Line shape narrowing in carbon dioxide at high pressures

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The description of the narrowing effect at high pressures is demonstrated on the example of CO$_2$-He absorption for Q-, P-, and R-branches and for the head of the R-branch. The problem is focused on the physical meaning of this phenomenon that should be associated with the angular and translation momentum transfer to matter from the photon absorbed. The effect is described in the approximation of the single line without the conventional line mixing. A narrowing function is introduced that links the absorption in the resonance region with the one in far wings. This function enlarges the absorption of a single line approximately in 20 times in far wings in comparison with the Lorentzian, independently of the type of molecule and pressures. The halfwidth of a single line is assumed to have a nonlinear pressure dependence and approaches to a saturated value at high pressures.

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I. INTRODUCTION

The present paper is devoted to the line shape narrowing or the so-called "line mixing effect" non less puzzling phenomenon of line shapes theories than the intriguing problem of extreme wings [1,2]. The narrowing of the absorption line shape for high enough pressures leads to the evident super-Lorentzian absorption near band centers and this effect had been first reported by Bloembergen, Purcell, and Pound [3] more than 50 years ago. At present, this phenomenon is known for many molecules, bands, in many spectral regions and has many applications (see, e.g., reviews by Lévy et al. [4] and by Spänkuch [5]). Near the band head, this effect had been observed by Grigor’ev et al. [6] for the band 3ν$_3$ of CO$_2$. The recent experiments and modelings of the line mixing for various bands and branches may be found in Refs. [7-10]. The above-mentioned papers [6-10] as well as ideas, experimental facts, and observations from Refs. [11, 12] are directly used in the present studies. The simplicity of computations that has underlined the importance of application of the line mixing in atmospheric studies had been pronounced in Refs. [11, 13, 14].

This paper continues our line shape exploration efforts devoted to investigations of CO$_2$ absorption in far wings and main results had been first announced on the Symposium IRS-2000 [15]. These studies are based on new theoretical ideas that are nearly to Ref. [16] and especially to Ref. [17] and they are aimed to characterize the absorption line shape in resonance and far wing regions by some common principles. The problem numerates many approaches for its decision with many ideas and we do not pretend to accomplish a comprehensive study of this question and even to outline some appreciable part of the pertinent works in these regions.

II. GENERAL PRINCIPLES AND THE LINE SHAPE

There is a conventionally established opinion that the Lorentz’s contour cannot describe actual molecular spectra. However, it seems that the problem is not so lucid. The matter comprises molecules that, in turn, are associated with many cavities in the form of two-level systems and any photon propagated within the matter feels these cavities, i.e., there is a probability that this photon will be captured by any of them. The latter means that any photon being in the vicinity of a molecule of interest with any frequency has a probability to interact with any cavity of this molecule, independently of the tuning wavenumber.

As a rule, the dispersion (Lorentzian) line shape was used to derive description of this interaction by methods of the wave mechanics. In fact, no contour other than the Lorentzian had been employed in the overwhelming majority of theories. For example, even the so-called Rozenkranz’s line shape [18] that is a basic approach for many sophisticated theories and techniques is not something else as the modified dispersion profile. Our recent results can encourage this idea, since the Lorentzian priority may cause the original description of the sub-Lorentzian properties of CO$_2$ absorption [15]. The exclusion may be the statistical line shape that uses ideas of the quantum theory, where the photon energy emitted or absorbed corresponds to the difference between two energy levels being in the statistically changing field of other particles [19]. However, the statistical line shape that is fruitful for description of the line wing broadening in plasmas, nevertheless, does not exclude the Lorentzian in the core part [20] as well.

The photon interaction with a two-level system can lead to the photon absorption, if the momentum and angular momentum have been conserved. However, the photon cannot interact with a molecule or molecules infinitely, because there is a need of time to transfer the momentum and angular momentum from photon to the molecule, because every molecule has the inertia that is determined by the mass or the inertia momentum. This
means that an act of absorption or emission begins, if the system is in a determined stationary state not in an intermediate position, and some time is needed in order the system due to its inertia can change its stationary states. This interpretation completely corresponds to the main principles of the quantum mechanics. A period of the angular and translation momentum transfer restricts the duration of the absorption by some minimal value, therefore the lifetime of the exited state to reckon in the conventional approaches is also not less than some minimal value.

