LINE PARAMETERS OF VOLCANIC GASES (CO2 AND CO): MEASUREMENTS AND CALCULATIONS

T.M.Petrova, V.M. Deichuli, N.N. Lavrentieva, N.A. Lavrentiev, A.Z. Fazliev

V.E. Zuev Institute of Atmospheric Optics, Russian academy of sciences, Siberian branch, 634021 Tomsk, Russia

Introduction

When studying volcanic activity, knowledge of the carbon oxides dynamics in the surface layers of the atmosphere is necessary. These studies are conducted when recording solar atmospheric spectra using ground stations equipped with FTS spectrometers. To record the solar spectra, we need data on the broadening coefficients of the lines of CO, CO_2, and H_2O broadened by the main atmospheric gases, such as nitrogen, oxygen, and carbon dioxide, the latter being released during volcanic activity.

The absorption of $^{12}C^{16}O_2$ in the spectral region 9340–9650 cm^{-1} was measured on a Bruker IFS 125HR Fourier spectrometer, combined with a multi-pass measuring cell. A large array of the coefficients of broadening and shift of the lines of the 20032−00001 band was obtained.

The broadening coefficients of the carbon monoxide and dioxide lines, as well as the water vapor lines were calculated. Two calculation methods were used: a semi-empirical method, based on the semiclassical impact theory of line broadening, and supplemented by the introduction of a correction factor, the parameters of which were determined using experimental data [Mol. Phys. 102 (2004)], as well as the average frequencies method [Opt. Atmosphere Ocean. 28 (2015)]. The lines half-widths were calculated for room temperature (296 K) and for the Earth's atmosphere temperature range. The calculations were performed for a wide range of rotational quantum numbers J (up to 100). For each half-width the temperature exponents were calculated. Experimental and calculated are in a good agreement.

Semi-empirical approach

The semi-empirical method [1] simplifies the semi-classical Robert-Bonamy expressions to an Anderson-type form via introducing effective correction factors. These factors, chosen in a convenient parameterized form, account for the real trajectory curvature, vibrational dependence and corrections to the scattering matrix. The model parameters are fitted on some experimental data and their values are further used to compute the line-widths for other sets of rotational quantum numbers (the vibrational dependence of line-broadening coefficients is negligible for most molecular systems and the parameters adjusted on one vibrational or rotational band can be safely used for other vibrational bands).

The semi-classical half-width γ_{if} associated with the optically active $i \to f$ transition are given by

$$\gamma_{if} - i\delta_{if} = \frac{n_2}{c}\sum_2 \rho(J_2)\int_0^\infty d\upsilon\,\upsilon f(\upsilon)\int_0^\infty db\,b\,S(b)$$

with the interruption function

$$S(b) = 1 - \sum_{2'}\sum_{m,m'} \frac{(J_f 1 m_f q | J_i m_i)(J_i 1 m_i q | J_i m_i)}{(2J_f+1)(2J_i+1)} \langle J_i m_i J_2 m_2 | T | J_i m_i' J'_2 m_2' \rangle \times$$

$$. \quad \times \langle J_f m_f' J_2' m_2' | T | J_f' m_f' J_2' m_2' \rangle$$

The half-width can be expressed as

$$\gamma_{if} = A(if) + \sum_{i'l} D^2(ii'|l)P_l(\omega_{ii'}) + \sum_{f'l} D^2(ff'|l)P_l(\omega_{ff'}) + \ldots$$

where

$$A(if) = \frac{n}{c}\sum_2 \rho(J_2)\int_0^\infty \upsilon F(\upsilon) b_0^2(\upsilon, J_2, i, f)\,d\upsilon$$

The efficiency function $P(\omega)$ can be represented as

$$P_l(\omega) = \frac{n_2}{c}\sum_k \rho(J_2)\sum_{l',J_2'} A_{ll'} D^2(J_2 J_2'|l') F_{ll'}\left(\frac{2\pi c b_0(J_2,i,f)}{\upsilon}(\omega + \omega_{J_2 J_2'})\right),$$

$$P_l(\omega_{ii'}) = P_l^A(\omega_{ii'}) C_l(\omega_{ii'})$$

where correction factor $C_l(\omega)$ is usually taken in the following forms:

1) $C_1(\omega_{JJ'}) = \frac{c_1}{c_2\sqrt{J}+1}$ for linear molecules, symmetric and asymmetric tops

(H_2O-N_2,O_2,H_2O; O_3-N_2,O_2; CO_2-N_2O,CO_2; CH_3Cl-CO_2);

.

