

Line broadening of SO₂ and CO₂ volcanic activity gases in the Earth's atmosphere

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Abstract. Calculations of the CO₂-broadening coefficients of sulfur oxide lines by the semi-empirical method [Mol. Phys. 102 (2004) 1653] and averaged energy difference method [Atmosph. Ocean. Optics 28 (2015) 403] are presented. In this work, 41 lines are considered, the rotational quantum number J varies from 14 to 51. Calculations of the line widths are carried out for room temperature (296 K), and also for the temperature range typical for the Earth's atmosphere. There is good agreement with the literature data. The carbon dioxide lines broadening coefficients induced by nitrogen, nitrogen oxide, carbon monoxide and carbon dioxide at room temperature ($T = 296$ K) are obtained for a wide range of the rotational quantum number J (up to 100). The temperature exponents are calculated for every line widths. The calculations were performed by a semi-empirical method, based on the semiclassical impact theory of line broadening and modified by introducing additional correction factor whose parameters can be determined by fitting the broadening or shifting coefficients to the experimental data.

1 Introduction

Dynamics studies of SO₂ and CO₂ volcanic activity is an actual problem. Such research is performed by recording solar spectra of the atmosphere using ground stations equipped with FTC spectrometers. Registering solar spectra requires data on the broadening coefficients of SO₂ lines broadened by the main atmospheric gases, such as nitrogen and oxygen, and CO₂, which is released during volcanic activity.

To calculate the CO₂ broadening coefficients of SO₂ lines we have used two methods: semi-empirical (SE) technique [1] and the averaged energy difference (AED) approach [2]. The carbon-dioxide line broadening coefficients were obtained applying the first method only. The semi-empirical method was developed to calculate line broadening parameters of asymmetric top molecules and it was successfully applied for H₂O-N₂, -air, HDO-air colliding systems [2]. The averaged energy difference method allows the calculation of line widths with acceptable precision without the need for a complicated calculation scheme. The approach is based on matching the so called coupled energy state difference with a line broadening value. The averaged energy differences for lines with experimentally-determined collision-induced widths are then used to match averaged state energy

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differences to line broadening values using a fitting formula. The idea of the approach is in the selection from the whole calculation scheme of parameters that reflect the influence of the buffer particles on the internal state of the absorbing molecule. And the parameter formed from them was called the average energy difference of coupled states (the averaged frequency of collisional transitions).

2 Theoretical background

1.1 Semi-empirical method

The semi-empirical approach is a parametric modification of the semi-classical theory [1]. The rotation-vibration line half-width in the semi-classical theory can be represented by the expression

$$\gamma_{fi} = A(f, i) + \sum_l \sum_{i'} D^2(ii'|l) P_l(\omega_{ii'}) + \sum_l \sum_{f'} D^2(ff'|l) P_l(\omega_{ff'}), \quad (1)$$

where $A(f, i) = \frac{n}{c} \sum_r \rho(r) \int_0^\infty v f(v) b_0^2(v, r, i, f) dv$ – is the summand in which the dependence on the cut-off parameter b_0 is explicitly shown, n – is the density of perturbing molecules, $\rho(r)$ – is the population of the level r , r – is the set of quantum numbers of the perturbing molecule, v – is the relative collision velocity, $D^2(ii'|\lambda)$ and $D^2(ff'|\lambda)$ – are transition strengths related to the scattering channels $i \rightarrow i'$ and $f \rightarrow f'$ for the dipole ($l=1$), and quadrupole ($l=2$) types of transitions, $P_\lambda(\omega_{ii'})$ – are the efficiency functions, $\omega_{ii'}$, $\omega_{ff'}$ – and are the scattering channels corresponding to transitions from the upper and lower levels.