The relaxation time $\tau_{\text{rot}}$ of the excited rotational state $i$ into a lower state $j$ or the lifetime of the excited rotational state $i$ in presence of the lower state $j$ is on average determined as

$$\tau_{\text{rot}}^{ij} = \frac{1}{2c\gamma_{\text{rot}}}$$

(2.1)

where $c$ is the light velocity (cm/c) and $\gamma_{\text{rot}}^{ij}$ is the halfwidth (cm$^{-1}$) of the rotational line $ij$. Let us omit the superscripts in Eq. (2.1) in further. On average, the rotational angular momentum transfer time cannot be shorter than some limits that are determined as reciprocal separation between rotational lines,

$$\tau_{\text{rot}} \geq \tau_{\text{rot}}^{\text{min}} = \frac{1}{2c\gamma_{\text{rot}}^{\text{max}}},$$

(2.2)

where the saturation halfwidth $\gamma_{\text{rot}}^{\text{max}} \sim \Delta\omega_{\text{rot}}$, and $\Delta\omega_{\text{rot}}$ is this mean separation. The similar relationships must be for the translation momentum transfer time

$$\tau_{\text{vib}} \geq \tau_{\text{vib}}^{\text{min}} = \frac{1}{2c\gamma_{\text{vib}}^{\text{max}}} \approx \frac{1}{c\Delta\omega_{\text{vib}}}$$

(2.3)

where $\gamma_{\text{vib}}$ and $\Delta\omega_{\text{vib}}$ should be regarded as the halfwidth of the selected vibrational band and the separation between bands, respectively. Our assumption consists of that the minimal duration of the rotational or vibrational relaxation is related to the conservation laws of the angular or translation momentum, respectively.

The finitely collision duration hypothesis [19, 21] is distinguished from our assumption. It was used to be fruitful for explanation of the line mixing [22] in CO$_2$ and the wing absorption in H$_2$O [23]. However, this idea may find objections from the point of view of collision and statistical theories [19, 20]. The main reason is that the impact approximation (infinitesimal collisions) describes good the line shape nearly resonances, where transitions are caused by slow molecules, i.e., with finitely collision time, but this approximation is lame in wings that must be reasoned by rapid collisions, i.e., with the infinitesimal collision time. While according to the finitely collision duration, the effect could be inverse. Though these objections have a paradoxical character, indeed, they are serious because the collision duration mostly relies on the relative velocity of molecules not their internal properties.

The paradox may be removed by the fact that the duration of the photon interaction differs from the collision time and the hypothesis in our edition means that there is a minimum limit of time of the photon interaction with a molecule. The angular or translation momentum transfer from photon to the molecule or vice versa must be occurred during this time that because of the molecule inertia cannot on average be less than the minimum limit.

Note that for the determination of the separation between lines or bands in CO$_2$ molecule, the forbidden transitions must not be formally taken into account. These mean they do not change the number of channels that could be appropriate for the momentum transfer. Certainly, the pressure-induced absorption is here ignored. The appearance of the supplement resolved lines (e.g., rotational lines in Q- branches of the perpendicular bands in CO$_2$) enlarges the transfer time minimal limit under the channels of interest. The supplement lines effect the narrowing of the line shape that formally approves the name of the "line mixing" in Q-branches. Comparing the different branch, thereby one may conclude that weak lines between strong lines decrease the transfer time limit and strong lines increase this limit. The transfer time limit determined by the far lines always should not be greater than those done by adjacent lines. The role of the adjacent lines always should be more significant than "interaction" between far lines and, as one can see in Section V, the adjacent lines mostly determined the effect of narrowing of the lines in bands at high pressures.

### III. PRESSURE-DEPENDENT LINE HALFWIDTH

There is a well established empirical fact that the line shape of a single line is described by the Voigt contour at any pressures of interest and adjustments of the line parameters stored in databases are practically carried out by this profile. The collision halfwidth of a single line strongly depends on pressure (Fig. 1). The database contains the values of $\gamma_{\text{atm}}$ that equals to $\gamma (p) - \gamma_0$ (Fig. 1) at $p$ equal to 1 atm. The halfwidths at other pressures $\gamma (p)$ is as a rule determined by the linear law including high pressures, where experimental evaluation is difficult.

