Semiempiric approach for calculation of the H_2O and CO_2 line broadening and shifting

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ABSTRACT

A semiempiric approach for spectral line halfwidths and shifts calculation is proposed. This approach is based on the Anderson approximation and includes the correction factors whose parameters can be determined by fitting the broadening or shifting coefficients to the experimental data. This allows sufficiently accurate predictions of the parameters of line profiles, which were not measured. The coefficients of the CO_2 and H_2O spectral lines broadening and shifting by air and nitrogen pressure are calculated, as well as the coefficients of their temperature dependence. The calculated coefficients agree satisfactorily with measured values.

Key words:

Line profile, broadening and shifting coefficient, temperature exponent

I. INTRODUCTION

Various problems of atmospheric physics, astrophysics, flame spectroscopy and laser physics require a knowledge of spectral line parameters for water vapor and carbon dioxide in a wide temperature range for different vibrational bands from the mid-infrared to the visible spectral region. For example, the amount of information needed for calculation of atmospheric transparency in the region of the water vapor resonance polyad includes several thousands of spectral lines. An even greater number is needed for calculating the spectra of flames (as well as spectra of planets), because in this case one needs the information on spectra at the temperature of 2000–3000 K, which include a large number of hot bands.

It is known that the halfwidths of molecular spectral lines only slightly depend on vibrational quantum numbers. The typical difference in the halfwidths of different bands is as small as several percent. Therefore, the broadening coefficients can be calculated for only one band and then extrapolated to other vibrational bands. At the same time, the shift coefficients can vary significantly from one band to another. Calculations should therefore be performed for every band separately, or the shifts should be determined by some interpolation procedure. The temperature exponents of line halfwidths can also vary widely depending on the rotational quantum numbers because of the strong temperature dependence of the population of the lower energy level. These parameters are different for different values of quantum numbers. Therefore, the amount of calculations for compilation of a more complete database increases by several orders of magnitude.

The Anderson theory (*1*) employs the simplest (straight path) representation of the relative motion and the intermolecular potential is taken as the long range expansion. The Anderson method distinguished by the relative simplicity of calculations has proved its efficiency in description of line broadening processes for molecules like HCl-DCl, H_2O-H_20, H_2O-CO_2 and etc. characterized by so-called strong interactions, when the distance of closest approach is less than the interruption parameter of the Anderson theory ($r_c < b_0$, r_c - distance of closest approach and b_0 – Anderson interception radius). The N_2 molecule has no dipole moment and in the case of H_2O-N_2, CO_2-N_2 colliding pairs the dipole-quadrupole interaction becomes the main factor in line broadening, and other weaker interactions (such as quadrupole-quadrupole interactions etc) begin to play an important role.

For the case of weak interactions ($r_c > b_0$) this method does not provide a good description, and therefore several authors proposed various versions of cut-off-free method taking into account increasingly subtle effects (atom-atom potential, trajectory curvature, accounting for the imaginary part of the interruption function for broadening calculation (Refs.(*2*-*4*)).

Robert and Bonamy have developed (*2*) a semi-classical cut-off-free theory (RB) which takes into account a more realistic potential as a sum of an atom-atom short-range potential and an electrostatic long-range potential. They use an effective parabolic trajectory instead of the straight-line trajectory of the Anderson theory. Details of the intermolecular interaction at short distances and of the bending of the trajectory were found to be important for close collisions (small b) and their consideration in the formalism proved to bring significant improvements in the calculations.

Gamache *et al. (3)* have proposed a new improvement in the RB-theory, known as the complex Robert-Bonamy formalism (CRBF), which takes into account simultaneously the real and imaginary parts of the interruption function. They found that the imaginary part of the interruption function, which defines the lineshift, provides an important contribution to the H_2O halfwidths.

In our work *(4)*, an exact trajectory (ET) model has been proposed. It allows one to use a more accurate trajectory model in the semi-classical calculation of line broadening parameters. This model was successfully used by Buldyreva *et al. (5,6)* in the calculation by RB-method.

These versions of the cut-off-free method describe the processes rather well, but due to the complexity of the calculations, do not allow visualizing and analyzing processes occurring in colliding molecules, in particular, the effect of compensation for contributions of different scattering channels in the pressure-induced shift. Therefore, it seems useful to correct the Anderson method *(1)* in some way to eliminate its main disadvantages. In this paper, we propose a semiempiric method based on the Anderson theory to calculate broadening and shifting coefficients of the water vapor and carbon dioxide spectral lines and their temperature exponents.

