Influence of temperature on the collision broadening of IR spectral lines of CO$_2$ molecules

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Abstract. **The method of diode laser spectroscopy is used to measure the widths of the IR spectral lines of CO$_2$ molecules within wide ranges of temperatures ($T = 170 – 600$ K) and rotational quantum numbers ($J \leqslant 82$). It is established that the existing quasi-classical models of collision broadening cannot describe all the experimental results. An improved model is offered that takes into account departures of the trajectories of moving particles from straight lines and an increase in the effective broadening cross section at small relative particle velocities due to orbital collisions. The model contains no free fitting parameters and satisfactorily describes experimental data. The scheme of averaging the broadening cross sections over the relative velocities of particles is refined.**

1. Introduction

The interaction of radiating particles with surrounding atoms and molecules causes a collision broadening and shift of spectral lines. The character of such interactions depends on the relative velocity of particles and, in our opinion, has not been sufficiently studied for molecular spectra. This work is devoted to experimental and theoretical investigations of the collision broadening of IR spectral lines of a CO$_2$ molecule taken as an example. This molecule plays an important role in various devices, technologies, energy transfer processes in atmosphere, etc. The data on the line profiles of this molecule are systematically discussed in the literature. The CO$_2$ molecule serves as a test molecule in spectroscopy.

With the development of the Fourier and high-resolution laser IR spectroscopy techniques, spectroscopic data bases have appeared (e.g., HITRAN-92, HITRAN-96 [1, 2]). The theoretical description of line profiles in molecular spectra and methods for extrapolating data are based on the classical Anderson approach [3], which was subsequently systematised in [4]. This model was named the ATC approximation and finds its application up to now (see

also [5]). As the experimental data have been accumulated, the model have been modified. From the viewpoint of physics, the most important modification was introduced in paper [6] (the RB model). The results of calculating the CO$_2$ linewidths using these models agree as a whole, but none of them describes the total set of the experimental data for a wide range of rotational quantum numbers $J_i \leqslant 80$. Discrepancies are clearly pronounced but do not exceed $15\% – 20\%$. A more significant fact is that the available systematic experimental data refer to room temperatures. For this reason, we studied the collision broadening of CO$_2$ emission lines in an extended temperature range.

2. Experimental

The transmission of carbon dioxide at 4.5 μm [$V_1V_2^lV_3 \rightarrow V_1V_2^l(V_3+1)$ vibrational transitions] was measured at temperatures 170 and 600 K. The measurements were performed with an IR diode laser spectrometer with a spectral resolution of $\sim 10^{-4}$ cm^{-1} described in papers [7, 8]. To assign the spectral lines and determine the gas and vibrational temperatures, a program for comparing the experimental and calculated transmission was developed [9]. Figs 1a and 1b show fragments of experimental and calculated CO$_2$ transmission spectra (a discharge in CO$_2$), respectively. The following notation of spectral lines is used: the three first figures correspond to the isotope composition of molecules (626 – ^{16}O^{12}C^{16}O, 636 – ^{16}O^{13}C^{16}O, etc.), and then the designations of the lower vibrational level and the rotational transition follow.

The program makes it possible to find the widths of spectral lines (see the inset in Fig. 1a) and select the collision components. For this purpose, the working segment of the spectrum was recorded and was used to determine the gas temperature T (details are in [9]) and, consequently, the FWHM of the Doppler component $\Delta v_{1/2}^D$. The FWHM of the collision component was determined from the total FWHM of the Voigt profile and $\Delta v_{1/2}^D$. To control the spectrometer operation at a low CO$_2$ pressure ($p \leqslant 1$ Torr) and room temperature, a Doppler profile of the ^{13}C^{16}O$_2$ line was recorded. Its FWHM was $\Delta v_{1/2}^D = 2.1 \times 10^{-3}$ cm^{-1}, which corresponded to $T = 300$ K.

The transmission in the ranges $2259.4 – 2260.5$ cm^{-1} and $2264.3 – 2265.3$ cm^{-1} was studied under conditions of a glow-discharge plasma. In this case, the rotational temperature T_r identified with the gas temperature was 600 ± 30 K, the vibrational temperatures of the symmetric and deformational modes were $T_1 = T_2 = 650 \pm 30$ K, and the vibrational temperature of the antisymmetric mode was $T_3 =$