The part of the curve for small and moderate pressure less than, e.g., $p_L$ is presented in Fig. 1, following Ref. [24]. We believe that the Lorentzian should be a basic contour of the line shape generated in this paper. Let us assume that the halfwidth of the Lorentzian at high pressures is deviated from being linear on pressure (Fig. 1) and approaching to the saturation value not being greater than some value proportional to the parameter $\gamma_{\text{rot}}$ (2.2). Therefore, it reaches the saturation at some critical pressure $p_s$ as one sees in Fig. 1. Because of line overlapping, it is impossible to measure this halfwidth at high pressures and, thereby, to extrapolate the Voigt line shape on high pressures. In order to verify this hypothesis, two estimations of the CO$_2$ absorption in mixtures with helium have been made at the critical density $p_s = 135.8$ atm (Fig. 2a) and $p = 657.1$ atm (Fig. 2b). The Lorentzian
halfwidth in these computations (Figs. 2a and 2b) was the same. The latter does not concern the far wings used for absorption anticipation in the inter-band region. The description of the model and calculation details will be considered in Sections IV and V, respectively.

![Graph](image)

**FIG. 1.** A hypothetical behavior of the pressure-dependent collision halfwidth of a single line demonstrates the main hypothesis of existence of the minimum time limit of the photon interaction with a molecule. The definition of the saturated value $\gamma_{rot}$ follows from Eq. (2.2) as the separation between rotational lines, that approximately becomes equal to this value at some critical pressure $p_s$, when the rotational structure of spectrum is not noticeable. The pressure interval $[p_D, p_L]$ indicates the quasi-linear region that is mostly applied to the experimental measurements of the collision halfwidth.

**IV. NARROWING FUNCTION**

Interesting observations may be found in a few papers [11,12] (see other cites in Ref. [12]). The absorption peak of the bands studied by the Lorentzian method is underestimated in two times [12] at those minimal pressures, when the fine rotational structure of the bands becomes unnoticeable. The absorption in near wings is overestimated also in two times independently of pressures, Q-branch line spacing, and wing wavenumbers [11,12]. These facts tell us that the narrowing effect is weakly dependent on molecular properties similar to the exponential behavior revealed for CO$\_2$ far wings absorption (a few examples of these computations are reported in Ref. [15]).

Applying the methods of probes and errors, we found out that the dispersion line shape of the line $i$ has to be multiplied by some factor-function $\Gamma_i (\omega, p)$ and by the exponential factor $\Gamma_i (\omega)$ for $\omega \geq \omega_i$ or by $1 - \Gamma_i (\omega)$ for $\omega < \omega_i$, where $\omega_i$ is the resonance wavenumber (frequency) of the line $i$. The exponential factor is not essential near the resonance spectral region and it is not considered in details in this communication. In turn, let the narrowing function be responsible for redistribution of the intensity in the line shape, that may be associated with the momentum transfer. This narrowing factor-function $\Gamma_i (\omega, p)$ at pressures $p \geq p_s$ (Fig. 1) has the form

$$\Gamma_i (\omega, p)_{p \geq p_s} = (1/4)^{x_i},$$

where the power $x$ is determined as follows:

$$x_i = x_{\text{min}}, \text{ if } |\omega - \omega_i| \leq a \gamma;$$

$$x_i = x_{\text{max}}, \text{ if } |\omega - \omega_i| \geq b \gamma;$$

$$x_i = \frac{|\omega - \omega_i| - c \gamma}{b - c \gamma} x_{\text{max}}, \text{ if } b > |\omega - \omega_i| > c \gamma;$$

$$x_i = \frac{c \gamma - |\omega - \omega_i|}{c \gamma - a} x_{\text{min}}, \text{ if } a < |\omega - \omega_i| \leq c \gamma.$$  

![Graph](image)

**FIG. 2.** Verification of the main hypothesis of the minimum time limit of the angular momentum transfer on the example of the two calculations of the absorption coefficient in the central region of the band $\nu_3$ near 4.3 $\mu$m in mixtures with helium. Densities: (a) $n_{CO_2} = 1.63 \times 10^{-5}$ Am and $n_{He} = 124.3$ Am (135.8 atm); (b) $n_{CO_2} = 2.73 \times 10^{-5}$ Am and $n_{He} = 603.4$ Am (657.1 atm). Experiment by Ozanne et al. [9] was performed at the temperature 298 K.

