RESULTS OF COMPARATIVE ANALYSIS OF CALCULATED AND EXPERIMENTAL CO AND NO SPECTRAL LINE HALF–WIDTHS USING RATC, BR, AND ATC MODELS

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The line half–widths of CO *and* NO *broadened by* N_2 *and* CO *pressure as well as self–broadened were obtained using the elastic collision model, which assumes that the molecules travel along straight trajectories with the velocities being dependent of the rotational states of the absorbing molecule. It is shown that within the experimental error the results of our calculations of the line half–widths agree fairly well with the experimental data for different spectral regions. Comparison of our results with the data obtained by Bonamy–Robert and Anderson–Tsao–Curnutte models is also presented.*

Our previous paper[1] described a refined version of the Anderson–Tsao–Curnutte–Frost model (RATCF). Unlike the well–known ATC model[2] and the extended Frost formulation[3] (ATCF), our refined version of the ATCF model was based on the assumption that the rotational motion of the absorbing molecule changes its translational velocity. The refinement made it possible in example of calculations to reproduce with good accuracy the experimental broadening (γ) and shift (δ) parameters of the CO_2 lines corresponding to the rovibrational transitions for virtually any spectral interval.

This paper reports the results of the application of our RATC model to calculation of the half–widths (γ) of the spectral lines of the slightly–polar diatomic molecules of CO and NO. The values of γ thus obtained are compared with those calculated by the well–known Bonamy–Robert[4,5,6] (BR) and Anderson–Tsao–Curnutte[2] (ATC) models and with a number of experimental data. Examined in this paper is only the half–width (γ) derived by the RATC model. Therefore, *F* is omitted in the abbrevation of our model, since the Frost formulation refers to the spectral line center shift δ.

The molecules of CO and NO are known to possess the dipole moment μ. Therefore, the half–widths of their rovibrational lines written according to Ref. 1 in the form

$$\gamma_{if} = \frac{N}{2c}\,\nu_2(i,\,f)\,b^2(i,\,f)\sum_g r_g[\eta(i,\,f) + S_2'] \,,$$

$$\eta = 1 - [b_{\mathrm{gk}}/b(i,\,f)]^2 \,, \qquad S_2' = S_{2i}' + S_{2f}' + S_{2m}' \,, \tag{1}$$

with

$$S_2' = \sum_t \frac{2}{h_t - 2}\,\frac{\lambda_{2t}(b_{\mathrm{mid}}(i,\,f),\,\nu_2(i,\,f),\,f_{\mathrm{n}})}{b_t^h(i,\,f)} = \sum_t \frac{2S_{2t}}{h_t - 2}$$

are determined by a number of interactions (S_{2t}) which, in the self–broadening case, incorporate S_{21q} dipole–quadrupole, S_{2qq} quadrupole–quadrupole, $S_{2\mathrm{dis}}$ dispersion, S_{211} dipole–dipole, and S_{2q1} quadrupole–dipole contributions while in the presence of a foreign buffer gas (N_2 or O_2) they incorporate only the first three contributions (S_{21q}, S_{2qq}, and $S_{2\mathrm{dis}}$). The notation in Eq. (1) the same as in Ref. 1. For the convenience the bar atop the parameters in the formulas and the subscript *min* used with the impact parameter *b* are omitted. The initial molecular parameters employed for the calculation of γ are listed in Table I.

TABLE I. Molecular parameters used in the calculations of γ.

Gas	μ, *D*	*q*, *D*Å	*E*, 10^{-12}erg	B_0 (cm^{-1})	α* (Å^3)	$\alpha_{\|\|}$ (Å^3)	$\alpha_{\perp}$ (Å^3)	$\alpha_{\|\|} -$ $\alpha_{,}$(Å^3)
CO	0.112 Ref. 4	4.0	22.59 Ref. 4	1.923 Ref. 4	1.95 Ref. 4	2.63 Ref. 4	1.625 Ref. 4	0.975 Ref. 4
NO	0.158 Ref. 5	1.7	15.22 Ref. 5	–	1.74 Ref. 5	2.26 Refs. 5,6	1.42 Refs. 5,6	0.84 Refs. 5,6
N_2	–	3.6	24.85 Ref. 5	2.0 Ref. 4	1.75 Ref. 5	–	–	0.93 Ref. 5
O_2	–	3.0	20.03 Ref. 5	1.438 Ref. 4	1.6 Ref. 5	–	–	1.14 Ref. 5

* The values α correspond to the vibrational ground state.