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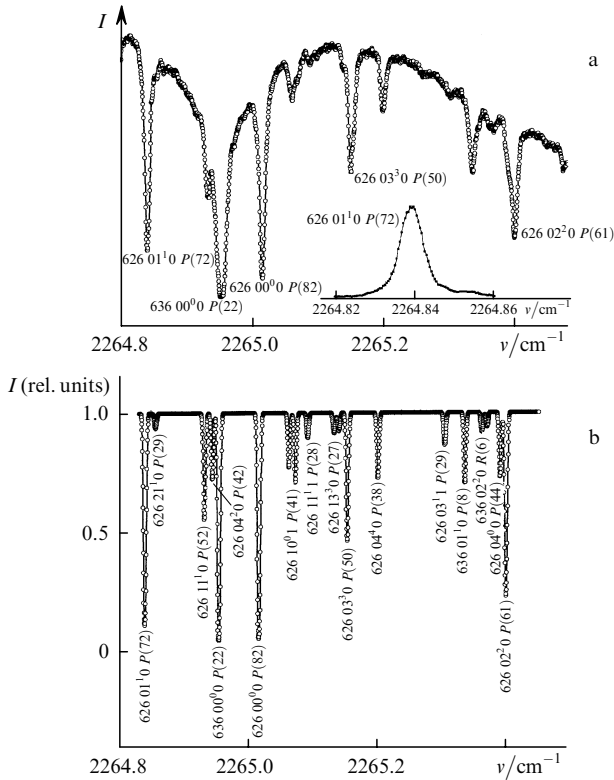
Figure 1. Fragments of the (a) experimental and (b) calculated spectra of a discharge in CO_2 at a pressure $p = 20$ Torr and a current $i = 5$ mA.

900 ± 50 K. The experiments in plasma were conducted at comparatively low pressures ($p = 20$ Torr), at which the Doppler broadening predominated (the Voigt parameter a is < 1). At higher p, the spectrum became more complex, making the line profile measurements more difficult. Therefore, the width of the collision component was determined with an error of $10\% - 20\%$ despite precise measurements of the initial profile widths. The degree of CO_2 dissociation was minimised by the gas circulation and was within 5%. Measurements were carried out in a glow discharge at a current $i = 5$ mA in water-cooled glass discharge tubes with a 0.5-cm inner diameter and a 0.8-cm outer diameter. The total length of each tube was 11 and 6 cm, and the lengths of the discharge zones were 10 and 5 cm, respectively. Kovar electrodes were placed in side branches. The probe laser beam was 1 mm in diameter, and the measured characteristics corresponded to the axial discharge zone.

Measurements at 170 K were performed in quartz cells (without a discharge) 20 and 5 cm long cooled by ethanol, which, in turn, was cooled by liquid nitrogen. The temperature was monitored by the pressure of saturated CO_2 vapours $p_s(170\ \text{K}) = 77.55$ Torr [10]. The transmission of CO_2 in the ranges $2283.4 - 2285.2$ and $2286.2 - 2287.0$ cm^{-1} was studied. Under such conditions, a collision broadening was dominant, and the parameter a_{min} was 5.56 [the $626\ 00^00\ P(66)$ line]. The difference between the calculated half-width of the collision component and the initially measured half-width was smaller than the measurement error. For the $626\ 00^00\ P(66)$ line, the measured half-width is $\Delta v_m = (11 \pm 1.0) \times 10^{-3}$ cm^{-1}, and the calculated half-width of the Lorentzian component is $\Delta v_{1/2}^L = 10.7 \times 10^{-3}$ cm^{-1}. Therefore, we identified the measured quantity with the collision half-width of the spectral line.

3. Results and discussion

3.1 Comparison of calculations with the experiment

Fig. 2 shows the dependences of the collision half-width of CO_2 lines on the rotational quantum number J_i of the lower vibrational state for the P-branch of the $00^00 \rightarrow 00^01$ transition in CO_2 in this gas at $T = 296$ K and $p = 1$ atm. The results of calculations from papers [11] (ATC approximation) and [12] (RB approximation) and the averaged experimental data from the HITRAN data base [1, 2] are plotted. One can see that both models yield close results that agree with the experimental data at $J_i < 20$. As a whole, the ATC model is valid up to $J_i < 40$. At $J_i > 40$, the agreement deteriorates and the discrepancy between the calculation data according to the two models reaches 40%. Nevertheless, the agreement between the experiment and theory remains satisfactory ($\pm 20\%$).
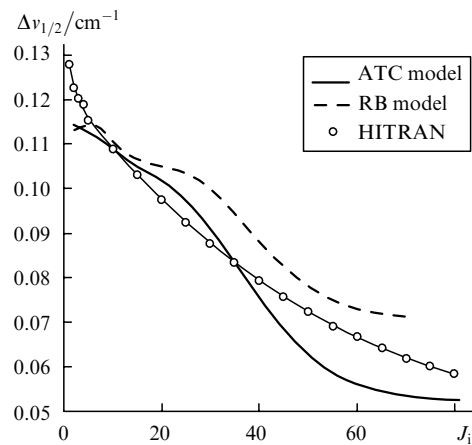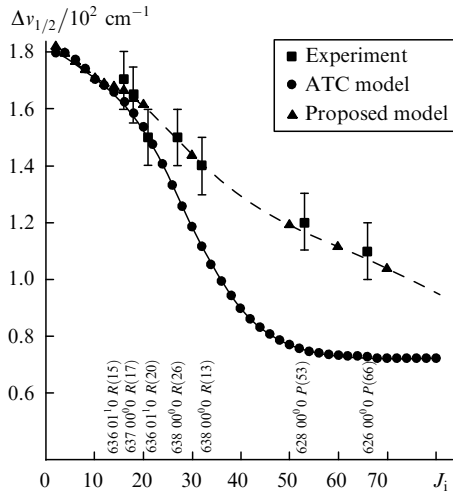