The dimensionless parameters $a$, $b$, and $c$ are shown in Fig. 3. The ordinary Lorentzian halfwidth $\gamma$ in Eqs. (4.1-3) at pressures ($p \geq p_s$) is equal to the constant $\gamma_{rot}^s$. Then, $\gamma = \gamma_{rot}^s$ at these pressures. The parameters $x_{\text{max}}$

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and \( x_{\min} \) were studied by method of probes and errors near some values, so that, the following equations would be valid

\[
\Gamma_{\max}(\omega, p)_{p \geq p_s} = (1/4)x_{\min} = 4,
\]

and

\[
\Gamma_{\min}(\omega, p)_{p \geq p_s} = (1/4)x_{\max} = 0.1.
\]

Thus, \( x_{\min} = -1 \) and \( x_{\max} = \ln 0.1/\ln 0.25 \).

![FIG. 3. The line shape regions for constructing the narrowing function \( \Gamma_\ast(\omega, p)_{p \geq p_s} \) (4.1).](image)

The factor 2 at the factor-function \( \Gamma_\ast \) is included in the function (4.1). Without this factor, the function (4.1) has a simple assignment. In comparison with the Lorentzian line shape with the saturation halfwidth \( \gamma_{rot} \), it increases the intensity by factor 2 in the region less than the parameter \( a \) (Fig. 3) and, in comparison with the Lorentzian line shape having the ordinary halfwidth, it decreases the absorption in wings by the factor 0.05 for the wavenumber more than parameter \( b \) (Fig. 3). The functions (4.2) and (4.3) are sewing together the factors 2 and 0.05. The calculations of the spectrum at pressures \( p \geq p_s \) are fulfilled along with the Lorentzian having the saturation halfwidth \( \gamma_{rot} \), therefore the parameter \( x_{\max} \) is determined in the computational algorithm as

\[
x_{\max} = \ln (0.1/\gamma_{rot}) / \ln 0.25,
\]

where the \( \gamma \), as above, is the conventional Lorentzian halfwidth linear to the pressure. In all our computations, e.g., in Fig. 2, the relation \( \gamma_{rot} = 3.92 \Delta \omega_{rot} \) is used. The separations \( \Delta \omega_{rot} \) are different for different types of band branches.

The parameter values \( a, b, \) and \( c \) for estimations in Fig. 2 are specified as 0.72, 3.92, and 1.2. The discrepancies in Fig. 2b between data calculated and measured may be explained by existence of the inter-branch narrowing effect found out in paper by Qzanne et al. [9]. Following ideas of the present paper, one may foresee that this effect for the photon interaction with matter should be elucidated by existence of the minimum time limit of the translation momentum transfer. Its rates may be different for molecules in states with different angular momenta. Somewhat other behavior for the branch interactions are modelled for the 3p\( \beta \) band and we will come back to this question in Section V.C.

The narrowing function may be assumed as the function controlled the probability (rate) of the transition in a two-level system and that should be independent on the intermolecular interactions. The latter is not unexpected. The resonance nonlinear interaction of radiation with matter that produces the transition probability oscillating with the Rabi frequency [25] also does not depend on the intermolecular forces. According to this resonance approximation, the probability in far wings must be also oscillated, but with the detuning frequency [25]. Moreover, the classical impact theories of the line shape by Lorentz, Lenz, and Weisskopf [19] are based on the phase interruption due to strong impacts between molecules, that destroys the emission in a two-level system. The existence of this long-term emission was not clear in the classical theories, but it may be replaced in a modern representation by the oscillating probability that is caused by altering of level populations with the Rabi frequencies. In this interpretation, the emission and absorption may be considered by the similar technique.

Two different mechanisms of the angular momentum transfer have to be accounted for the central region and wing of the line shape, respectively. Let us interpret these mechanisms by a hypothesis of the paper [17]. Let two coherent photons [17] interact with a molecule as a fluctuation of four [17] or five photons. The latter was used for calculations in Ref. [15]. Let the angular momentum transfer occurs during the rotation of the polarization plane of one coherent photon on right angle in respect to the second coherent photon. Thus, two coherent photons or the whole fluctuation from four-five photons partake in the angular momentum transfer. The absorption rate (probability) being normalized in any reasonable theory per one photon also increases in two times.