II. TECHNIQUE OF CALCULATION

According to the Anderson theory the half-width γ_{if} associated with the $i \to f$ transition can be written as

$$\gamma_{if} = B(i,f) + \sum_l D^2(ii'|\,l\,)\, P_l^A(\omega_{ii'}) + \sum_l D^2(ff'|\,l\,) P_l^A(\omega_{ff'}) + \dots, \qquad [1]$$

where

$$B(i,f) = \frac{n}{c} \sum_k \rho(k) b_0^2(k,i,f) \qquad [2]$$

is the averaged ‘‘interruption part” of a half width, $D(ii'|l)$, $D(ff|l)$ are the transition strengths (reduced matrix elements) associated with multiple of rank l , and

$$P_l(\omega) = \frac{n}{c} \sum_k \rho(k) \sum_{l',k'} A_{ll'} D^2(kk'|l') F_{ll'}\left(\frac{2\pi c b_0(k,i,f)}{\mathrm{v}} (\omega + \omega_{kk'}) \right) \qquad [3]$$

is the efficiency function for the scattering channel $i \rightarrow i'$ or $f \rightarrow f'$ (if the frequencies $\omega_{ii'}$ and $\omega_{ff'}$ are substituted). The $A_{ll'}$ are the parameters for the ll'- type interaction. For example, in the case of the dipole – quadrupole interaction ($l = 1, l' = 2$)

$$A_{12} = \frac{16q^2}{45\mathrm{h}^2 \mathrm{v}^2 b_0^6 (k, i, f)} \quad . \qquad [4]$$

For the shifting coefficient the formulae are similar. In equations [1]-[4] n is the number density of perturbing molecules, $\rho(k)$ is the thermal population of level k, and k is the set of quantum numbers of the perturbing molecule, v is the average relative collision velocity, b is the impact parameter, and $F_{ll'}$ are the resonance functions.

The sums in [3] include the transitions of different tensor type (dipole, quadrupole and other) and can be represented as products of two different factors $D^2(ii'|1)$ and $P_l^A(\omega)$. The transition strengths $D^2(ii'|\ell)$ and $D^2(ff'|\ell)$ adapted to the scattering channels $i \rightarrow i'$, $f \rightarrow f'$ depend only on the wave functions of the lower and upper states of the radiative molecule, and they can be regarded as well-known quantities.

The expansion coefficients in Eq.[1], $P_l(\omega_{ii'})$ and $P_l(\omega_{ff'})$ can be regarded as efficiency for a given scattering channel, they depend on the intermolecular potential, and the trajectory of relative motion, the energy levels and the wave functions of the perturbing molecule. While intramolecular factors $D(ii'|l)$ and $D(ff'|l)$ are well known, the intermolecular interaction parameters are determined with worse accuracy. It is useful to divide the terms in Eq.[1] into the well known and only approximately known quantities and to refine the latter by fit to experimental data. Appendix gives the justification of such consideration.

Taking into account that $P_l(\omega)$ is a smooth function of the frequency ω, it seems to be consistent to represent it in the form:

$$P_l(\omega) = C_l(\omega) P_l^A(\omega), \qquad [5]$$

where $P_l^A(\omega)$ is the efficiency function of the Anderson theory and $C_l(\omega)$ is an correction factor, which should be determined from fitting to experimental data. The function $P_l^A(\omega)$ remains the most important term of the calculations, and it determines all main contributions to the broadening, and the factor $C_l(\omega)$ is a small correction.

It worth to note that the determination of model parameters is not a simple curve fitting, because the correcting term obtained from fitting to only a few values of the broadening coefficient for some band does not solely describe the experimental data in this band, but is the only factor including two parameters that describes line broadening for the whole variety of bands for the colliding couple (in our case, H_2O-N_2 or CO_2-N_2).

IV. DISCUSSION

The semiempiric method has been used to calculate broadening of water vapor and both line parameters (broadening and shifting) of carbon dioxide spectral lines and their temperature exponents.