Figure 2. Collision half-widths of spectral lines obtained in experiments (averaged HITRAN data) and calculated using the ATC and RB models versus rotational quantum number J_i for the P-branch of the $00^00 \rightarrow 00^01$ transition in CO_2 molecules at $T = 300$ K and $p = 1$ atm.

Fig. 3 presents the collision half-width of the CO_2 lines as a function of J_i measured at $T = 170$ K and $p = 77.6$ Torr and the results of our calculation in the ATC approximation using the data from [11]. At $J_i < 20$, the agreement between the calculation and experimental data is satisfactory, but, as J_i increases, the discrepancy between these data becomes significant. At $J_i > 40$, this discrepancy is 50%. Thus, the modern calculation scheme does not ensure an adequate description of the experimental data. This stimulated us to analyse the existing models for linewidth calculation with the purpose of their possible improvement.

3.2 Analysis of the existing models

In quasi-classical models, the colliding molecules move along classical trajectories, and quantum relations are used only for analysing the internal degrees of freedom. In the case of a collision broadening, the line shape is described by a Lorentzian

$$P(v) = \frac{1}{\pi} \frac{\Delta v_{1/2}(\text{i} \rightarrow \text{f})}{(v - v_{\text{if}} + \Delta_{\text{if}})^2 + \Delta v_{1/2}^2(\text{i} \rightarrow \text{f})}. \tag{1}$$

Figure 3. Experimental and calculated (using the ATC approximation and the model proposed in this paper) dependences of the collision half-widths of CO_2 spectral lines on J_i at $p = 77.6$ Torr and $T = 170$ K.

The state i(f) is determined by a set of vibrational and other quantum numbers $V_i(V_f)$ and by the rotational quantum number $J_i(J_f)$. The line half-width $\Delta v_{1/2}(i \to f)$ and shift Δ_{if} (in cm^{-1}) are related to the frequency of optically active collisions through the equations

$$\Delta v_{1/2}(i \to f) = \frac{1}{2\pi c} n_B v \sigma_R(v, i \to f),$$

$$\Delta_{if} = \frac{1}{2\pi c} n_B v \sigma_I(v, i \to f), \tag{2}$$

where c is the velocity of light; v is the relative velocity of particles; and n_B is the density of line-broadening particles B. The complex effective cross section of optically active collisions $\sigma(v, i \to f)$ is defined as the sum of partial cross sections $\sigma(v, i \to f, V_B, J_B)$ over all possible states V_B, J_B of the broadening particles B:

$$\sigma(v, i \to f) = \sigma_R(v, i \to f) + i\sigma_I(v, i \to f)$$

$$= \sum_{V_B, J_B} \rho(V_B, J_B)\sigma(v, i \to f, V_B, J_B), \tag{3}$$

where $\rho(V_B, J_B)$ is the relative population of the state V_B, J_B of particles B;

$$\sigma(v, i \to f, V_B, J_B) = \int_0^\infty S(b, v, i \to f, V_B, J_B) 2\pi b \, db; \tag{4}$$

b is the impact parameter; and $S(b, v, i \to f, V_B, J_B)$ is the interruption function. Its real part determines the probability of a phase disturbance or emission interruption, and the imaginary part determines the probability of a spectral line shift at the $i \to f$ transition upon a collision with a $B(V_B, J_B)$ molecule. This work is devoted only to the analysis of spectral line broadening. The function $S(b, v, i \to f, V_B, J_B)$ is calculated in the second approximation of the perturbation theory [3, 4]:

$$\text{Re}S(b, v, i \to f, V_B, J_B) = S_2(b) = S_2^{outer}(b) + S_2^{middle}(b). \tag{5}$$