Another mechanism should be assumed in wings. Perhaps, the act of the direct photon-molecule angular momentum exchange is impossible for big detuning frequencies for a short period. The angular momentum transfer in wing regions is delayed via an act of the photon-photon angular momentum exchange, i.e., between two fluctuations. The rate (probability) normalized per one photon should be less for the absorption act in \((1/4)^2(1/5)^2\) times. We have found this value as equal to 1/20.

Thus, the physical meaning of the puzzling narrowing effect should be associated, first of all, with the quantum representations in the form of the photon fluctuations. The latter is also confirmed by the absorption modeling in wings [15]. The line mixing method based on the Fano’s approach of the relaxation matrix [26] was in general successful in the line shape theory, but its physical meaning should not be obligatory concluded as the interference of lines. Exact calculations of cross-relaxation
constants in CO$_2$ by Petrova et al. [27] showed that they about in two-five orders of magnitude less than diagonal ones and cannot explain the narrowing effect at proper moderate pressures of N$_2$. Supplement hypotheses as, e.g., the statistical representation [18] must be incorporated and, then, the ad hoc and semiempirical parameters would have been included for practical calculations as it has been made in many works.

The narrowing is closer to definition of the rotational and vibrational relaxation. However, the technique of this relaxation must consider collisions that are occurred during the momentum transfer, i.e., for transitions of active molecules from one stationary state to another. This can be on average observed at high pressures. Since the quantum mechanics admits consideration only of observable quantities assigned for states with orthogonal functions, the problem becomes serious. Whether the apparatus of quantum mechanics, e.g., in the form of the density matrix, suffices to describe the effect of the collisions for the intermediate states? How means the possible photon fluctuations related to a two-level system can be incorporated in the theory?

V. VALIDATING THE NARROWING FUNCTION

In fact, the narrowing function together with the exponential form of the line shape reveals a good coincidence of the calculated absorption with the experimental data in the wing region [15]. In order to verify the narrowing function in the central region, the absorption coefficients are regarded for the Q-, P-, R-branches of CO$_2$-He mixtures. Our modelings of absorption in far wings show [15] the mixture of CO$_2$ with helium may be assumed with weak nonlinear absorption [16] and then it is convenient for validating the narrowing function hypothesis. The exponential form as well has the lesser impact in the central region.

A. $\nu_3$ band region

Such calculations for the $\nu_3$ band are depicted in Fig. 2. The narrowing function acts on the Lorentzian with the halfwidth $\gamma_{He} = 0.52 \gamma_{N_2}$. This value is the same as in our calculations for the mixture of CO$_2$ with helium in far wings [15] and it is nearly to the experimental value evaluated in Ref. [2]. The saturated value of the halfwidth $\gamma_{rot}^s$ is equal to 3.919$\Delta \omega_{rot}$, where for the $\nu_3$ region the $\Delta \omega_{rot}$ is specified as 1.2 cm$^{-1}$ that approximately is the mean separation between rotation lines in the R-branch. The parameter $b$ (Fig. 3) is 3.92.

On the whole, a good coincidence of data calculated and experimental is observed (Fig. 2a), but the same predicted for the higher pressure in Fig. 2b is worse. These computations are performed with the same saturated halfwidth $\gamma_{rot}^s$ for all pressures greater than some critical pressure $p_s$ equal 135.8 atm. Contrary to the latter, the absorption estimation in far wings is with the narrowing function that comprises $1/20^{th}$ from the Lorentzian contribution with the conventional halfwidth linear to pressure. The value of the latter is also $0.52 \gamma_{N_2}$. The worse coincidence of the two compared plots in the center of Fig. 2b should be associated with the inter-branch mixing effect introduced in Ref. [9]. In our interpretation the latter should arise due to a lower time limit (2.3) of the translation momentum transfer to active molecules from the photon absorbed.