The transition strengths are defined only by the properties of the absorbing molecule: multipole moments and wave functions. The efficiency functions depend mainly on the interaction of colliding molecules, namely, on the intermolecular potential and on the trajectories of the relative motion of the molecules. The expression for the efficiency function has the form

$$P_l(\omega_{ii'}) = \frac{n}{c} \sum_r \rho(r) \sum_{l', r'} A_{ll'} D^2(rr'|l') F_{ll'} \left(\frac{2\pi c b_0(r, i, f)}{v} (\omega_{ii'} + \omega_{rr'}) \right). \quad (2)$$

In the semi-empirical method, a correction factor to the function P_l is introduced:

$$P_l(\omega) = C_l(\omega) P_l^A(\omega). \quad (3)$$

Here, the efficiency function $P_\lambda^A(\omega)$ that is obtained from the Anderson–Tsao–Curnutte theory is used as an initial approximation. Using $P_\lambda(\omega)$ in form (1) permits one to take into account the corrections that are connected with the absence of high-order terms of the expansion of the intermolecular potential, the short-range part of the interaction potential, high-order multipole moments, curvature of trajectories etc. In this paper, the correction factor was used in the following form:

$$C_l = \frac{c_1}{c_2 \sqrt{J} + 1}, \quad (4)$$

where c_1 and c_2 are the fitting parameters determined from the comparison of the results of the calculation with the measured half-widths.

1.2 Averaged energy difference method

In the frame of the modified RB (Robert-Bonamy) formalism the expressions of half-widths are given by Ma et al. [3]:

$$\begin{aligned} \gamma &= \frac{n}{2\pi c} \int_0^{+\infty} \nu f(\nu) d\nu \int_0^{+\infty} 2\pi b db [1 - \cos(S_1 + \text{Im} S_2)] e^{-\text{Re} S_2} \\ &\approx \frac{n\bar{\nu}}{2\pi c} \int_0^{+\infty} 2\pi b db (1 - e^{-\text{Re} S_2}). \end{aligned} \quad (5)$$

It is well known that $\text{Re}(S_2)$ consists of three terms: $\text{Re}(S_{2,outer,i})$, $\text{Re}(S_{2,outer,j})$, and $S_{2,middle}$. An explicit expression for $S_{2,outer,i}$ is given by Ma et al. [4]:

$$\begin{aligned} S_{2,outer,i} &= \frac{1}{h^2(2i+1)} \sum_{i_2} \rho(i_2) \int_{-\infty}^{\infty} dt \int_{-\infty}^t dt' \sum_{i' i_2'(m)} \int d\Omega_{\alpha} \int d\Omega_{\beta} e^{i(\omega_{i'} + \omega_{2i_2'})(t-t')} \\ &\times \langle i m_i i_2 m_{i_2} | \alpha \rangle V_{\alpha}(\vec{R}(t)) \langle \alpha | i' m'_i i'_2 m'_{i_2} \rangle \\ &\times \langle i' m'_i i'_2 m'_{i_2} | \beta \rangle V_{\beta}(\vec{R}(t')) \langle \beta | i m_i i_2 m_{i_2} \rangle, \end{aligned} \quad (6)$$

where quantum indices i and i' associated with the absorbing molecule represent pairs of the quantum numbers J_i , τ_i and $J_{i'}$, $\tau_{i'}$ used to specify the energy levels of the initial and final states. The term $S_{2,outer,i}$ may be written in form:

We neglected the effects from the perturbed gases and introduced a simpler version of the averaged energy differences between the line of interest and other coupled lines defined by

$$\begin{aligned} \bar{\omega}_f(L_1 K_1 K'_1) &= \frac{1}{W(L_1 K_1 K'_1)} \left\{ \sum_{i' \tau'} (2i'+1) D(i \tau' i' \tau'; L_1 K_1) D(i \tau' i' \tau'; L_1 K'_1) f(\omega_{i \tau' i' \tau'; L_1 K_1 K'_1}) \omega_{i \tau' i' \tau'; L_1 K_1 K'_1} \right. \\ &\left. + \sum_{f' \tau'_f} (2f'+1) D(f \tau_f f' \tau'_f; L_1 K_1) D(f \tau_f f' \tau'_f; L_1 K'_1) f(\omega_{f \tau_f f' \tau'_f; L_1 K_1 K'_1}) \omega_{f \tau_f f' \tau'_f; L_1 K_1 K'_1} \right\}, \end{aligned} \quad (7)$$

where $W(L_1 K_1 K'_1)$ is the sum of the weighted factor given by

$$\begin{aligned} W(L_1 K_1 K'_1) &= \sum_{i' \tau'} (2i'+1) D(i \tau' i' \tau'; L_1 K_1) D(i \tau' i' \tau'; L_1 K'_1) f(\omega_{i \tau' i' \tau'; L_1 K_1 K'_1}) \\ &+ \sum_{f' \tau'_f} (2f'+1) D(f \tau_f f' \tau'_f; L_1 K_1) D(f \tau_f f' \tau'_f; L_1 K'_1) f(\omega_{f \tau_f f' \tau'_f; L_1 K_1 K'_1}). \end{aligned} \quad (8)$$