In the ATC approximation, it is assumed that particles move along rectilinear trajectories at a constant velocity, and the potential of interaction between molecules is electrostatic. Under such conditions, expressions for calculating S_2^{outer} and S_2^{middle} are given in [3, 4]. A linear symmetric molecule CO_2 has no dipole moment, and the first non-vanishing term in the expression for V_e [3, 4] corresponds to the quadrupole–quadrupole interaction. At $b \to 0$, the function $S_2^{ATC}(b) \sim 1/b^n \to \infty$ (for electrostatic potentials, $n > 1$); therefore, in [3], b_0 is determined from the condition $S_2^{ATC}(b_0, v, i \to f, V_B, J_B) = 1$ and it is assumed that

$$S_2(b, v, i \to f, V_B, J_B)$$

$$= \begin{cases} S_2^{ATC}(b, v, i \to f, V_B, J_B) & \text{for } b \geqslant b_0, \\ 1 & \text{for } b < b_0. \end{cases} \tag{6}$$

Thus, within the framework of the ATC theory,

$$\sigma^{ATC}(v, i \to f, V_B, J_B) = \pi b_0^2(v, i \to f, V_B, J_B)$$

$$+ \int_{b_0}^\infty S_2^{ATC}(b, v, i \to f, V_B, J_B) 2\pi b \, db. \tag{7}$$

A critical impact parameter b_m corresponding to the gas-kinetic molecular diameter is introduced in [3]. It is used instead of b_0 at $b_0 < b_m$ (as a rule, b_m serves as a free parameter in practical calculations). The divergence (6) elimination procedure is not quite correct, but its physical meaning is clear: for collisions with $b < b_0$, the probability of phase disturbance or radiation interruption is almost unity, and the introduction of b_m makes it possible to indirectly take into account nonelectrostatic short-range intermolecular forces. Another obvious difficulty of the ATC model consists in the fact that the assumption of the molecular motion along rectilinear trajectories at a constant velocity is not valid*.

Another version of the quasi-classical model was proposed in [6] (the RB model), where the expression for $S_2(b)$ was derived using the theorem of coupled clusters:

$$S_2^{RB}(b) = 1 - (1 - S_{2, fB iB}^L) \exp[-(S_{2, iB} + S_{2, fB} + S_{2, fB iB}^C)], \tag{8}$$

where $S_{2, fB iB}^L = S_{2nd}^{middle}$; $S_{2, fB iB}^C = S_{2d}^{middle}$; $S_{2, iB} + S_{2, fB} = S_2^{outer}$; and S_{2nd}^{middle} and S_{2d}^{middle} are nondiagonal ($J_B' \neq J_B$) and diagonal ($J_B' = J_B$) S_B^{middle} terms, respectively. Note that $S_2^{RB}(b)$ holds a finite value at $b \to 0$. The trajectory of particles' motion is determined by the expansion of the vector $r(t) = r_A(t) - r_B(t)$ [$r_A(t)$ and $r_B(t)$ are the radius–vectors of optically active molecules A and molecules B] into a time t series near the point of the closest approach r_c with second-order infinitesimal terms retained. The interaction potential was represented as the sum of a multipole electrostatic potential and the partial Lennard-Jones atom–atom potentials. General relations for calculating $S_2^{RB}(b)$ are presented in [6] for such a potential and parabolic trajectories.

The calculation in the RB model is a much more complex problem than in the ATC approximation: there

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*The influence of the curvature of the trajectories of moving colliding particles was analysed in [13–15]. However, the attention was drawn mainly to line shifts.

appears a significant number of parameters of atom–atom potentials, the determination of which represents a special problem. In the RB approximation, the divergence of the function S_2^{RB} (8) at $b \to 0$ is eliminated. Note that the term $1 - S_{2,fBiB}^L$ in (8) was obtained in the second approximation of the perturbation theory, i.e., at $|S_{2,fBiB}^L| \ll 1$. It can be shown that this assumption is violated at $J_i \gg 1$ (or $J_f \gg 1$). In other words, as $J_i (J_f)$ increases, we can expect an increase in the systematic error in the RB approximation, which is considered as a possible cause of the discrepancy between the calculation and experimental data (see Fig. 2).

3.3 Scheme proposed for linewidth calculation

Our aim was to take into account possible distortions of trajectories at small impact parameters and to preserve the physical clearness of the ATC model. The problem is split into two parts. First, one should determine the form of the function $S_2(b)$ satisfying the following conditions: at $b \to 0$, $S_2(b)$ holds a finite value that does not exceed unity, and $S_2(b) = S_2^{ATC}(b)$ at $S_2(b) \ll 1$. The second stage of this problem is the calculation of matrix elements of the form $\langle V_i J_i m_i, V_B J_B m_B | V | V_i' J_i' m_i', V_B' J_B' m_B' \rangle$, where V is the interaction potential of the colliding particles and m_j is the magnetic quantum number, taking into account the trajectory distortions and the effect of short-range nonelectrostatic forces.

