THE EFFECT OF CHANGE OF THE VELOCITY OF THE ABSORBING MOLECULE ON THE ACCURACY OF CALCULATION OF THE HALF−WIDTHS AND THE SHIFTS OF THE SPECTRAL LINES BASED ON THE RATCF MODEL

V.V. Zuev and A.I. Petrova

Institute of Atmospheric Optics,
Siberian Branch of the Academy of Sciences of the USSR, Tomsk
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It has been shown using the molecules CO_2 *and* CO *as an example that if the change of the velocity* $(\Delta v = |v(i) - v(f)|)$ *of the absorbing molecule in the quantum transition from the state i to the state f is at a level of* $0.2 \cdot 10^4$ *cm/s, then the results of calculation of the parameters of the half−width* γ *and the shift* δ *of the spectral lines based on the refined Anderson−Tsao−Curnutte−Frost (RATCF) model in terms of the velocity* $v(i, f)$ *averaged over the states* i *and* f *lie within the limits of the experimental error obtained for the functional dependence* $f(v(i), v(f))$.

Strictly following the theoretical RATCF model, it is necessary to take into account the molecular velocities individually for the states i and f ($v(i)$ and $v(f)$) in order to calculate the half−width (γ) and the shift (δ) of the spectral absorption line of a gas molecule at the frequency w_{if}. However, such an approach is more labor−intensive, especially in calculating the shift δ, since we must know not only the value $\delta(v(i, f))$, but also the correction $\Delta = \delta(v(i, f)) - \delta(v(i), v(f))$ (see Ref. 1) calculated with the help of the ATCF approach.[1−3]

The performed comparative analysis of the calculated parameters γ and δ of the CO_2 molecule calculated on the basis of the functional dependences $f(v(i), v(f))$ and $f(v(i, f))$ has shown the following:

1) when the velocity of the absorbing molecule changed by $\Delta v = |v(i) - v(f)| \simeq 0.2 \cdot 10^4$ cm/s the half−widths of the lines at the frequencies ω_{if} were independent of the way of determining $\gamma(\gamma(v(i, f)) \approx \gamma(v(i), v(f)))$;

2) with such a value of Δv the maximum deviation of the line center shifts $\Delta = \delta(v(i), v(f)) - \delta(v(i, f)) = \pm 2.0-1.5 \cdot 10^{-3}$ cm^{-1}·atm^{-1} was observed for the first three lines of the R−branch ($J_i = 0, 2, 4$) which was within the limits of the experimental error $\pm 4.0 \cdot 10^{-3}$ cm^{-1}·atm^{-1}.

The generality of the first conclusion is confirmed by the data in Table I where the half−widths of the vibrational−rotational lines of the CO molecule broadened by two different molecules are presented.

In this case as well as for the broadening by CO_2 molecules the change of the velocity of the CO molecule in the transition from the state i to the state f is at the same level ($\Delta v \approx 0.2 \cdot 10^4$ cm/s), and the parameters γ calculated in terms of the velocity $v(i, f)$ averaged over the states i and f do not differ virtually from $\gamma(v(i), v(f))$ (compare the values in the columns 1 and 2, and 3 and 4 in Table I to each other).

As to the line center shifts of CO, the mean experimental error (Δ_{exp}) in determining δ_{CO} may significantly exceed the experimental values of the line shifts in the 0−2 vibrational band center (see Table II). For this reason, there is no sense to refine the values of δ in this case; it is sufficient to determine $\delta(v(i, f))$ in terms of the velocity $v(i, f)$.

TABLE I. The values of γ (in units 10^{-2} cm^{-1}·atm^{-1}) for the R−branch of the 0−2 band of C0.

J_i	CO−N$_2$		CO−CO	
	$\gamma(v(i, f))$	$\gamma(v(i), v(f))$	$\gamma(v(i,f))$	$\gamma(v(i), v(f))$
1	8.247	8.247	10.42	10.42
2	7.373	7.363	9.571	9.568
3	7.009	7.009	9.399	9.399
4	6.698	6.692	9.229	9.224
5	6.506	6.503	9.042	9.040
6	6.437	6.437	8.829	8.829
7	6.445	6.448	8.559	8.558
8	6.460	6.460	8.249	8.246
9	6.439	6.439	7.913	7.911
10	6.380	6.380	7.583	7.581
11	6.285	6.284	7.291	7.285
12	6.158	6.159	7.028	7.023
13	5.997	5.994	6.790	6.787
14	5.815	5.812	6.565	6.561
15	5.608	5.605	6.337	6.334
16	5.387	5.384	6.104	6.101
17	5.156	5.156	5.872	5.870

TABLE II. The experimental values of δ and Δ_{exp} of the 0−2 band for the first four values of J_i (in units of 10^{-3} cm^{-1}·atm^{-1}) taken from Ref. 4.

$R(J_i)$		0	1	2	3
CO−CO	δ	0.45	−1.0	−2.2	−3.0
	Δ_{exp}	±0.913			
CO−N$_2$	δ	−	−1.4	−3.0	−3.8
	Δ_{exp}	±1.37			

Thus, if the change of the velocity of the absorbing molecule is insignificant ($\Delta v \approx 0.2 \cdot 10^4$ cm/s) while the error in the measurement of the shift is large ($\gtrsim 40-100\%$ of the value δ), then the calculation of the half−widths and shifts of the lines according to the simpler formulas for $\gamma(v(i, f))$ and $\delta(v(i, f))$ (see Ref. 1) is quite justified.

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