^o	46.6	20.8	4.64	6.56	8.24	1.91	2.7	3.40
	1200 K ^o	37.3	20.5	5.73	7.46	9	2.77	3.61	4.36

* $\sum_i^n S_i / S_T \cdot 100\%$, S_T – integrated intensity at given temperature T , $\sum_i^n S_i$ – sum of intensities of the rotational transitions within the band; n – number of the lines in the band; [] – source of the constants of the Hamiltonian which were used in calculation.

In the current work, we presented the results of calculating the PSL of sulfur-containing gaseous compounds, corresponding to the rotational transitions. These data can be used as the reference in the active and passive methods of the remote sounding in the terahertz range of electromagnetic waves.

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