In the first part of the problem, we used the results of paper [16] to obtain the following expression for $S(b)^*$:

$$S(b) = 1 - \exp\left\{ -i(\Delta_i - \Delta_f) - [S_{2,iB}^{outer} + S_{2,fB}^{outer} + S_{2,iBfB}^{middle}] + \frac{1}{2}(\Delta_i - \Delta_f)^2 \right\}, \quad (9)$$

where Δ_i and Δ_f are the first-order terms in the ATC theory that describe the orientation-averaged shifts of the states i and f caused by the interaction with a particle $B(V_B, J_B)$, and $S_{2,iB}^{outer}$, $S_{2,fB}^{outer}$ and $S_{2,iBfB}^{middle}$ have the same form as similar terms in the ATC theory [3, 4]. The function $S(b)$ written in the form (9) holds a finite value at $b \to 0$, and in the limit of $S_2^{outer} + S_2^{middle} \to 0$, we have $S_2(b) = S_2^{ATC}(b)$.

Describing the translational motion of colliding molecules, we take into account their interaction using the Lennard-Jones potential

$$V_{LD} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (10)$$

with the known constants ε and σ [17]. At large b, the attraction leads to a situation in which the distance of closest approach is $r_c < b$; at small b, a short-range repulsion results in $r_c \approx \sigma$. The relation between r_c and b for potential (10) follows from the laws of conservation of energy and momentum:

$$b = r_c \left\{ 1 - \frac{8\varepsilon}{\mu v^2} \left[\left(\frac{\sigma}{r_c} \right)^{12} - \left(\frac{\sigma}{r_c} \right)^6 \right] \right\}^{1/2}, \quad (11)$$

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*There are errors in the final expressions for $S(b)$ in [16] [see formulas (2.17) and (2.18)] caused by an inaccurate consideration of the contribution of diagonal matrix elements of the isotropic part of the potential. Here, we present the expression that takes into account the introduced corrections.

where μ is the reduced mass of the colliding molecules. Let us introduce dimensionless variables

$$R = \frac{r}{\sigma}, \quad \beta = \frac{b}{\sigma}, \quad K = \frac{E}{\varepsilon}, \quad (12)$$

where E is the energy of the relative motion of molecules. The two-body problem with the interaction potential (10) is reduced to the analysis of a one-dimensional motion of a particle with a mass $m = \mu\sigma^2/\varepsilon$ and a total energy K in the field of the effective potential [18]

$$V_{eff} = \frac{K\beta^2}{R^2} - \frac{4}{R^6} + \frac{4}{R^{12}}. \quad (13)$$

As follows from (13), there exists such a critical value $(K\beta^2)_{cr} = 2.4624$ that, for $K\beta^2 < (K\beta^2)_{cr}$, a potential barrier forms in the curve of the effective potential energy V_{eff} (13). If $K > 4/5 = 0.8$, then the system passes over the barrier at any impact parameter. If $K < 4/5 = 0.8$, then there exists such β_{cr} that, at $\beta \leqslant \beta_{cr}$, the system surmounts the barrier (an almost central collision takes place) and, at $\beta > \beta_{cr}$, the barrier is not surmounted. The collisions at $\beta \leqslant \beta_{cr}$ are called orbital, because the particles move along helical trajectories. In the aforementioned parabolic approximation [6], in the vicinity of the point of the closest approach r_c, we have

$$r(t) \approx \left(r_c^2 + v_c'^2 t^2 \right)^{1/2}, \quad (14)$$

where $v_c'^2 = v_c^2 + F_c r_c / \mu$; and v_c and F_c are the relative velocity and force at the point of closest approach r_c, respectively. It follows from (14) that, near r_c, a curvilinear motion can be approximately described as a motion along an equivalent straight line with an impact parameter r_c and a 'fictitious' velocity v_c'. This method allows us to use the ATC relations for calculating $S_2(b)$ by replacing b by r_c and v by v_c'. For potential (10),

$$v_c' = v \left\{ 1 + \frac{8\varepsilon}{\mu v^2} \left[5 \left(\frac{\sigma}{r_c} \right)^{12} - 2 \left(\frac{\sigma}{r_c} \right)^6 \right] \right\}^{1/2}. \quad (15)$$

Let us analyse the motion of molecules with $K \leqslant 0.8$, when β_{cr} exists. At $\beta \leqslant \beta_{cr}$, particles experience a central collision with a relative kinetic energy $E \geqslant \varepsilon$. Note that the de Broglie wavelength $\lambda = h(2E\mu)^{-1/2}$ [λ (in Å) $= 6.59 \times (\varepsilon/k)^{-1/2}$] corresponding to such a motion is much smaller than the characteristic distance for the particle interaction [i.e., the constant σ of potential (10)] for the majority of molecules. In particular, for a CO_2 molecule, $\varepsilon/k = 205$ K and $\sigma = 4.07$ Å [17]. Consequently, particles always move along classical trajectories in the vicinity of the point of closest approach r_c.