CO_2. The calculations for CO_2-N_2 were performed with a correction factor $C_l = \left\lfloor c_1/(c_2\sqrt{j_f}+1)\right\rfloor$ describing in a simple manner the J-dependence of the efficiency function:

$$P_l\left(\omega_{ff'}\right) = P_l^A\left(\omega_{ff'}\right)\left\lfloor c_1/(c_2\sqrt{j_f}+1)\right\rfloor, \qquad [6]$$

where c_1, c_2 are the fitting parameters. For the CO_2-N_2 system, the parameters ($c_1 = 1.25$ and $c_2 = 0.23$) were obtained from the fit of broadening coefficients for several lines of the ν_3

band. It was found that such a simple modification of the Anderson theory allowed us to reproduce correctly the measured broadening and shifting coefficients.

In the case of the CO_2 – N_2 collisions, the main contribution to broadening and shifting is due to interaction between the quadrupole moment of carbon dioxide (3.41 DA) and the quadrupole moment of nitrogen (1.4 DA). We have also taken into consideration the induction and dispersion terms of the polarization potential. It was found by the direct calculations that the higher electrostatic interactions give negligible contributions both to line broadening and to lineshifting.

Figure 1a shows the halfwidths of CO_2 lines (in the case of broadening by nitrogen) calculated by three different methods in comparison with the experimental data *(7)*. It is seen that calculations by the Anderson-Tsao-Curnutte (ATC) method do not agree with the measured values for high J. Calculations by the more accurate cut-off-free method *(8)* are closer to the experiment, but also disagree with the experimental data at $J > 25$. At the same time, the values obtained using the semiempiric method coincide with the experimental ones within the measurement error for all the considered lines.

Using obtained parameters (c_1 and c_2) numerous calculations for the CO_2-N_2 colliding system were performed. The calculations provide a good description of the line broadening and shift coefficients for the whole range of CO_2-N_2 bands. Figure 1b shows the calculated and measured *(7,9)* line shifts for R-branches of the ν_3 and $3\nu_3$ bands. When calculating the shifts, we used one more fitting parameter – the mean dipole polarizability in the excited vibrational state. This parameter is responsible for the contribution of the isotropic part of the potential to the shift value. The isotropic part is, in turn, responsible for the vibrational dependence of the shift coefficient. First of all, we would like to note the presence of a strong vibrational effect. At excitation of three quanta of the asymmetric stretching mode, the polarizability changes from 2.601 to 2.683 A^3. At the same time, the shift of lines corresponding to the same rotational transitions changes more by a factor of mere than three. The rotational dependence of the shift coefficients proves to be almost linear. It is well reproduced by our calculations (the rotational dependence is determined by the parameters a_i, which were found by fitting line halfwidths). The agreement between the calculated and experimental data is rather good. The calculated values, as a rule, coincide with the experimental ones within the measurement error (the typical measurement error is ±0.001 cm^{-1}/ atm).

The studies of the temperature dependence of CO_2 line halfwidths reported in *Refs. (10,11)* were performed for temperatures from 300 to 900 K. The exponents of the temperature dependence *N′* and *N″* are determined from the equations

$$\begin{aligned}\gamma(\mathrm{T}) &= \gamma(300)\left(\frac{\mathrm{T}}{300}\right)^{-\mathrm{N}'} \\ \delta(\mathrm{T}) &= \delta(300)\left(\frac{\mathrm{T}}{300}\right)^{-\mathrm{N}''}\end{aligned} .$$

Temperature dependence of the broadening coefficient for the R(42) ν_3 band is presented in Fig 2. Our calculations made with the same correction parameters (c_1 and c_2) agree well with the experiment.

$\underline{H_2O.}$ The line width calculations of water vapor lines took into account the dipole-quadrupole interaction between the H_2O dipole moment (1.8549 D for the ground vibrational state, 1.8233 D and 1.8926 D for the (010) and (301) vibrational states) and the quadrupole moment of the perturbing molecule, and the quadrupole-quadrupole interaction ($Q_{bb}(H_2O) = -0.13$, $Q_{cc}(H_2O) = -2.50$, $Q_{aa}(H_2O) = 2.63$ DA with a, b, and c representing the inertia axes with the usual convention). The rotational and centrifugal distortion constants of the water molecule vibrational states were taken from Ref. *(12)* and the parameters for the dipole moment operator needed for calculation of the transition strength (induced by collisions) were taken from Ref. *(13)* (see also Ref. *(14)* for the dipole moment operator of

XY_2 molecules). It was found from the fit to experimentally measured widths that the correction parameters for the H_2O-N_2 pair are the following: c_1 = 1.15 and c_2 = 0.3, the C_0 factor from Eq. [A8] for B(i,f) was taken equal to 1.