Temperature dependence

The temperature-dependence characteristics were determined for the interval 200–400 K.

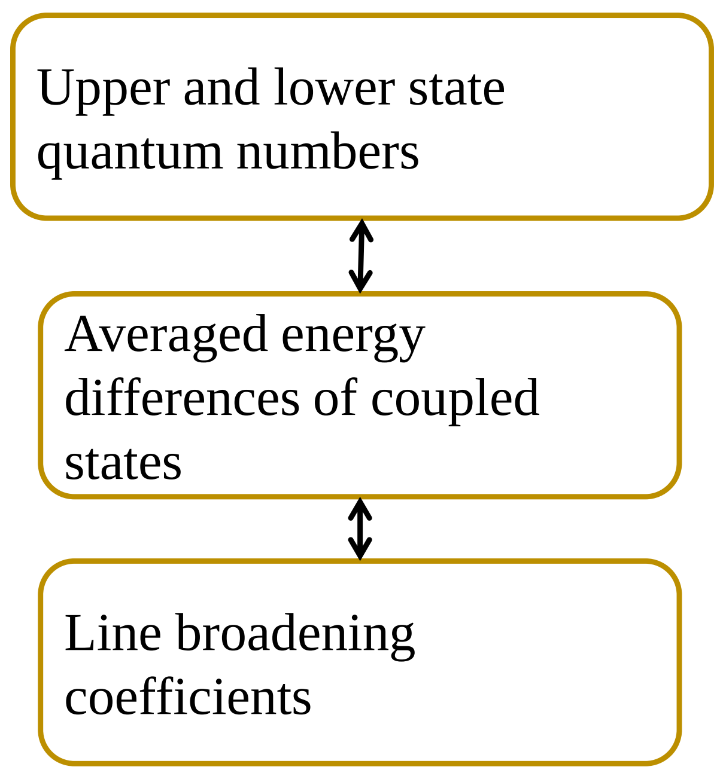
The usual relation for temperature dependence of broadening and shifting coefficients are given by

$$\gamma(T) = \gamma(T_0)\left(\frac{T_0}{T}\right)^N$$

.

Averaged energy difference approach

Basic idea



Upper and lower state quantum numbers

Averaged energy differences of coupled states

Line broadening coefficients

Based on the modified RB formalism, the expressions of the half-widths are given by

$$\gamma = \frac{n_b}{2\pi c}\int_0^{+\infty} vf(v)dv \int_0^{+\infty} 2\pi b db[1 - \cos(S_1 + \operatorname{Im} S_2)e^{-\operatorname{Re} S_2}] \quad (1)$$

$$\approx \frac{n_b \bar{v}}{2\pi c}\int_0^{+\infty} 2\pi b db(1 - e^{-\operatorname{Re} S_2}).$$

$$S_{2,outer,i} = \sum_{L_1 K_1 K_1' L_2}\int_{-\infty}^{\infty}\int_{-\infty}^{t} dt\,dt' G_{L_1 K_1 K_1' L_2}(t,t') W^{(a)}_{L_1 K_1 K_1'}(t-t') W^{(b)}_{L_2}(t-t').$$

In the above expression, two functions which are independent of the potential are defined by

$$W^{(a)}_{L_1 KK'}(t) = \sum_{i'\tau'}(2i'+1)D(i\tau i'\tau'; L_1 K)D(i\tau i'\tau'; L_1 K')e^{i\omega_{i\tau_i i'\tau_i'}t},$$

where quantum indices i and i' associated with the H_2O 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.