When calculating the effective broadening cross section, we should take into account the anisotropic part of the interaction potential

$$V = V_{mol} + V_e, \quad (16)$$

where $V_{mol} = V_{iso} + V_{aniso}$ is the nonelectrostatic potential with the isotropic part $V_{iso} = V_{LD}$. It can be shown that, due to its central symmetry, the isotropic part of the potential V_{mol} [i.e., potential (10)] cannot cause transitions between states of optically active molecules. A natural

assumption is that the anisotropic part of the intermolecular potential V_{aniso} has a sufficiently short range; i.e., the range of its action is $R \sim 1$. The particles with a relative collision energy $E \geqslant \varepsilon$ that surmount the potential barrier fall within this region. If the rotational quantum of a molecule is $2\tilde{B}J_i \ll E$ ($\tilde{B}$ is the rotational constant), then the rotational transitions occur upon each collision, when the molecules approaching each other reach a distance $R \sim 1$. This condition means that, ignoring a specific form of V_{aniso}, we can confidently consider that $S_2(b) = 1$ at $R \sim 1$. The rotational constant for CO_2 molecules is $\tilde{B} = 0.39$ cm^{-1} [1]; therefore, we restricted ourselves to rotational quantum numbers $J_i \sim 80$.

Abstracting from the line shift problem, we will assume that $\Delta_i \approx \Delta_f$. Then, it follows from (9) that

$$S_2(b) = 1 - \exp\left[-\left(S_{2,iB}^{outer} + S_{2,fB}^{outer} + S_{2,iBfB}^{middle}\right)\right]. \quad (17)$$

Thus, at $K \leqslant 0.8$,

$$\sigma(K, V_B, J_B) = \pi\sigma^2 \left\{ \beta_{cr}^2(K) \right.$$

$$\left. + 2\int_{R_{cr}(K)}^{\infty} S_2(R_c, K) R_c \left[1 + \frac{4}{K}\left(\frac{5}{R_c^{12}} - \frac{2}{R_c^6}\right)\right] dR_c \right\}. \quad (18)$$

Here, we have changed from the integration over the reduced impact parameter β to the integration over the reduced distance of closest approach R_c. In (18), the quantity $R_{cr}(K)$ is the distance of closest approach at $\beta = \beta_{cr}$. The parameters β_{cr} and R_{cr} determine [in view of (12)] a local minimum of function (13). In particular, at fixed K,

$$R_{cr}(K) = \left\{0.2\left[1 - \left(1 - \frac{K}{0.8}\right)^{1/2}\right]\right\}^{-1/6}, \quad (19)$$

and $\beta_{cr}(K)$ can be found from (11). It can be shown that, for $K > 0.8$,

$$\sigma(K, V_B, J_B) = 2\pi\sigma^2$$

$$\times \int_{R_c^{min}(K)}^{\infty} S_2(R_c, K) R_c \left[1 + \frac{4}{K}\left(\frac{5}{R_c^{12}} - \frac{2}{R_c^6}\right)\right] dR_c, \quad (20)$$

where $R_c^{min}(K)$ is the minimum distance of closest approach at a given K. It can be easily shown that

$$R_c^{min}(K) = \left[\frac{2}{1 + (K+1)^{1/2}}\right]^{1/6}. \quad (21)$$

Expressions (3) and (17)−(21), together with the expressions for calculating the functions $S_{2,iB}^{outer}$, $S_{2,fB}^{outer}$, and $S_{2,iBfB}^{middle}$ [4], make it possible to determine the widths of molecular spectral lines taking into account the features of the translational motion of colliding molecules.

3.4 Comparison with experiment

The above relations were derived at a fixed relative velocity v of colliding particles. Let us define the procedure of averaging over velocities, because, as shows the analysis of the reference data, a unified approach to this problem is absent. Let us assume that the absolute-velocity v_a distribution for optically active particles is a Maxwellian one.