Here μ and q are dipole and quadrupole moments, *E* is the ionisation energy, B_0 is the rotational constant of the ground molecular state, α is the average polarizability, and $\alpha_{ê}$ and $\alpha_{,}$ are the parallel and perpendicular polarizability, respectively.

An attempt to compare our calculated values of $\gamma_{\mathrm{CO\text{-}N_2}}$ with those obtained by the BR–model revealed that the data on $\gamma_{\mathrm{CO-N_2}}$ obtained in Refs. 7–9 in different years did not agree (see Table II with $m = J_i$ for the *P*–branch and $J_i + 1$ for the *R*–branch). Note that the values of $\gamma_{\mathrm{CO-N_2}}$ were obtained on the basis of different interaction potentials, e.g., $V = V_{\mathrm{at-at}} + V_{qq} + V_{LD}$ (Ref. 7) or $V = V_{\mathrm{at-at}} + V_{qq}$ (Refs. 8 and 9). Furthermore, in contrast to our initial values of $q_{\mathrm{CO-N_2}}$ given in Table I, Robert and

Bonamy[7] used different parameters $q_{CO} = 2.23\ D$Å and $q_{N_2} = 1.5\ D$Å.

TABLE II. The values of the CO *line half–widths at* $T = 300$ K (10^{-3} cm^{-1}·atm^{-1}).

m	Our calcula–tion	Bonamy–Robert		Calcu–lation	Experiment				
		Ref. 7	Ref. 8	Ref. 9	Ref. 10	Ref. 11	Ref. 12	Ref. 13	Ref. 14
				CO–N$_2$					
1	82.85	71.0	–	–	–	82.2	84(3)	80(3)	84(1)
3	70.04	67.0	76.5	71.8	69.6	73.0	–	–	–
7	64.5	63.0	65.0	64.5	60.7	68.0	–	–	–
12	61.6	59.5	60.0	59.7	56.4	60.0	–	–	–
				CO–O$_2$					
1	75.5	–	76.0	–	–	–	67(3)	71(3)	–
				CO–CO					
1	104	–	100	–	–	–	87(3)	–	–

Compiled in Fig. 1 are the results of calculations of $\gamma_{CO-N_2}(J_i)$ for the P–branch of the fundamental CO band obtained by our RATC model (solid curve), BR–model[7] (dushed curve), and ATC model (dash–dot curve). Circles, triangles, and squares depict experimental values measured by various authors.[10,11,15,16,17] Comparison of our values with those obtained by Bonamy and Robert shows that they agree for intermidiate values of J_i but differ substantially for $J_i < 5$ and for $J_i \geq 15$. It is also evident that our values of γ reproduce the experimental data fairly well. The discrepancy between the values calculated by the BR model and the experiment for small J_i seems to be due to the disregard of the two tcontributions in the interactions, namely, S_{21q} and $S_{2\text{dis}}$, in this model. For the quantum numbers $J_i \geq 15$ of the CO molecule there appears the condition $b_{gk} < b_{\min} < 1.5b_{gk}$ (Table III), such that the mechanisms of the curvature of the trajectory of the colliding molecules and the effect of the short–range part of the interaction potential on broadening become effective in the physical BR–model. Account of these mechanisms in Refs. 7–9, however, does not provide the agreement between the calculated and experimental data for large J_i even though the quadrupole moment of the nitrogen molecule was fitted.

The curve calculated by our model[1] on the assumption of the straight trajectory of colliding molecules reproduce better the experimental dependence of $\gamma_{CO-N_2}(J_i)$ for $J_i \geq 15$ than the curves calculated by the BR model.