Where D(iτi'τ';L K) is defined by

$$W^{(b)}_{L_2}(t) = \sum_{i_2 i_2'}(2i_2+1)(2i_2'+1)\rho_{i_2} C^2(i_2 i_2' L_2, 000)e^{i\omega_{i_2 i_2'}t},$$

The functions introduced above are:

$$G_{L_1 K_1 K_1' L_2}(t,t') = \frac{\hbar^{-2}}{4\pi(2l_1+1)^2(2l_2+1)^2}(-1)^{K_1+K_1'}\sum_L (-1)^{(L_1+L_2+L)}(2L+1) \quad (7)$$

$$\times u(L_1 L_2 L; K_1; R(t)) u(L_1 L_2 L; K_1'; R(t')) P_L(\cos\Theta_{tt'}).$$

$$\operatorname{Re}(S_{2,outer,i}) = \sqrt{\frac{\pi}{2}}\sum_{L_1 K_1 K_1' L_2}\{\sum_{i_2 i_2'}(2i_2+1)(2i_2'+1)\rho_{i_2} C^2(i_2 i_2' L_2, 000)\}$$

$$\times\{\sum_{i'\tau'}(2i'+1)D(i\tau i'\tau'; L_1 K_1)D(i\tau i'\tau'; L_1 K_1')\} H_{L_1 K_1 K_1' L_2}(\omega_{i\tau i'\tau'} + \omega_{i_2 i_2'}). \quad (8)$$

Then, we can estimate how values of Re(S_2) vary with different lines of interest. We introduce coupled state energy differences between a H_2O line of interest and other coupled lines defined

$$\overline{\omega}_{if} = \frac{1}{W}\left\{\sum_{i'}(2i'+1)D^2(ii'|l)f(\omega_{ii'})\omega_{ii'} + \sum_{f'}(2f'+1)D^2(ff'|l)f(\omega_{ff'})\omega_{ff'}\right\} \equiv \omega'$$