It is known [19] that the distribution function for the velocities v of perturbing particles relative to the optically active molecule depends on the velocity v_a:

$$\psi(v/v_a) = \frac{2v}{\pi v_a \bar{v}_p} \left\{ \exp\left[-\frac{4}{\pi}\left(\frac{v - v_a}{\bar{v}_p}\right)^2\right] \right.$$

$$\left. - \exp\left[-\frac{4}{\pi}\left(\frac{v + v_a}{\bar{v}_p}\right)^2\right] \right\}, \quad (22)$$

where $\bar{v}_p$ is the average absolute velocity of perturbing particles. When the dependence of the broadening cross section on the velocity v is taken into account, the collision-induced line broadening becomes inhomogeneous: the ensemble of particles is split into groups $f(v_a)dv_a$, and an individual Lorentzian profile with a half-width

$$\langle \Delta v_{1/2}(i \to f, v_a) \rangle = \int_0^{\infty} \Delta v_{1/2}(i \to f, v) \psi(v/v_a) dv \quad (23)$$

corresponds to each group.

The resulting profile for the whole ensemble of particles must be determined by the expression

$$\Phi(v) = \frac{1}{\pi} \int_0^{\infty} \frac{\langle \Delta v_{1/2}(v_a) \rangle f(v_a) dv_a}{(v - v_{if})^2 + \langle \Delta v_{1/2}(v_a) \rangle^2}. \quad (24)$$

However, it is often assumed that the line shape caused by a collision broadening has, as a whole, a Lorentzian profile with the half-width

$$\langle \Delta v_{1/2} \rangle = \frac{n_B}{2\pi c} \langle v\sigma_R(v, i \to f) \rangle. \quad (25)$$

The averaging in (25) is performed over relative velocities v. To simplify calculations, the averaging over the Maxwellian distribution is replaced in most papers (e.g., [6, 20, 21]) by a simpler relation

$$\Delta \tilde{v}_{1/2} = \frac{n_B}{2\pi c} \bar{v}\sigma_R(\bar{v}, i \to f), \quad (26)$$

where $\bar{v} = (8kT/\pi\mu)^{1/2}$ is the average relative velocity (average particle approximation).

The averaging procedure was discussed many times (e.g., in [19, 22]), but possible errors due to simplifications (25) and (26) were not analysed even within the ATC approximation and all the more within the RB model. The amount of calculations in the scheme proposed by us is close to that in the ATC model, and we evaluated these errors. Fig. 4 presents the calculated errors

$$\Delta(J_i) = \frac{\Delta v_{1/2}(J_i) - \langle \Delta v_{1/2}(J_i) \rangle}{\Delta v_{1/2}(J_i)} \quad (27)$$

for the P-branch of the $00^00 \to 00^01$ transition in CO_2 at $T = 170$, 300, and 600 K. In (27), the quantity $\Delta v_{1/2}(J_i)$ is the true half-width of the profile (24), and $\langle \Delta v_{1/2}(J_i) \rangle$ is the averaged half-width (25). As we see, the error is $\Delta(J_i) < 0$. As a whole, its magnitude is small ($< 4\%$), but it should be taken into consideration in precise measurements.

Fig. 5 shows the results of our calculation of the collision half-width $\Delta v_{1/2}(J_i)$ for the P-branch of the $00^00 \to 00^01$ transition at $T = 300$ K and $p = 1$ atm. The constant
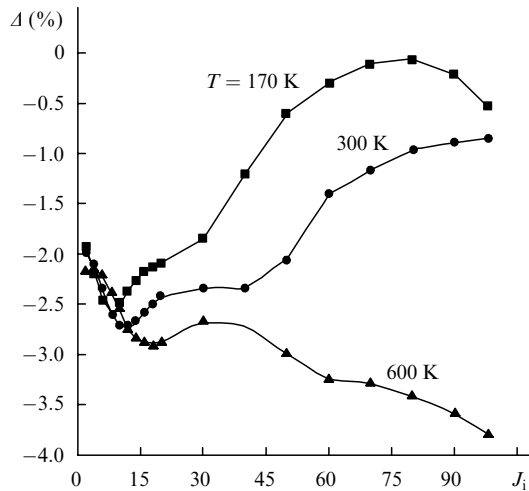
Figure 4. Relative error Δ as a function of J_i for CO_2 at various T.

Figure 6. Experimental and calculated (using the ATC and proposed models) dependences of the collision half-widths of CO_2 spectral lines on J_i at $p = 20$ Torr and $T = 600$ K.