B. Q-branch of the $\nu_2$ band region

Thus, the halfwidth $\gamma_{He} = 0.52 \gamma_{N_2}$ is occurred in all our developments [15]. Let us apply it to absorption estimation in Q-branches (Figs. 4, 5). The absorption contour for the pressure $p_{He} = 49.6$ atm is adjusted by the fitting of the halfwidth (Fig. 4) and the value $\gamma_{He} = 0.35 \gamma_{N_2}$ has been obtained. Then, the critical pressure $\gamma_{He} = 37.2$ atm has been predicted. Indeed, the calculations at this pressure and with $\gamma_{He} = 0.52 \gamma_{N_2}$ approximately yield the double absorption in comparison with the Lorentzian, if the contribution of the P- and R-branches is not taken into account. The parameter $c$ is equal to 1.2 for the Q-branch, also $a = 0.6$ and $b = 8$. In order to compare effects in different branches, their values are chosen to be close to those used for computations in other bands (e.g., Fig. 2) and it is clear that their adjustment could improve the spectrum retrieval, although the calculations in the Q-branch are weakly sensitive to the parameter $b$.

FIG. 4. Application of the main hypothesis of the minimum time limit of the angular momentum transfer to calculations of the absorption coefficient in the central region of the band $\nu_2$ near 14 $\mu$m (620-700 cm$^{-1}$) in mixtures with helium (experiment by Boissoles et al. [10]). The pressure $p_{CO_2}$ is 4.2 Torr. The pressures of He $p_{He}$ is 49.6 atm. The temperature is 296 K. The double absorption in Q-branch without contributions of P- and R-branches in comparison with the Lorentzian is evaluated for the pressure of He equal 37.2 atm. The halfwidth $\gamma_{He}$ of the CO$_2$-He absorption lines is 0.52$\gamma_{N_2}$. The path length is 3.85 cm.
and spectral regions. In any case, they are greater than the halfwidth values has been accomplished in Ref [10]. The pressure of He $p_{He}$ is 9.85 atm. The temperature is 296 K. The double absorption in comparison with the Lorentzian is obtained only for the halfwidth of the CO$_2$-He absorption lines $\gamma_{He} = 0.64\gamma_{N_2}$ (compare with Fig. 4). The path length is 3.85 cm.

According to Ref. [10], the double absorption becomes at pressure $p_{He} = 9.85$ atm (Fig. 5). However, the parameter $\gamma_{He}$ equals to 0.52$\gamma_{N_2}$ and we do not enable to obtain the double absorption (Fig. 4) with the parameters defined in Fig. 3. The strong line by line analysis of the halfwidth values has been accomplished in Ref [10]. Our testing of the Lorentzian contribution for many samples in Ref. [10] show that these values [10] slightly differ ($\gamma_{He} \approx \gamma_{N_2}$) from those stored in databases [28, 29]. These discrepancies are different [10] for various branches and spectral regions. In any case, they are greater than our value $\gamma_{He} = 0.52\gamma_{N_2}$. In turn, our value 0.52$\gamma_{N_2}$ successfully applied to many regions is near to the experimental value of 0.59$\gamma_{N_2}$ by Burch et al. [2]. Certainly, the conventional cutoff, e.g., no wings greater than 600 cm$^{-1}$, is used in all calculations with the Lorentzian. The narrowing problem based on the Lorentzian priority shows in Fig. 5 that evaluation of the Lorentz’s halfwidth is significant and it is deserved for detailed studies. Hitherto the rough relationship $\gamma_{He} = 0.52\gamma_{N_2}$ suffices to describe main features of the effect of interest. The spectroscopic information stored in the database GEISA-97 [28] (see also Ref. [29]) is used in all computations.

C. 3$\nu_3$ band region

Computations in the 3$\nu_3$ region are presented in Fig. 6. The pressure of helium (Fig. 6a) is approximately the same as in Fig. 2a and it may be associated with the critical pressure for the P-branch. Thus, the absorption must be reckoned with the $\gamma_{He} = 0.52\gamma_{N_2}$ in the P-branch region. We also found that for the R-branch that contains a strong head near the branch center this parameter is 0.2$\gamma_{N_2}$. This means that the Lorentzian halfwidths for lines in R-branch reaches its saturation values at pressures in 0.2/0.52 times lesser than for lines of P-branch. Thus, there are two intervals in the 3$\nu_3$ region that may be described with the different parameters. The parameter $c$ is 1.6 and 1.2 for the P- and R-branches, respectively. The parameter $b$ is the same for two branches, $b = 8$. The absorption modeling in the P-branch may be considered as being extrapolated from other regions, but the absorption in the head of the R-branch is fitted. The extrapolation is demonstrated in Fig. 6b for the higher pressures.