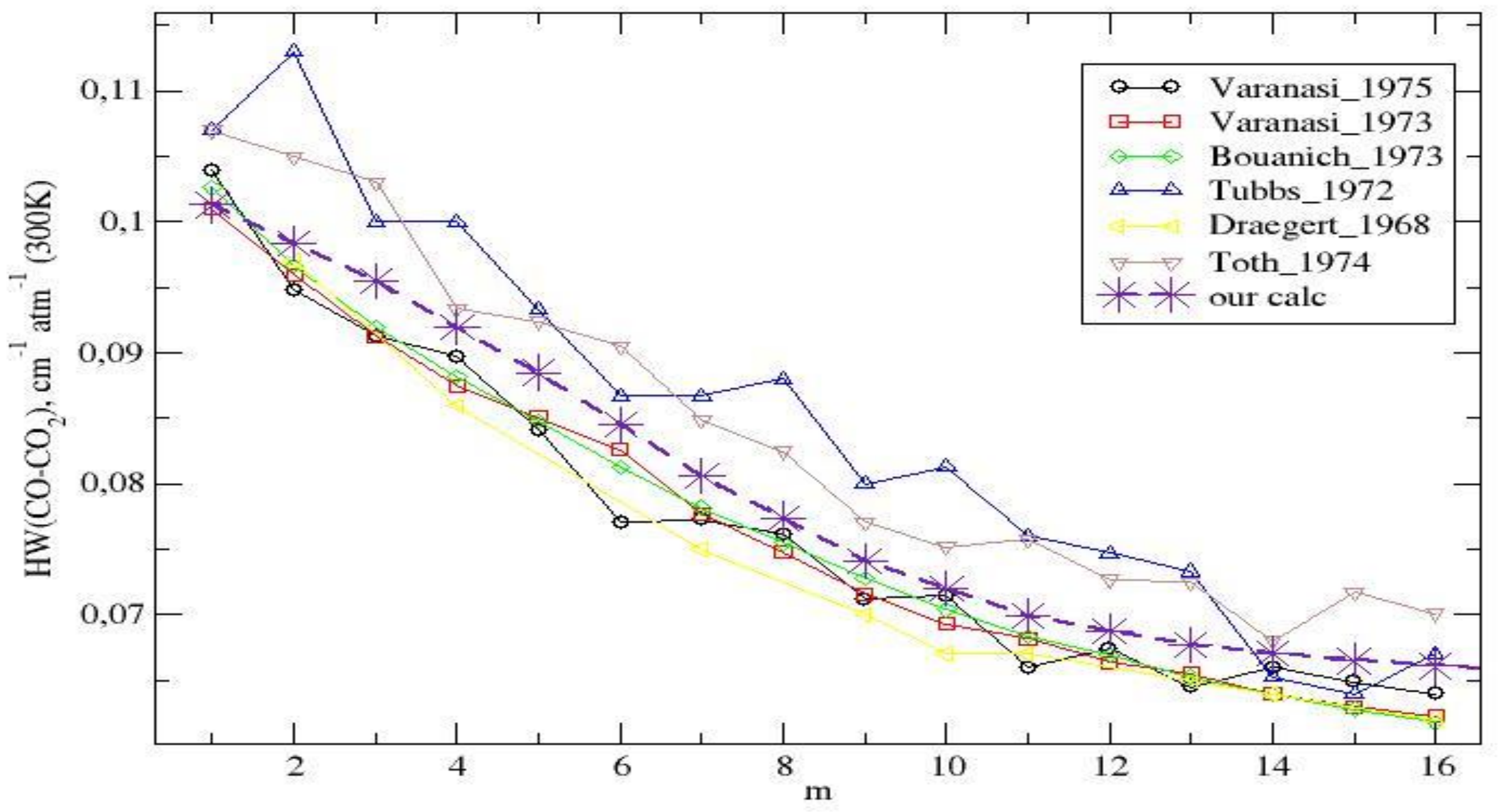
by

$$W = \sum_{i'}(2i'+1)D^2(ii'|l)f(\omega_{ii'}) + \sum_{f'}(2f'+1)D^2(ff'|l)f(\omega_{ff'})$$

