

ANALYSIS OF THE CONTRIBUTIONS OF INTERACTIONS TO THE SHIFTS OF ROTATIONAL-VIBRATIONAL CO AND NO LINES USING THE RATCF MODEL

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Based on the use of the RATCF model which enables one to account for the dependence of the absorbing molecular translational velocity on the rotational quantum number J , we have calculated the shifts of the absorption line centers in the vibrational band 0-2 for the molecular media CO-CO, CO-N₂, NO-NO, and NO-N₂. A comparison made between the calculated and experimental values showed good agreement.

The determination of the line center shifts (δ) for the entire spectral range is much more difficult problem in comparison with the problem of calculating the half-widths (γ) of rotational-vibrational CO and NO lines solved by us.⁴ Thus, in order to determine the parameters δ one should take both imaginary parts of the collisional cross sections (\tilde{S}_l) and S_{2t} (Refs. 1-3) into account. In addition, according to the model,³ the line center shifts depend strongly on the translational velocity of the absorbing molecule ($v_1(J_i)$), which varies as the rotational number J_i increases.

The relation for the line shift accounting for $\tilde{S}_l = \tilde{\lambda}_l/b_l^h$ and $S_{2t} = \lambda_{2t}/b_t^h$ and the average relative velocity of interacting molecules $v_2 = (i, f) = f(v_1(i, f), \bar{v}_2)$ for the spectral transition $i \rightarrow f^3$

$$\delta_{if} = -\frac{N}{2c} v_2(i, f) b^2(i, f) \sum_g \rho_g \sum_l \frac{\tilde{\lambda}_l(b_{\text{mid}}(i, f), \tilde{f}_n)}{b_l^h(i, f)} \times \left[\frac{2}{(h_l - 2)} - \sum_t \frac{2}{(h_l - h_t - 2)} \frac{\lambda_{2t}(b_{\text{mid}}(i, f), f_n)}{b_t^h(i, f)} \right] \quad (1)$$

depends on the minimum impact parameter $b(i, f)$, of the closet approach of the molecules in the process of collision when they move at the velocities $v_1(i, f)$ and \bar{v}_2 . Note that the parameters h_l and h_t acquire different but definite values³ depending on the type of intermolecular interaction (e.g., for \tilde{S}_{1dis} the parameter $h_l = 5$ and for S_{2pp} $h_t = 4$, etc.).

Solid curves in Figs. 1 and 2 show plots of $\delta(J_i)$ for R- and P-branches of spectral band 0-2 of CO, calculated from Eq. (1) for the collisions CO-CO and CO-N₂. Circles represent the experimental values of the shifts δ ,⁷ vertical bars denote experimental errors, which as can be seen are rather large. This fact, unfortunately, makes it difficult to compare quantitatively the calculated and

experimental values of δ . On the whole, as can be seen from Figs. 1 and 2, the values of δ calculated using the RATCF model, are practically within the experimental error.

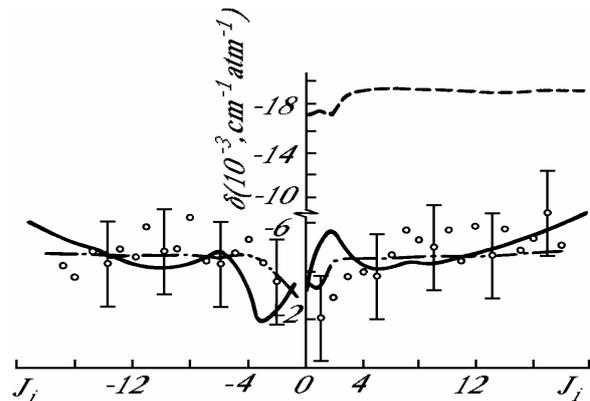


FIG. 1. Line shifts in the 0-2 band of CO-N₂, $T = 300$ K. Circles correspond to the experiment,⁷ solid curves correspond to Eq. (1) at $\Delta\alpha = 0.085$, dash-dot curves denote the ATCF model at $\Delta\alpha = 0.015$, and dashed curves denote the ATCF model at $\Delta\alpha = 0.085$.

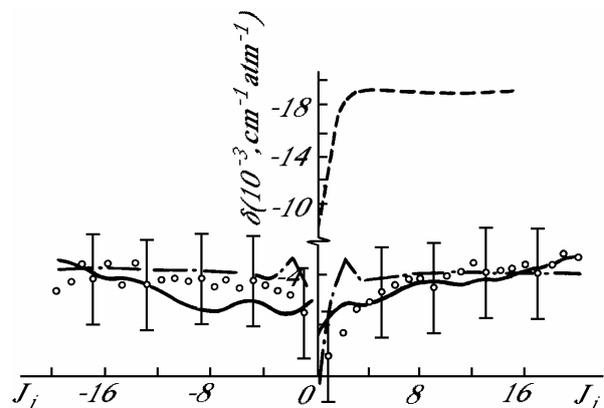


FIG. 2. Line shifts in the 0-2 band of CO-CO, $T = 300$ K. The notation is the same as in Fig. 1.