We obtain a certain effective quantity $\bar{\omega}_f(L_1 K_1 K'_1)$ characterizing the influence of interaction on the absorbing molecule. In fact, we carry out the averaging of frequencies of collisional transition over scattering channels with matrix elements of the dipole moment and resonance functions as weights (weighted arithmetic average). It should be noted that the averaging is performed over all collisional transitions, related to initial and final states.

The next step is to compare by the averaged frequency of collisional transitions with experimental line widths, to determine the model parameters we applied the reference data [5]. Then we plot the dependence of measured line broadening coefficient versus the average frequency of collisional transitions. If we use the experimental data of high quality, we have a smooth monotonic curve which is easily approximated to a simple analytical expression. Curve smoothness directly depends on the data quality. We can see such example in the paper [2], where the case of N_2 -broadening of water vapour line is present

and very accurate measured data are used. In case of SO₂-CO₂ system we do not have as good a situation, (Fig. 1), these data are not a perfect fit to a smooth curve.

Now it is easy to determine the approximation of the line broadening coefficient for this system:

$$\begin{aligned} \gamma_{if} &= -0.000963 \cdot \bar{\omega} + 0.1663 & \text{for } \bar{\omega}_{if} < 46, \\ \gamma_{if} &= -0.000609 \cdot \bar{\omega} + 0.1500 & \text{for } \bar{\omega}_{if} \geq 46. \end{aligned} \quad (9)$$

Comparison of computed using approximation (9) values with available experimental data and semi-empirical calculations are given in Fig. 1, it will be discussed later.

The calculation requires spectroscopic SO₂ molecule constants, for the ground and the first excited states they are taken from [18]. The mean dipole moments in the ground state $\mu = 1.627$ D, quadrupole moment $Q = 4.4$ D Å, the mean dipole polarizability $\alpha = 3.78$ Å³ are taken from [19,20].

3 Results and discussion

Calculations of SO₂-CO₂ broadening coefficients are performed for 41 rotational-vibrational lines, rotational quantum numbers of J varies from 14 to 51. Our data agree satisfactorily with measured values. The root mean square deviations (RMSD) of calculated line widths from measured values [5] are 0.012 cm⁻¹atm⁻¹ for AED method and 0.011 cm⁻¹atm⁻¹ for SE method, discrepancy is less than 8%.

It is seen that experimental values [5] are characterized by larger dispersions than theoretical ones. The discrepancies increase with higher rotational quantum numbers and the differences can be positive or negative. For example, the discrepancy in the line width with $J=49$ reaches 29%.

The temperature dependences of line broadening coefficients are of crucial impact for radiative transfer modelling of air near volcanoes and of planetary atmospheres. The calculated line widths were fitted to the available experimental data at the room temperature (296 K), and then using obtained parameters the broadening coefficients have been computed at the temperatures of 150 K, 200 K, 250 K, and 350 K. The semi-empirical method yields realistic results and SE calculations for numerous molecular systems show that the model parameters c_i are not temperature-sensitive.

After the determination of the line half-width at different temperatures, by the usual least-squares method the temperature exponents N for the broadening coefficients were derived according to the expression

$$\gamma = \gamma_0 \left(\frac{T_0}{T_k} \right)^m, \quad (10)$$

with the reference temperature $T_0 = 296$ K.

We note that the deduced N values are very sensitive to the precision of half-widths, especially for narrow lines: even small errors in the determination of γ induce large uncertainties in N . The bulk of the extracted temperature exponents with their uncertainties computed for $K_a=14$ is shown in Fig. 2. The calculated temperature exponents of line broadening at $K_a=14$ vary from 0.450 to 0.669. The general tendency of the temperature exponent variation is a sharp increase with the rotational quantum number till $J \sim 25$ then the values are almost constant and the exponents of some lines increase slightly again at high J quantum numbers.