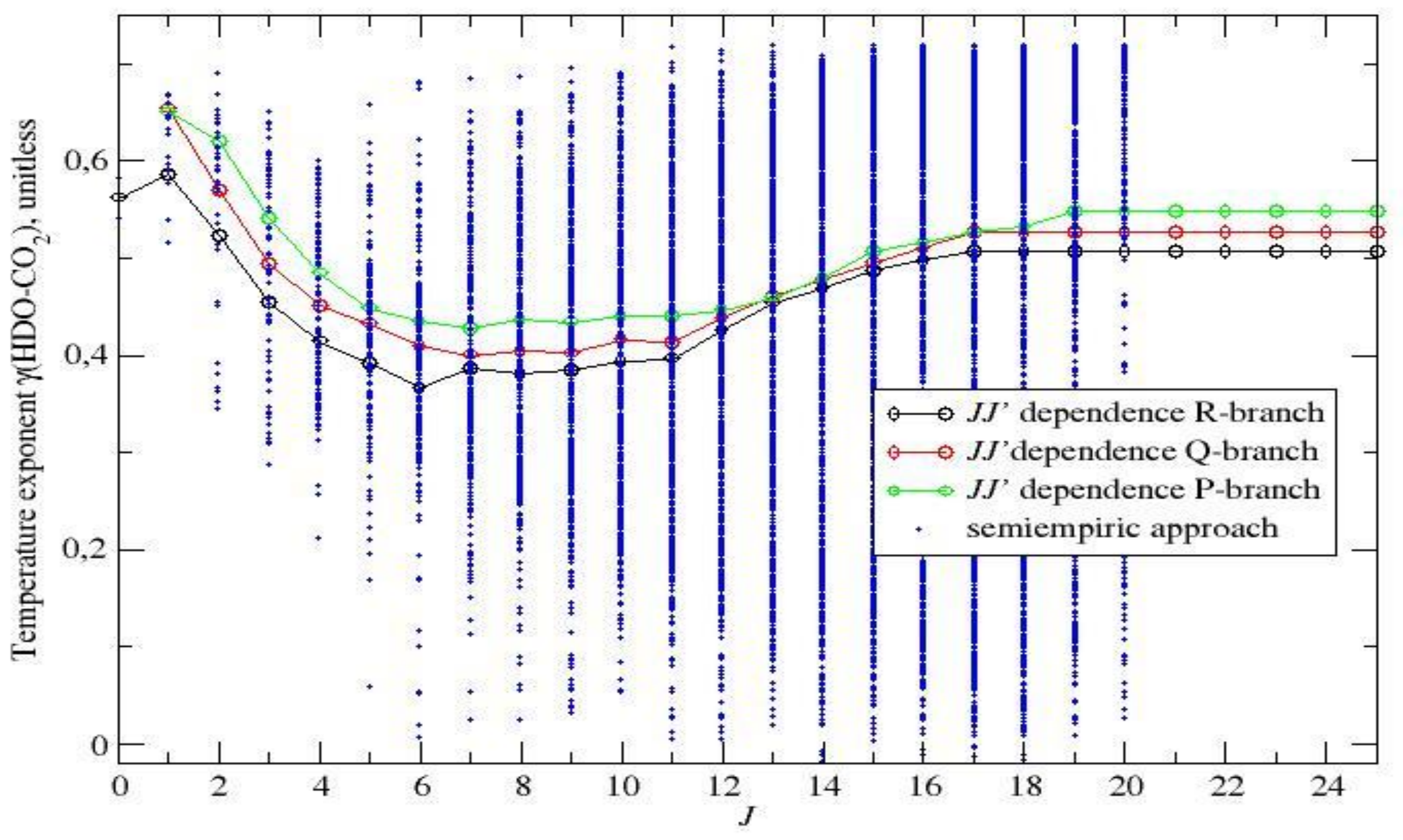
Calculations were made considering contributions of the dipole-quadrupole and quadrupole-quadrupole interactions.