To analyse the J-dependence of the broadening and shifting coefficients, we have examined different sub-branches from the spectrum: R(1,1), R(1,-1), R(-1,1), R(3,-1) and so on, formed according to definite combinations of the quantum numbers. Here R(1,1) denotes the sequence of transitions belonging to the R-branch with $K'_a - K_a = 1$, $K'_c - K_c = 1$ having different values of J and K_a (J, K_a and K_c are the rotational quantum numbers of the lower vibrational state whereas J′, K'_a and K'_c are those for the upper state of a transition). The strongest sub-branches are R(1,1), R(1,-1) and R(-1,1), so it was possible to get from the experiment the J-dependence for the corresponding type of transitions up to J=15. As it is seen in the Fig.3, calculations for broadening coefficients both for low rotational quantum numbers K_a=0,1 and for high K_a=7,8 are in a good agreement with experimental values of Toth (15). Anderson method does not allow to properly account for the measured values. Recently high accuracy data were obtained using a diode laser spectrometer *(16)*. For two measured lines from this work (1859.704 cm^{-1} and 2087.408 cm^{-1}) the broadening coefficients are the following: 0.07456(38) cm^{-1}/atm and 0.06975(9) cm^{-1}/atm. They agree with our calculations (0.073 cm^{-1}/atm and 0.068 cm^{-1}/atm respectively).

In order to test our approach, we have calculated broadening and shifting coefficients of the H_2O lines in the $3\nu_1+\nu_3$ band and compared with measured data and calculated using a complex version of Robert-Bonamy theory (CRBF) data from Ref. *(17)*. The comparison of our calculations and those of *Ref (17)* with experimental data is presented in Table 1 and in Fig. 4. As it is seen both methods of calculation give practically the same accuracy as for the broadening and shifting coefficients of water vapor.

Table.1. Root mean square in calculations (*Ref. (17)* and present paper) for broadening and shifting coefficients of the H_2O lines in the $3\nu_1+\nu_3$ band

Parameter	Calculations *(17)*	Present calculations
γ	0.00055	0.00049
δ	0.00037	0.00037

The approach presented above was used for numerous calculations of line contour parameters and their temperature exponents in the cases of H_2O-N_2, CO_2-N_2 and CO_2-O_2 colliding systems (*Refs. 18-21*). The results of calculations for CO_2 lines are included in the carbon dixide spectroscopic data banks which is freely accessible via the Internet (high temperature version: ftp://ftp.iao.ru/pub/CDSD-1000, for atmospheric applications: http://spectra.iao.ru or ftp://ftp.iao.ru/pub/CDSD-296).

The comparison of calculated and experimental data shows that our approach gives an accuracy of calculation close to that reached by the Full Complex Implementation of Robert-Bonamy theory. The semiempiric technique remains the main advantage of the Anderson method: clear physical meaning and the possibility to calculate separately the contributions of different types of intermolecular interactions and different scattering channels to the contour parameters. The last aspect allows us to analyse the vibration-rotational dependence of line broadening and shifting coefficients.

V. ACKNOWLEDGEMENTS

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APPENDIX A

The general expression for the half width within the semiclassical spectral line broadening theory (24) is:

$$\gamma_{fi} = \mathrm{Re}\left\langle 1 - e^{-S(b)} \right\rangle_{Av} \quad , \qquad \text{[A1]}$$

where corner brackets denote the averaging over collisions, velocities and buffer gas states:

$$\left\langle \ldots \right\rangle_{Av} = \frac{n}{2\pi c} \sum_k \rho(k) \int_0^\infty v dv \int_{r_m(v)}^\infty 2\pi r_c \left(\frac{v'_c}{v} \right)^2 dr_c \ldots$$

S(b) is the complex interruption function which may includes both the short-range atom-atom and the long-range electrostatic interactions.

One can see, that *S(b)* involve the values which are well known or can be calculated with satisfactory accuracy, say $S_g(b)$ and values which are not well determined and which can be only approximately modeled, $S_p(b)$. These can be those terms in *S(b)* that are connected with accounting for the short-range interaction potential or badly known high-order electrostatic potential. One can divide the interruption function into two parts

$$S(b) = S_g(b) + S_p(b) \qquad \text{[A2]}$$

Our idea is to use the experimental data for correction of the $S_p(b)$.