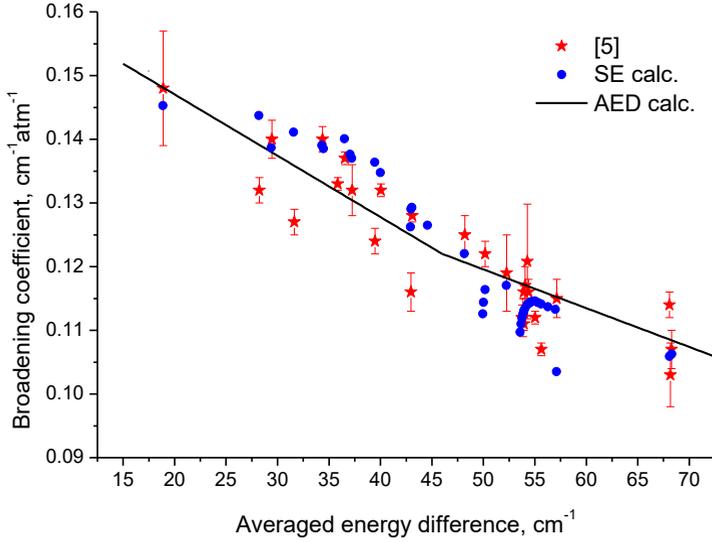


Fig. 1. CO₂-broadening coefficient of SO₂ line as functions of averaged frequency of collisional transitions.

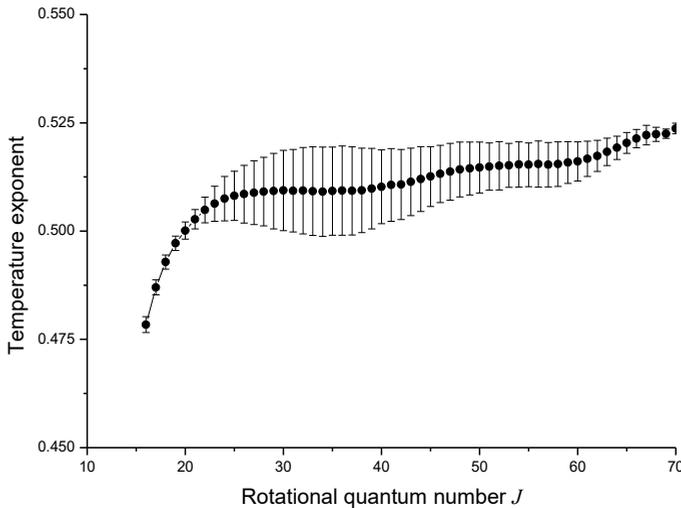


Fig 2. Semi-empirical temperature coefficient versus the upper rotational quantum number J for RQ -branch-line broadening for SO₂-CO₂ system.

To determine semi-empirical parameters in the case of carbon dioxide self-broadening, the measured values [6] were used. The half-widths from the HITRAN spectroscopic database [7] and from [6] are in good agreement with our calculated data (Fig. 3). The N₂-, N₂O-, CO- and CO₂-broadening coefficients of CO₂ lines, are calculated for the transitions of the R -, P -branches with upper rotational quantum numbers J up to 100 for ten temperatures in the interval from 300 to 700 K. The rotational dependence of the line widths for the CO₂-CO₂ system is stronger than for the CO₂-N₂O system, and, for $J < 56$, the values $\gamma_{CO_2-CO_2} > \gamma_{CO_2-N_2O}$. This is explained by the difference in the multipole moments and in the structure of the vibrational-rotational energy spectrum of the broadening molecules.