The calculations of $\delta(J_i)$ for the 0–2 band of CO were performed using Eq. (1) with the same molecular parameters as those employed for the half-widths $\gamma(J_i)$ in Ref. 4. Using the polarizability changes in the transition of the absorbing molecule changes in the vibrational state V_i to the state V_f $\Delta\alpha = \alpha_f - \alpha_i = 0.085$, we have calculated $\delta(J_i)$ by the standard ATCF model^{5,6} with the same initial molecular parameters and types of interactions. The results for R -branch are depicted in Figs. 1 and 2 by dashed lines. As can be seen, the values of δ_{ATCF} are about 3 times as large as the results of the RATCF-model calculations and the experimental data. In order to fit the values of δ_{ATCF} to the experiment, a smaller value of $\Delta\alpha$ should be used. Thus, for example, the fitted values of δ_{ATCF} (the dash-dot curve in Figs. 1 and 2), which fall within the range of experimental values, were obtained at $\Delta\alpha = 0.015$. This is 5 times as small as the initial data. Such a discrepancy is due to the fact that the standard ATCF approach ignores the dependence of the velocity of the absorbing molecule on the quantum states i and f during the collisions.

It should be emphasized that the published data for δ calculated by the conventional ATCF approach disregard the contributions of the real part of the collisional cross sections S_{2t} ($S_{2\mu\mu}$, $S_{2\mu q}$, $S_{2q\mu}$, S_{2qq} , and S_{2dis}) and take into account the contributions of its imaginary part solely, namely, \tilde{S}_{1dis} , \tilde{S}_{2mm} , \tilde{S}_{2mq} , \tilde{S}_{2qm} , and \tilde{S}_{2qq} . The subscripts μ , q , and dis refer to dipole, quadrupole and dispersion interactions, respectively. Let us examine the effect of accounting or neglecting the contribution of the third- and fourth-order interactions ($S_{2t} \neq 0$ or $S_{2t} = 0$) in calculations of the values δ by the RATCF model (Eq. (1)) for the R -branch in the first overtone band of CO. The calculated results are presented in Table I. As can be seen the neglect of the contributions of S_{2t} leads, in this case, to an overestimation of the calculated values up to 30%.

Let us return to Fig. 2. In the region $J_i < 6$ the experimental behavior of $\delta(J_i)$ is distinctly seen, which for the R - and P -branches can be considered as an inverted mirror image. In order to answer the question which of the contributions is responsible for the extreme behavior of $\delta(J_i)$ in this region, let us run over the types of the intermolecular interactions S_{2t} and \tilde{S}_t . Since many authors restrict themselves in the estimation of S by the effect of S_{1dis} (S_{1ind}) only,^{7,8} let us first consider this very case. It appears that if the estimation of the shift is limited only by this contribution, the monotonic dependence of $\delta(J_i)$ is observed (dashed curve in Fig. 3) for both R - and P -branches.

If the effect of the imaginary part \tilde{S}_{2qq} on γ is estimated by our model, then a monotonic behavior of $\delta(J_i)$ is also observed at $\tilde{S}_{2qq} = 0$ (dash-dot curve in Fig. 3) without any appreciable extreme. Thus, the presence of the extreme for small J_i is unambiguously determined by \tilde{S}_{2qq} (the solid curve in Fig.3). It should be stressed that the resulting calculated value of δ shown in Fig. 3 by a solid curve do take into account the contributions of interactions up to the fourth order. Recall that, according to Table II, the absence of S_{2t} leads to a significant overestimation of the values of $\delta(J_i)$.

TABLE I. The calculated line shift for CO–CO and CO–N₂ by the RATCF model describing in Ref. 4 at $T = 300$ K ($10^{-3}\cdot\text{cm}^{-1}\cdot\text{atm}^{-1}$) for 0–2 band (R -branch).

J_i	$\delta_{\text{CO-CO}}$		$\delta_{\text{CO-N}_2}$	
	$S_{2t} \neq 0$	$S_{2t} = 0$	$S_{2t} \neq 0$	$S_{2t} = 0$
0	-1.5	-1.76	-3.17	-3.44
1	-2.5	-3.4	-5.01	-6.2
2	-3.04	-4.0	-5.7	-7.0
3	-2.6	-3.4	-4.7	-5.6
4	-2.7	-3.5	-4.1	-4.8
5	-3.1	-3.93	-4.1	-4.8
6	-3.41	-4.23	-4.17	-4.91
7	-3.6	-4.38	-4.27	-5.0
8	-3.63	-4.36	-4.35	-5.13
9	-3.6	-4.25	-4.41	-5.20
10	-3.55	-4.16	-4.53	-5.37
11	-3.53	-4.09	-4.67	-5.52
12	-3.59	-4.13	-4.8	-5.78
13	-3.73	-4.26	-4.93	-5.92
14	-3.88	-4.4	-5.10	-6.10
15	-4.05	-4.55	-5.30	-6.30
16	-4.18	-4.65	-5.5	-6.30
17	-4.31	-4.74	-5.7	-6.30
18	-4.47	-4.83	-5.9	-6.5
19	-4.67	-5.00	-6.20	-6.70
20	-4.85	-5.12	-6.47	-6.92

TABLE II. The values of $\delta_{\text{NO-N}_2}$ and $\delta_{\text{NO-NO}}$ obtained by the model of Ref. 1 at $T = 300$ K ($10^{-3}\cdot\text{cm}^{-1}\cdot\text{atm}^{-1}$). R -branch, 0–2 band.