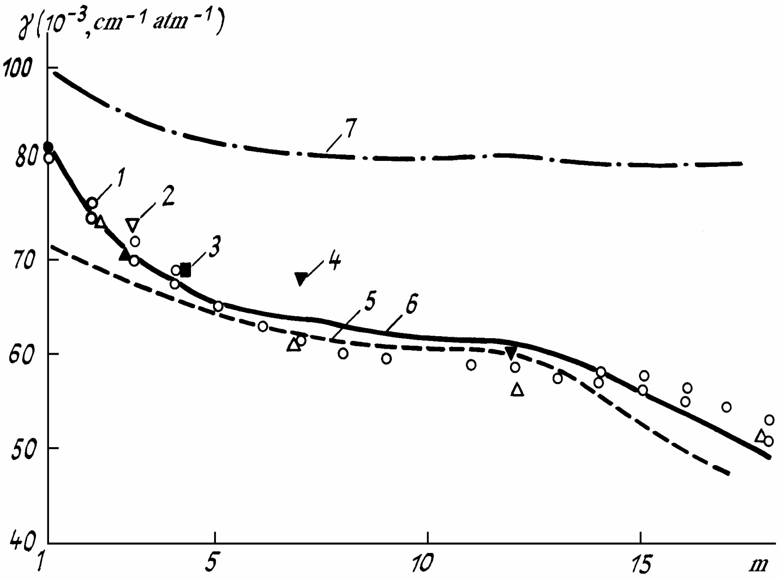

FIG. 1. γ_{CO-N_2} *for the fundamental band (the P–branch); 1) Refs 15 and 16; 2) Ref. 10; 3) Ref. 17; 4) Ref. 11, 5) Ref. 8; 6) Eq. (1); 7)* ATC *model with the same parameters as for calculations from Eq. (1)*

As was mentioned above, the dependence of $\gamma_{CO-N_2}(J_i)$ shown in Fig. 1 by the dash–dot line has been obtained by the theory of Ref. 2 using the same initial data (contributed interactions, molecular parameters, and the number of states of the buffer molecule) as those employed in the calculation by the model of Ref. 1. It is evident that the data calculated by the ATC model appreciably overestimate the experimental values of γ and fail to reproduce the behavior of the experimental data for $J_i \geq 12$. A good agreement between the calculations performed by our model and the experimental data is also observed for self–broadened spectral lines of CO (Table IV).

TABLE III. Impact parameters (Ð) for various gaseous media.

Mixture	b_{gk} Ref. 18	Our values	
		$b_{\min}(J_i = 0)$	$b_{\min}(J_i = 80)$
CO–CO	3.73	6.3	5.1
CO–N$_2$	3.73	6.2	5.0
CO–O$_2$	3.66	5.82	4.75
NO–NO	3.69	5.09	4.58
NO–N$_2$	3.71	5.07	4.45

TABLE IV. γ_{CO-CO} for the P–branch of the 0–1 band (10^{-3} cm^{-1}·atm^{-1}).

J_i	20	25	26	27	29
Eq. (1)	51.2	44.7	44.1	43.5	42.6
Ref. 19	–	48.2	45.9	46.3	46.7

TABLE V. Experimental values of γ_{NO-N_2} for the P–branch of the 0–1 *band* (10^{-3} cm^{-1}·atm^{-1}).

J_i	3.5	5.5	6.5	7.5	10.5	Refs.
	50.0	50.1	–	–	50.0	22
γ	–	61.2	55.8	54.4	–	23
	68.4	67.3	63.0	62.3	62.3	21

The experimental data have been obtained in Ref. 15 with an average error of $5\cdot10^{-3}$ cm^{-1}·atm^{-1} at $T = 293$ K. A comparison of the initial molecular parameters (Table I) shows that the values of the dipole moment μ_{NO} is 1.4 times as high as μ_{CO}. The experimental values of γ_{NO-NO}, however, (e.g., $\gamma[P(J_i = 1.5)] = 0.074$ cm^{-1}·atm^{-1}, see Ref. 20 are lower than the values of γ_{CO-CO} (e.g., $[P(J_i = 1)] = 0.087$ cm^{-1}·atm^{-1}, Ref. 13). Since the spectral line half–widths of both molecules are determined by the same molecular interactions with the dominant contribution of qq interaction, the value of the quadrupole moment must be lower by at least several times than q. This very ratio is given in Table I: $q_{NO}/q_{CO} \simeq 0.42$. It should be emphasized that in the works where the BR–model is used to calculate γ, the values of the quadrupole moments q_{NO} and q_{CO} are in close agreement: $q_{NO} = 1.8$ DÅ (Ref. 21) and $q_{CO} = 2.23$ DÅ (Ref. 7). Unfortunately, various authors reported different experimental values of γ measured for the same values of J_i (Table V).