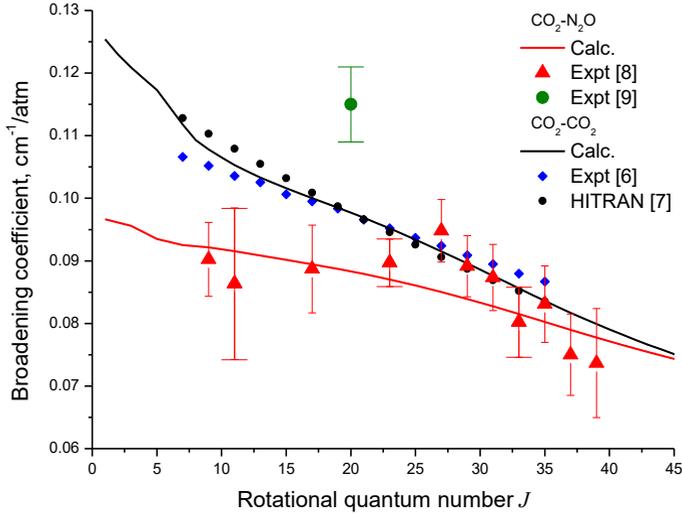


Fig. 3. Broadening coefficients as functions of the upper rotational quantum number J for the $\text{CO}_2\text{-N}_2\text{O}$ and $\text{CO}_2\text{-CO}_2$ systems.

Figure 3-4 demonstrates the good agreement of measurements [8] and our calculations for $\text{CO}_2\text{-N}_2\text{O}$, $\text{CO}_2\text{-CO}$ systems. The $\gamma_{\text{CO}_2\text{-N}_2\text{O}}$ and $\gamma_{\text{CO}_2\text{-CO}}$ theoretical half-widths of smoothly decrease from 0.0967 (for $J = 0$) to 0.0672 $\text{cm}^{-1}\text{atm}^{-1}$ (for $J = 80$) and from 0.1167 (for $J = 0$) to 0.0570 $\text{cm}^{-1}\text{atm}^{-1}$ (for $J = 80$), respectively; the behavior of the experimental values is similar. The root-mean-square deviation for $\text{CO}_2\text{-N}_2\text{O}$ system is 0.0045 $\text{cm}^{-1}\text{atm}^{-1}$.

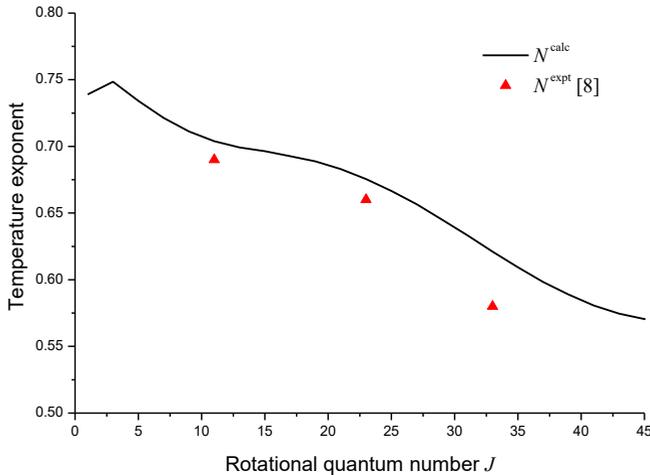


Fig. 4. Temperature exponents versus the upper rotational quantum number J for the N_2O -broadening of CO_2 lines.

The half-width of the line P(20) for the $\text{CO}_2\text{-N}_2\text{O}$ system that was measured in [9] is 0.115 $\text{cm}^{-1}\text{atm}^{-1}$ and, as seen from Fig. 3, is significantly larger than the values that were obtained in [8] and in this work. The half-widths for some buffer gases that are presented in [9] are also larger than other experimental data as, e.g., in the case of nitrogen broadening.

All temperature exponents for N₂O and CO broadening coefficients of CO₂ lines are smaller than 0.8. In the case of N₂O-broadening the experimental values [8] for the vibrational–rotational transitions R(10), R(22), and R(32) are equal to 0.69, 0.66, and 0.58, respectively, and the calculated temperature exponents vary within the interval from 0.569 to 0.748.

The temperature exponents are not monotonic functions of the rotational quantum number for both gas mixture: in the case CO₂-N₂O coefficient reaches the minimum value at $J = 47$. One can see that the experimental temperature exponents are less than the theoretical values for each of the three vibrational–rotational transitions; however, N^{calc} and N^{expt} have similar dependencies on J . The theoretical temperature exponents for CO₂ – N₂O system vary in the range of 0.59–0.75. For the coefficients m , the root-mean-square deviation is 0.026.

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