Let's use the Taylor expansion of the exponent $e^{-S_g(b)}$, then

$$\begin{aligned} \gamma_{fi} &= \mathrm{Re}\left\langle 1 - e^{-S_g(b)} e^{-S_p(b)} \right\rangle_{Av} = \mathrm{Re}\left\langle 1 - \left(1 - S_g(b) + S_g^2(b)/2! - \ldots\right) e^{-S_p(b)} \right\rangle_{Av} = \\ &= \mathrm{Re}\left\langle 1 - e^{-S_p(b)} \right\rangle_{Av} + \mathrm{Re}\left\langle S_g(b) e^{-S_p(b)} \right\rangle_{Av} + \frac{1}{2!} \mathrm{Re}\left\langle S_g^2(b) e^{-S_p(b)} \right\rangle_{Av} + \ldots \end{aligned} \qquad \text{[A3]}$$

Below we use the representation

$$S_g(b) = \sum_{l',i',k'} D^2(ii'|l) D^2(kk'|l') f_{ll'}(\omega_{ii'}, \omega_{kk'}) + \\ + \sum_{l',f',k'} D^2(ff'|l) D^2(kk'|l') f_{ll'}(\omega_{ff'}, \omega_{kk'}) , \qquad [A4]$$

where only dipole-dipole and dipole-quadrupole interactions are included.

The transition strengths do not depend on the variables that should be averaged, then one can obtain

$$\gamma_{fi} = \operatorname{Re} B(f,i) + \sum_{l}\sum_{i'} D^2(ii'|l) \operatorname{Re} P_l(\omega_{ii'}) + \sum_{l}\sum_{f'} D^2(ff'|l) \operatorname{Re} P_l(\omega_{ff'}) \qquad [A5]$$

where

$$B(f,i) = \left\langle 1 - e^{-S_p(b)} \right\rangle \qquad [A6]$$

$$P_l(\omega) = \left\langle \sum_{l'}\sum_{k,k'} D^2(kk'|l') f_{ll'}(\omega, \omega_{kk'}) e^{-S_p(b)} \right\rangle_{Av} \qquad [A7]$$

One can see that Eq.[A5] is similar to the Anderson expression for half width and one can represents it in the form

$$B(f,i) = B^A(f,i) \cdot C_0(f,i) \qquad [A8]$$

and

$$P_l(\omega) = P_l^A(\omega) \cdot C_l(\omega) \qquad [A9]$$

where $B^A(f,i)$ and $P_l^A(\omega)$ are usual Anderson terms where only dipole-dipole and dipole-quadrupole interactions are included.

The Eq. [A5] can be understood as a sum of terms connected with different scattering channels in radiative molecule with the efficiency function $P_l(\omega)$ given by Eq.[A7]. Form of the correction factors and fitting parameters in the Eqs. [A8]-[A9] can be determined by the fit to experimental data.

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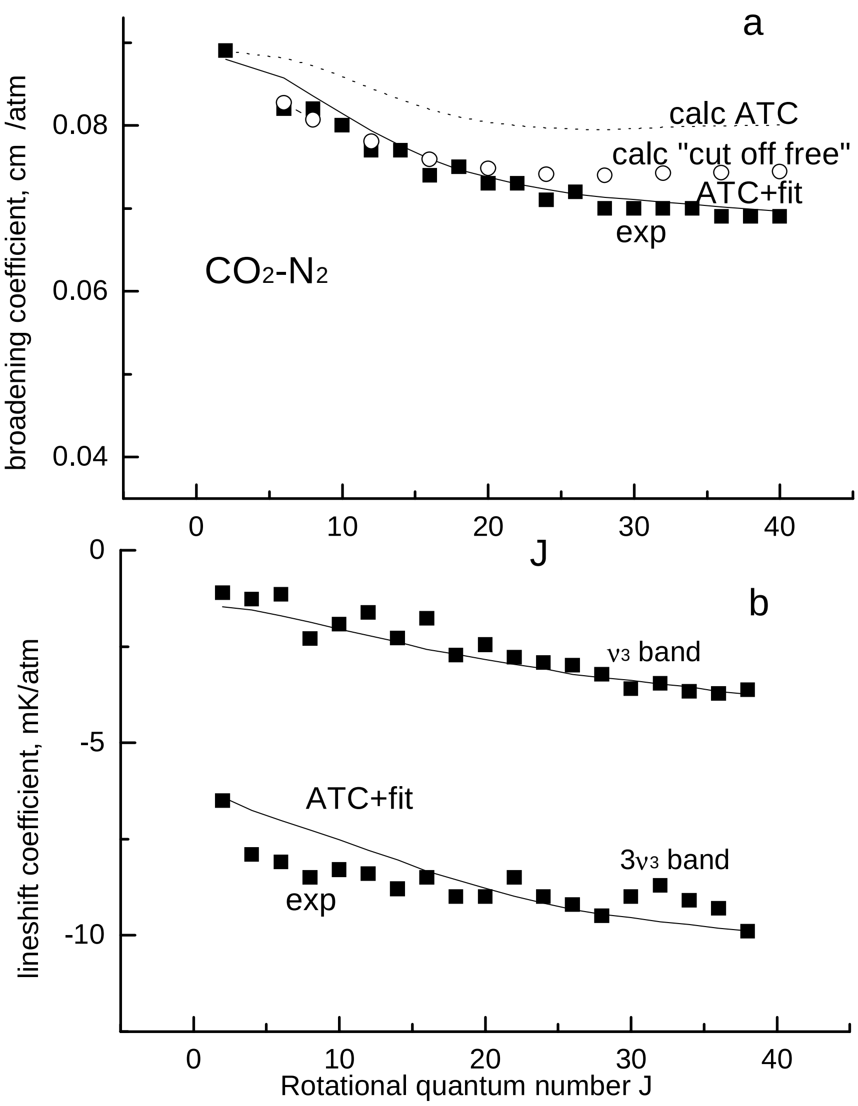