Contrary to data in Fig. 2b, the discrepancies in Fig. 6b have other character. The effect corresponds to the branch-broadening not the branch-narrowing as in Fig. 2b. Probably, the reorientation of the angular momentum of molecules, that concerns the inter-branch interaction, can lead to decrease of the period of the angular momentum transfer from photon to molecules. A trivial explanation also is not excluded that there is other set of the adjusting parameters, that allows us to obtain a description similar to that in Fig. 2b. A picture similar
to the small inter-branch narrowing effect is noticeable in Fig. 6a.

VI. SUMMARY AND CONCLUSION

The present studies and modelings followed confirm the main hypothesis of this communication that the Lorentzian halfwidth of absorption lines trends toward approaching to the saturation value at high pressures. Also, the lower time limit of the angular momentum transfer seems as an encouraged hypothesis with the reasonable physical meaning. We tried to follow the Lorentzian priority that, in our opinion, underlines the wave properties of the phenomena considered. However, as our modelings of absorption in the CO$_2$–He mixture show, the simple redistribution of the intensity in the band with the direct construction of the Lorentzian halfwidth $\gamma$, e.g., in the form

$$\gamma = \frac{\gamma_c \gamma_{rot}^s}{\gamma_c + \gamma_{rot}^s}$$  \hspace{1cm} (6.1)

does not properly describe the needed narrowing effect. Although this evident formula seems to produces the needed double absorption in the band center, for the halfwidth $\gamma$ could be equals to $\gamma_c/2$ at the critical pressure $p_c$, when $\gamma_c = \gamma_{rot}^s$; nevertheless the narrowing function (4.1) must be introduced for these aims. The halfwidth in Eq. (6.1) is equal to the conventional halfwidth $\gamma_c$ at small pressures and to the saturated halfwidth $\gamma_{rot}^s$ at high ones.

The Lorentzian priority is seen from the formula for "experimental" absorption coefficient that has been constructed in the following form

$$\alpha_{eff} (\omega) = \alpha (\omega) + \frac{1}{2x} \ln \left( 1 + \frac{b (\omega)}{2 \alpha (\omega)} (1 - \exp (-2 \alpha (\omega) x)) \right)$$  \hspace{1cm} (6.2)

that comprises two terms connected with linear and nonlinear absorption. The nonlinear absorption is large in water vapor, but it is small in mixtures of CO$_2$ with various broadeners, therefore the problem of the line shape may be first of all regarded as the sub-Lorentzian behavior of the linear absorption $\alpha (\omega)$ that is determined by the line by line summing over $n$ lines,

$$\alpha (\omega) = \sum_i n \left( p, \omega_i, T \right) FL (\omega, \omega_i, T) \times \left[ Ab (\omega, \omega_i, T, M = 5) \Gamma (\omega, \omega_i) \right]$$  \hspace{1cm} (6.3)

The conventional factor $n \left( p, \omega, T \right)$ is the molecule number in the lower state of the transition $i$ at the temperature $T$. This factor contains the Gibbs (Boltzmann) exponent. The full Lorentz line shape $FL (\omega, \omega_i, T)$ includes the integral intensity of the line at the temperature $T$ per one molecule. The universal narrowing function $\Gamma (\omega, \omega_i)$ is presented by Eq. (4.1) for high pressures. The Fermi (anti-Fermi) absorption factor $Ab (\omega, \omega_i, T, M)$ for the right (left) wing is taken with the $M = 5$. The parameter $M$ manifests the slope of the Fermi-distribution that presents an exponential form of the absorption in far wings. Since the exponential form is not essential in the resonance region, this factor as well as nonlinear absorption with the nonlinear absorption coefficient $b (\omega)$ is not considered in this communication. The Lorentzian priority is presented in Eq. (6.3) by the fact that the full Lorentz’s line shape enters Eq. (6.3) as a single factor.