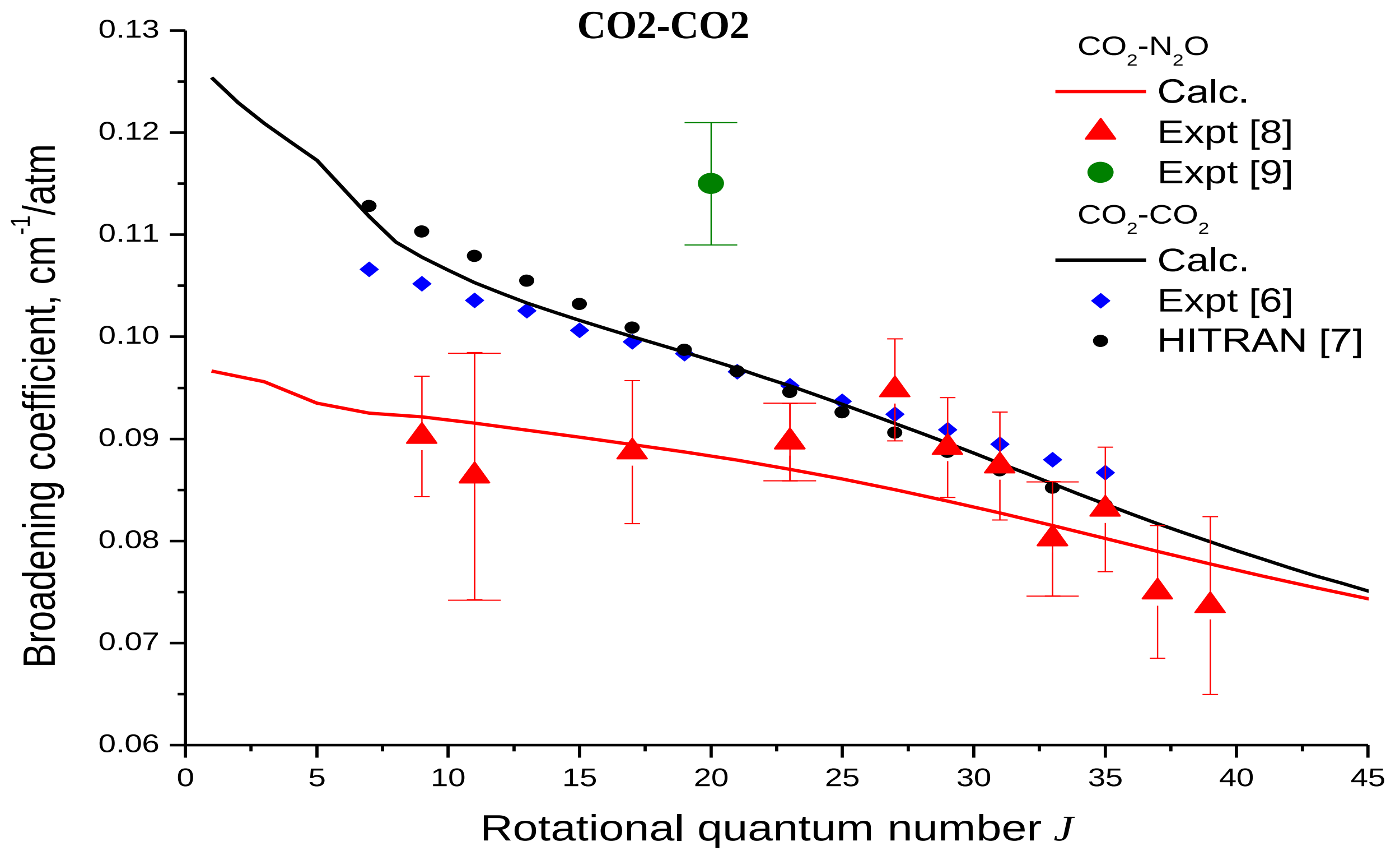
LINE BROADENING: CO-CO_2, CO_2-CO_2 H2O-CO_2,