Fig. 1. a) Halfwidths of CO_2 lines (broadening by nitrogen) calculated by three different methods and the experimental data: Anderson—Tsao—Curnutte method[1] (· ·), cut-off-free method[10] (o), our method (—), and experiment[9] (■).

b) Calculated and experimental line shifts for *R*-branches of ν_3 and $3\nu_3$ bands (designations are the same).

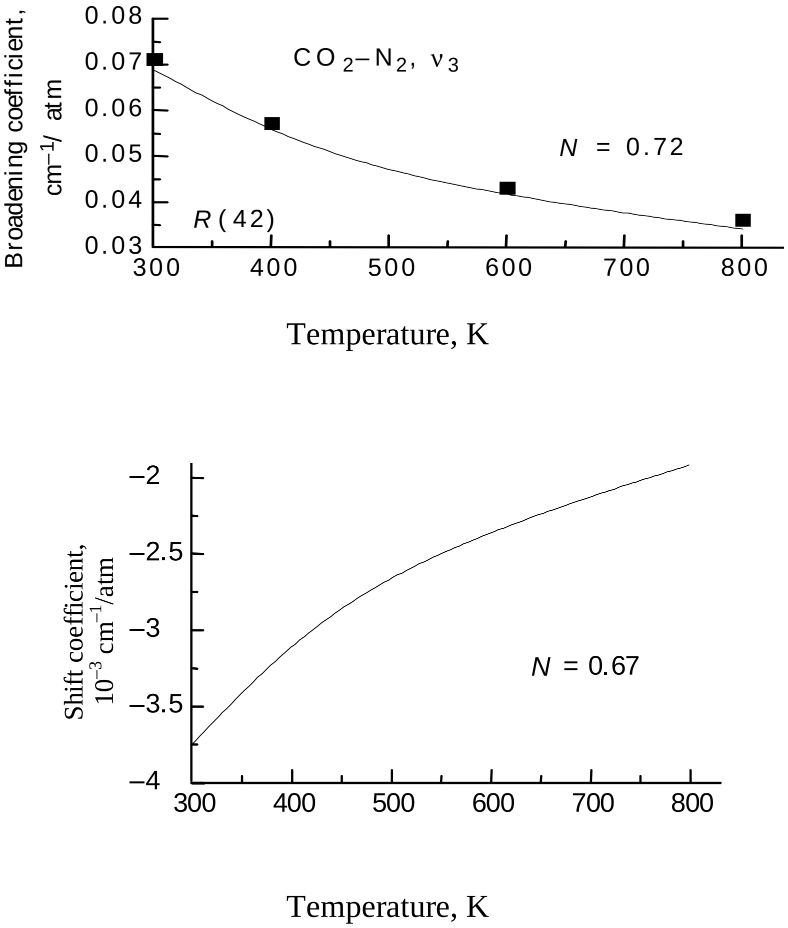

Fig. 2. Temperature dependence of line profile parameters of CO_2 (ν_3 band): broadening coefficients (upper panel) and shift coefficients (lower panel); calculation (—) and experiment[12] (   ).