Naturally, it brings about certain difficulties both in determining q_{NO} and in obtaining sought–for γ. We have taken the most recent experimental data published in Ref. 20 as the basis for our calculation. Figure 2 shows the values of γ for the R–branch of the 0–2 vibrational band of NO calculated using our model (Eq. (1)) in the cases of self–broadened lines (solid curve) and lines broadened by N_2 molecules (dashed curve). The filled circles indicate the line half–width for self–broadened lines and empty circles – for the lines broadened by N_2 molecules). It follows from Fig. 2 that in the case of broadening by N_2 molecules the decrease of γ with J_i is less pronounced than for self–broadened lines. This is attributed by the fact that the quadrupole–quadrupole interaction in the case of NO–N_2 medium has a stronger broadening effect for large J_i as compared to NO–NO medium, since q_{N_2} is approximately 2.1 times greater than q_{NO} (Table I).

TABLE VI. Line half–width for NO–NO *and* NO–N_2 *media for the Q– and P–branches of the 0–2 vibrational band (*10^{-3} cm^{-1}·atm^{-1}*).*

Transition	Self–broadening		broadening by N_2	
	Our calculations	Ref. 20	Our calculations	Ref. 20
Q (1.5)	68.6	71.0	–	–
Q (2.5)	70.4	69. 0	–	–
Q (3.5)	71.1	69.0	–	–
P (4.5)	71.3	69.0	58.0	59.2
P (5.5)	70.9	67.4	56.5	–
P (6.5)	68.4	67.9	55.4	58.1

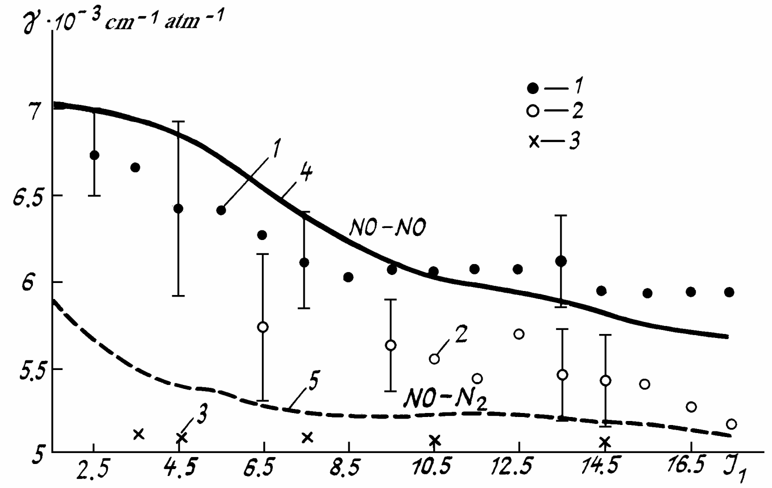

FIG. 2. Calculated and experimental dependences of $\gamma(J_i)$ *for the R–branch of the* 0–2 *vibrational band of* NO. *Experiment: 1)* NO–NO; *2)* NO–NO_2 *according to Ref. 20; 3)* NO–NO_2 *according to Ref. 22; Results of calculations from Eq. (1): 4)* γ_{NO-NO}; and, *5)* γ_{NO-NO_2}.

Quite good agreement is observed between our calculations and the experimental data published in Ref. 16 for the Q– and P–branches of the 0–2 vibrational band of NO (Table VI).

Thus, similar to the case of CO_2 (Ref. 1), the comparison of our results on the broadening of CO and NO spectral lines with the values of γ calculated by the BR and ATC models and with the experimental data allows us to draw a number of conclusions. First, in spite of the fact that the minimum impact parameters $b(J_i)$ for the molecular group under study (CO and NO) satisfies the inequality $b(J_i) < 1.5\mathrm{b}_{gk}$ for large

J_i, broadening is evidently determined by multipole intermolecular interactions. Second, our dependences of the parameters $\gamma_{\text{CO-NO}}(J_i)$ as well as previously obtained dependences $\gamma_{\text{CO}_2}(J_i)$ (Ref. 1) demonstrate an ample validity of our refined version of the physical model based on the assumption that for elastic collisions the molecules travel along straight trajectories with the velocities which depend on the rotational states of the absorbing molecule.

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