quadrupole moment of a CO_2 molecule is $Q_{CO_2} = -3.69D \times Å$ [20]. The calculation data for the ATC model [11] and HITRAN experimental data [1, 2] are also presented. Although, as was mentioned above, the ATC model gives a satisfactory agreement with the experiment at room temperature (the discrepancy between the calculation and experimental data was within 20 %), the plots in Fig. 5 show that this agreement has improved (the average disagreement is ~ 7 %). Note that the calculation results also describe well the linewidths with $J_i \sim 80$, where the contribution of the electrostatic interaction is not large.
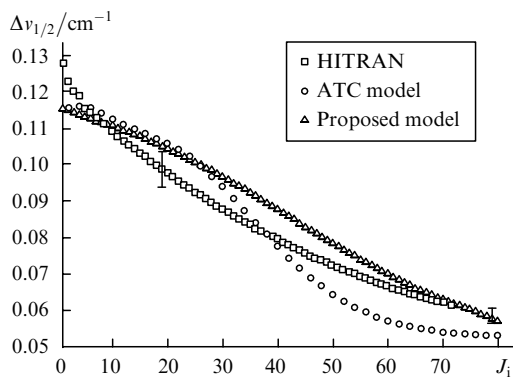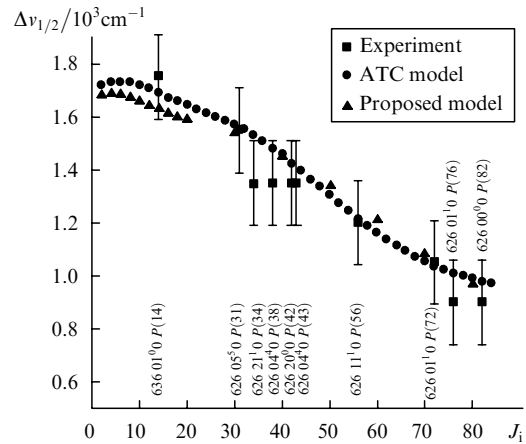

Figure 5. Collision half-widths of spectral lines obtained in experiments (averaged HITRAN data) and calculated using the ATC and proposed models versus rotational quantum number J_i for the P-branch of the $00^00 \rightarrow 00^01$ transition in CO_2 molecules at $T = 300$ K and $p = 1$ atm.

Fig. 6 shows the collision half-widths of lines versus J_i obtained in plasma measurements ($T = 600$ K, $p = 20$ Torr) and the calculated half-widths under the same conditions. The calculation and experiment agree well. A dependence obtained in the ATC approximation is also plotted. The effect of low-energy collisions at a high temperature is small, and the electrostatic interaction is efficient up to large J_i; therefore, both models yield close results.

Fig. 3, in which the calculation and experimental results at $T = 170$ K are compared, shows that, for $J_i < 20$, both our and the ATC models give close results corresponding to

the experimental data. On the contrary, at $J_i > 20$, the dependence predicted by the ATC model significantly differs from that observed experimentally, and the new model properly describes the experiment. Taking into account the above consideration, we can assert that, at low temperatures, the effect of low-energy collisions ($K \leqslant 0.8$) appreciably increases and it becomes necessary to take them into account. The calculated collision half-widths of CO_2 molecular spectral lines versus J_i at $T = 15$ K and $p = 1$ atm are shown in Fig. 7. The low-temperature conditions can be interesting when studying, for example, the upper atmosphere and gas-dynamic processes. Here, the discrepancy between the offered model and the ATC approximation is very large (at $J_i > 20$, the results differ by a factor of 2.5). Note that the line half-widths in this case are an order of magnitude larger than at room temperature. Special experiments for verifying these calculations are desirable.
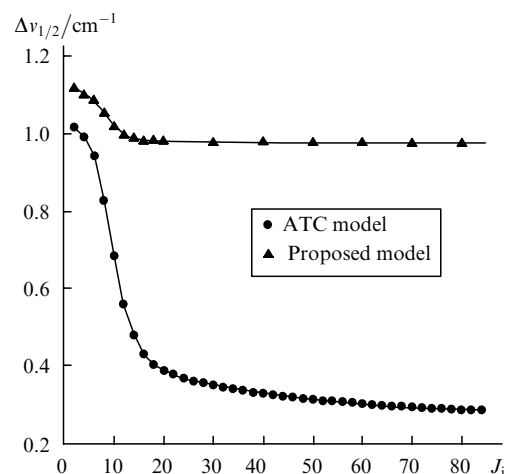

Figure 7. Dependences of the collision half-widths of CO_2 molecular spectral lines on J_i at $T = 15$ K and $p = 1$ atm calculated using the ATC model and the model proposed in this paper.

4. Conclusions

The widths of IR spectral lines of CO_2 molecules have been measured in wide temperature and rotational quantum number ranges using the diode laser spectroscopy technique. Analysis of the experimental results obtained and the available reference data suggests that it is necessary to improve the existing theoretical models.

We have proposed the calculation scheme that takes into account a deviation of the particle trajectories from rectilinear ones in a field of intermolecular forces and an increase in the effective broadening cross section in orbital collisions of particles with low translational energies, and satisfactorily describes the experimental results. The conditions under which the consideration of these collisions is especially important are specified. The calculations use a small number of initial parameters known from independent experiments and computations: constants of the Lennard-Jones intermolecular potential and constant molecular electrostatic multipole moments.

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