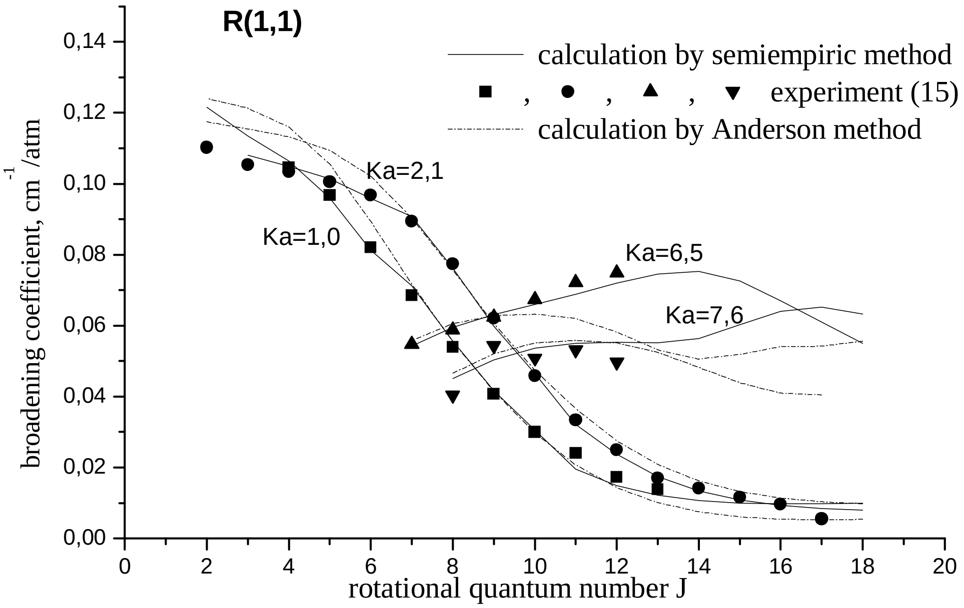

Fig.3. Comparison of calculated by two different methods (Anderson and semiempiric) broadening coefficients H_2O lines with experimental results *(15)*.

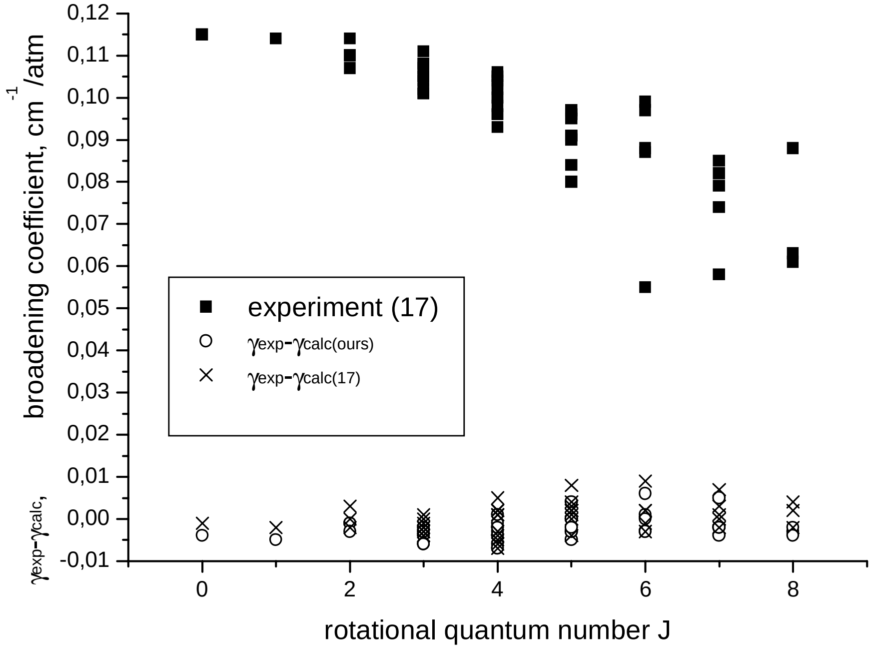

Fig.4. Comparison of calculated by two different methods (CRBF and semiempiric) broadening coefficients H_2O lines with experimental results *(17)*.