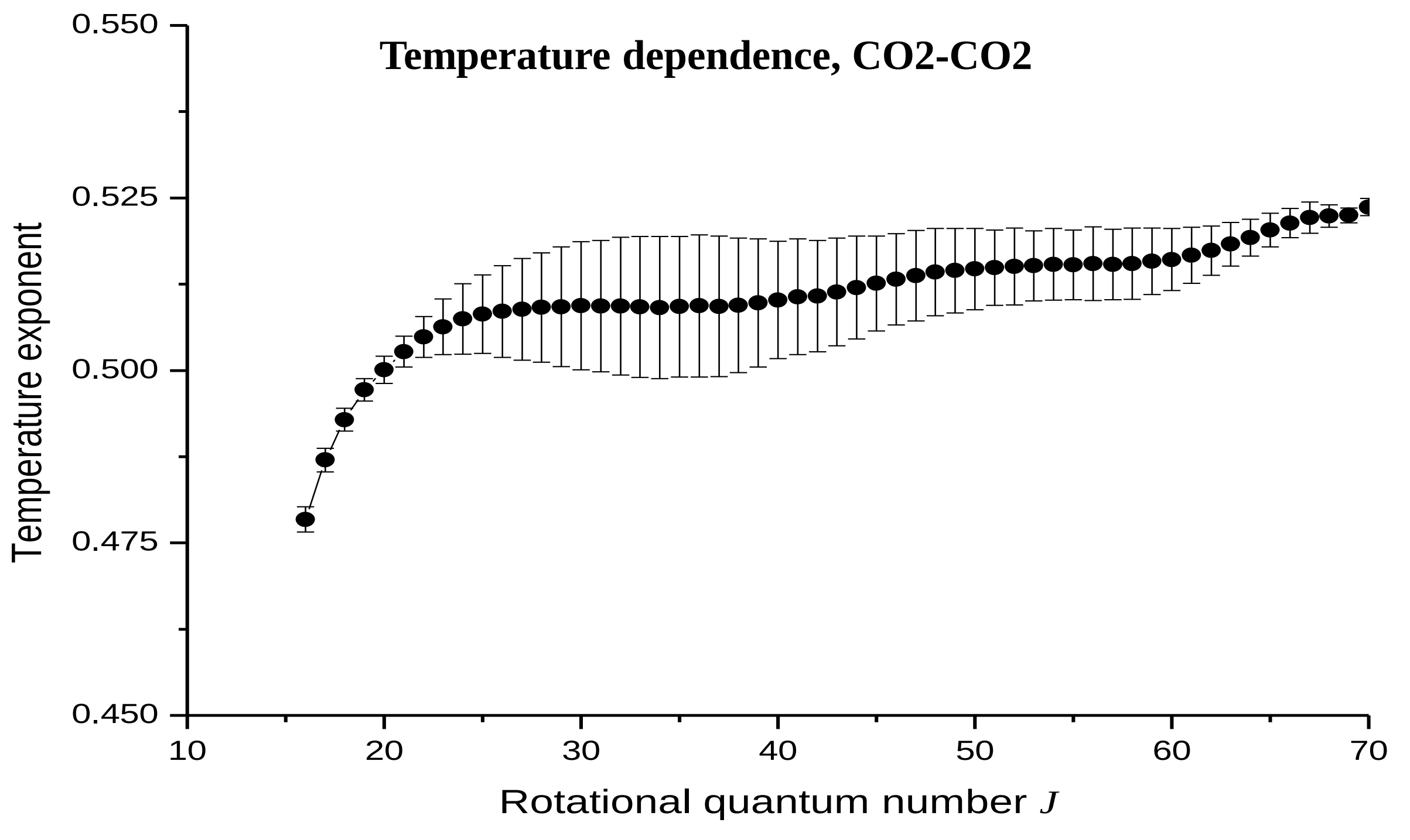
CO-CO2



H2O-CO2




CO2-CO2


Temperature dependence, CO2-CO2

References

[1] Bykov A.D., Lavrentieva N.N., Sinitsa L.N., Mol. Phys.,102, 1653–1658 (2004).

[2] Dudaryonok A.S., Lavrentieva N.N., Ma Q., Atm. Oc. Optics 28(6) 403-409 (2015).

[3] Varanasi P. // J. Quant. Spectrosc. Radiat. Transfer. 1975. V.15. P. 191-196.

[4] Borkov Yu., Petrova T. et al// JQSRT 2018 V.219 P.379-382

[5] Varanasi P. Addentum to "line-width measurements on CO in an atmosphere of CO2" // J. Quant. Spectrosc. Radiat. Transfer 1973. V.13(8). P. 823-824

[6] Bouanich J. P., Brodbeck C. // J. Quant. Spectrosc. Radiat. Transfer 1973.

Conclusions

Measurements and calculations of CO_2 broadening coefficients and their temperature exponents for CO_2, CO and H_2O lines were obtained for the temperature interval 150–350 K recommended for HITRAN. Calculations are performed using two methods: 1. the average energy difference method, 2. the semi-empirical approach, which is a modification of the impact theory performed by introduction of the empirical correction factor. Data are obtained for a large amount of rovibrational transitions J and K_a requested by spectroscopic databases. Theoretical coefficients agree satisfactorily with measured values. The calculations have demonstrated that the semi-empirical method provide a reasonable description of the variation of the broadening coefficients and their temperature exponents.

The capacity of the semi-empirical approach to reproduce available measurements of line-shape parameters and to extrapolate their values to higher J and K_a inaccessible experimentally can be also exploited to get line-shape characteristics for another spectral range of considered colliding system, such calculations for the other bands are in progress. We have computed line-lists for broadening coefficients as well as the corresponding temperature exponents for the temperature interval 200–400 K recommended for HITRAN.

The work was supported by the Russian Foundation for Basic Research (Grants No. 19-03-00389_a).