J_i	$\delta_{\text{NO-N}_2}$		$\delta_{\text{NO-NO}}$		Experiment from Ref. 9
	Our calculations	Experiment from Ref. 9	Our calculations	Experiment from Ref. 9	
	$S_{2t} \neq 0$	$S_{2t} = 0$	$S_{2t} \neq 0$	$S_{2t} = 0$	
0.5	-2.92	-3.36	-2.71	-2.90	
1.5	-3.47	-4.47	-3.33	-4.69	
2.5	-3.74	-5.00	-3.33	-4.73	
3.5	-4.16	-5.81	-3.31	-4.75	
4.5	-4.49	-6.40	-3.27	-4.76	
5.5	-4.63	-6.80	-3.29	-4.86	
6.5	-4.64	-6.95	-3.47	-5.15	
7.5	-4.65	-6.83	-3.70	-5.61	
8.5	-4.63	-6.78	-3.89	-6.06	
9.5	-4.59	-6.71	-4.07	-6.48	
10.5	-4.58	-6.71	-4.22	-6.73	

A further refinement of the shift values δ_{CO} could be based on:

- 1) the use of the direct integration with respect to the impact parameter in our RATCF model, unlike the standard ATCF approach,
- 2) the replacement of the average relative velocity $v(i, f)$ by the velocities $v(i)$ and $v(f)$,³ and
- 3) the decrease of the errors in the measurement of $v(i)$ and $v(f)$. At this stage, however, such a refinement

would make no sense because of lack of the available experimental values of δ with an adequate accuracy.

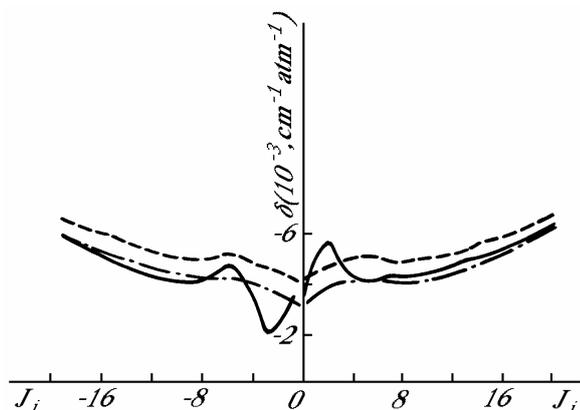


FIG. 3. The analysis of the anomalous behavior of the line shifts for the small values of J_i for the molecular medium CO-N₂ (0-2 band, $T = 300$ K). Solid curve corresponds to Eq. (1), dash-dot curve— to Eq. (1) at $S_{qq} = 0$, dashed curve— to Eq. (1), at $S_{idis} > 0$.

Similar to the case of CO, the calculation of the parameters of the rotational-vibrational line center shifts for NO in the vibrational band $V_i = 0 \rightarrow V_f = 2$, the vibrational dependence for the polarizability (α) was used

$$\Delta\alpha = \alpha_{V_f} - \alpha_{V_i} = \Delta V \cdot K_{\text{CO}(\text{NO})}, \quad (2)$$

where $\Delta V = V_f - V_i$. Given in Table II are the calculated values of $\delta_{\text{NO-N}_2}$ and $\delta_{\text{NO-NO}}$ for R-branch of the 0-2 band of NO and the experimental data from Ref. 9. It can be seen that the calculations at $S_{2t} \neq 0$ agree with experiment.

In the case in which the contribution of S_{2t} is ignored, the values of δ are overestimated by 40%. Finally, it should be noted that, in contrast to the behavior of $S_{\text{CO-N}_2}$ for small J_i , no extreme behavior of the dependence $S_{\text{NO-N}_2}(J_i)$ is observed.

Thus, our theoretical analysis of the effects of intermolecular interactions of different types and of the translational velocities of the absorbing molecule ($v_i(J_i)$) on the parameters of the spectral line center shifts ($V_i J_i \rightarrow V_f J_f$) for different molecular systems suggests the following conclusions:

1) The neglect of the S_{2t} contributions leads to a significant overestimation of δ -values (by 30-40%).

2) As the rotational number J_i increases, a slight change in the kinetic energy of the absorbing molecule increase the line center shift.

3) The pronounced extremum for small J_i which is observed for CO-N₂ is due to a strong influence of the \tilde{S}_{2qq} contribution.

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