![FIG. 7. The high pressure hypothetical line shape of a single line positioned at 1000 cm$^{-1}$ in the logarithmic scale has the simple form. The Lorentzian is the full Lorentz line shape. The exponential form is the Lorentzian with some Fermi or anti-Fermi factor. The full line shape is the Lorentzian with the narrowing function (4.1) and Fermi or anti-Fermi factor. The nonlinear absorption due to the specific line mixing (self-mixing for the single line) [16] that leads to increase of the absorption in near wings is not presented.](image)

The line shape of the single line for high pressures is depicted in Fig. 7. The rapid decrease of its value near the value $\gamma_{rot}^s$ that associates with the separation of the rotational line manifests the angular momentum transfer in the photon absorption act, i.e., due to the inertia momentum of molecules. Adding the nonlinear absorption increases the absorption in near wings and the non-Lorentzian line shape in Fig. 7 with this enlargement in the central region can resemble that what was called as the "generalized line shape" [31,32] (see also Ref. [33]). This is not surprising because the analysis of the experimental facts in far wings was the same as in our works as in Refs. [31-33]. Nevertheless, the methods and the explanation of these phenomena in these references are different from ours.

We try to utilize facts and observations from Refs. [11,12] illustrated the common absorption features inherited, in our opinion, to the interaction of the electromagnetic field with a two-level system and independent from intermolecular forces. As a result, the very simple formulas (6.2) and (6.3) allow one to provide the prompt computations of CO$_2$ absorption in the total spectrum region for various broadeners [15]. Only the exponential
form somewhat enlarges the chip time. As it is shown in Fig. 7, this form may be ignored for computations in the central region, e.g., in the Q-branches. In general, this approach should be useful, first of all, for atmospheric applications. Further parametrization of the narrowing function must be fulfilled for moderate pressures. This means that the detailed dependence of the halfwidth on pressure (Fig. 1) must be stipulated.

The studies of this paper help us to exhibit main problems of the line shape in the closed logical scheme as follows. The line shape is broadened in the electromagnetic fields, so that the absorption coefficient $k$ is described by the relation $k \sim 1/(\delta \omega^2 + \gamma^2 + \eta I)$, where $\delta \omega$ is the detuning wavenumber, $\gamma$ is the Lorentz's halfwidth, $I$ is the radiation intensity with the proportionality constant $\eta$. This relationship gets an origin from Ref. [34] and it presents the nonlinear absorption near the resonance region [25]. It is conventionally deemed as a formula that cannot describe the absorption in far wings. However, the expansion of this expression for far wings over the small third term in the denominator at small intensities can lead to the nonlinear absorption equation [16,17], if this expression is substituted for the $k$ in the Beer-Lambert law and the term of the second power of $I$ is omitted. The latter can be done, in our opinion, according to the causality principle [16,17]. Some observed features of the far wing absorption had been obtained [16,17,15] with the help of this nonlinear absorption. Thus, the nonlinear absorption as in the resonance region [34,25] as in the far wings [16,17] should have the same origin.

Also, the same technique for deriving the nonlinear constants should be occurred in both these regions. The rise of the so-called "collapse" of the wave function, the main paradox of the quantum mechanics [36], had been excluded in Refs. [16,17] via its compensation by the absorption (chaos). The appearance of the photon fluctuations associated with two-level systems [15] in the resonance region for the period, when the system changes stationary states, may be also associated with this "collapse" of two coherent photons and the increase of the absorption in two times in the resonance region may be formally considered in a linear theory as the compensation of this "collapse" effect.

The present remarks into the line shape theory should be attractive for a few reasons. Firstly, it agrees with the local photon fluctuation of five photons associated with a two-level system (used in Ref.[15] for far wing calculations). Secondly, there is a hope that old Einstein's hypothesis of the induced emission in the two-level system that requires consideration, at least, two photons in one act of the absorption/emission should be properly interpreted. Also, the problems of the interaction of radiation with matter, not only intermolecular interactions, have been highlighted as important in the line shape theory. The latter underlines a close connection of the absorption as in resonance regions as in wings with the classical impact theory by Lorentz, Lenz, and Weisskopf [19]. Still one question should be interesting. How means the technique of the density matrix could incorporate the local photon fluctuations or some radical changes should be required, if the present ideas will be admitted in the line shape theory?

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