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Shape of collision-broadened lines of carbon monoxide

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ABSTRACT

We consider lineshape of the rotational spectrum of a CO molecule under the conditions of prevailing collisional broadening. Several series of experimental data obtained at relatively high (up to 1000) signal-to-noise ratio of self-broadening and broadening by noble gases have been analyzed. We used for analysis several well known models beyond the Voigt profile. It is confirmed that the use of the Hartman–Tran profile needs certain requirements in order to obtain meaningful and unambiguous results. A simple numerical simulation is suggested to evaluate the result of the model usage for any particular set of experimental data. Parameters of the collisional line narrowing were obtained. It is shown that under the experimental conditions, deviations of the shape of the observed lines from the Voigt profile are solely due to the wind effect.

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1. Introduction

The instruments used for remote sensing of the atmosphere in the millimeter and submillimeter wave range from ground stations, airplanes and satellites allow one to obtain substantial data for weather forecasts and prediction of climate changes. For example, oxygen lines can provide atmospheric temperature profiles. The distribution of air humidity is determined from the lines of water vapor. Observation of the lines of minor gas constituents permits finding, for example, distribution of greenhouse gases, which is an important issue in the context of global warming. Correct interpretation of atmospheric absorption profiles requires accurate laboratory measurements of the corresponding parameters of spectral lines [1].

It is known that in most cases the traditional Voigt model is unable to ensure sufficient accuracy of the description of the absorption lines recorded with high signal-to-noise ratios (several hundreds or more). The actual line is somewhat higher and narrower than the corresponding Voigt profile [2]. Two fundamentally different physical mechanisms affecting the line shape are known, namely, the velocity changing collisions, i.e., collisional narrowing of Doppler broadened lines (Dicke effect) [3] and the speed dependence of the collisional relaxation of absorbing molecules (the so-called “wind” effect) [4]. These two effects occur simultaneously and manifest themselves in very similar ways. Therefore, it is extremely difficult to estimate their individual contribution to the shape of the experimental line, even if the signal-to-noise ratio is high [2].

Corresponding models have been developed to allow for these “subtle” effects. These models were frequently used to approximate experimental lines (see, e.g., Ref. [5] and the references therein). It was stated in several papers (see, e.g., Ref. [6]) that under certain conditions, experimental data can be approximated with the same accuracy by models allowing either for the Dicke effect, or for the wind effect only. At the same time, it was noted that in the majority of cases the models allowing only for the Dicke

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effect fail to reproduce the experimental data corresponding to the prevailing collisional broadening conditions [6,7]. The study of these issues on an example of the OCS spectrum [5] showed that, at least for pure gases of polar molecules and in the pressure range where the collisional broadening is dominant, the observed line shape (excluding some specific cases) is governed by the wind effect.

This paper is aimed at further studying of the collisional narrowing effects. Herein, we discuss the results of fitting the known models (the Galatry profile [8], the quadratic speed-dependent Voigt profile [9], the partially-correlated quadratic-speed-dependent hard-collision profile, also known as the Hartman-Tran profile [10,11]) to the experimental recordings of the CO molecule rotational lines.

The dipole moment of about 0.1 debye, the absence of the superfine structure of the lines, and rather wide intervals between successive lines of the rotational spectrum make the main isotopologue of the carbon monoxide molecule (CO) extremely attractive for laboratory studies [12,13]. Due to the fact that CO is one of the major atmospheric pollutants, which is often related to large emissions of CO_2, its study is important from the viewpoint of the greenhouse effect and global climate issues [14,15]. Moreover, since it is the second most common molecule (after H_2) in the interstellar medium, CO plays an important role in the evolution of molecular gas clouds, where active star formation takes place; therefore, studies of its spectrum are of great importance for astrophysics [16].

The experimental details and features of the measurement method are described briefly in Section 2. In Section 3, the line-shape models are considered. Section 4 presents different aspects of analysis of the obtained data and their comparison with the results of earlier works. The main findings of the study are summarized in the Conclusion.

2. Details of the experiment

The CO spectrum rotational lines ($J=1\leftarrow0$ at 115,271.2018(5)[1] MHz, $2\leftarrow1$ at 230,538.0000(5) MHz, $3\leftarrow2$ at 345,795.9899(5) MHz, $4\leftarrow3$ at 461,040.7682(5) MHz, $5\leftarrow4$ at 576,267.9305(5) MHz and $7\leftarrow6$ at 806,651.806(5) MHz) were studied at room temperature (296–300 K) under self-pressure broadening conditions. Additionally, the $J=2\leftarrow1$ line was studied under the conditions of broadening by pressure of noble gases, specifically, xenon (Xe), krypton (Kr), and neon (Ne).

The experimental recordings of absorption lines were obtained by using a backward-wave oscillator (BWO) based spectrometer with radio acoustic detection of absorption (RAD spectrometer). The principle of the spectrometer operation and its features are described in detail in Refs. [18,19]. Continuous-wave coherent radiation is produced by a BWO. The BWO radiation frequency is stabilized and controlled by a phase-lock-loop system with reference to the harmonic of a microwave synthesizer. To increase the stability and accuracy of frequency setting, the synthesizer is synchronized with a rubidium clock. The use of a highly stable, digitally tunable radiation source, as well as synchronous detection of the amplitude-modulated absorption signal allows efficient averaging of the useful signal and recording of the absorption profiles with the signal-to-noise ratio sufficient for the precise line-shape analysis.

Details of spectra recordings, preparation of gas mixtures, and detailed description of the data processing method can be found in Ref. [5] and the references therein. The experimental conditions are specified in Table 1. The experimentally obtained profiles were analyzed by means of varying parameters of the model functions with the use of minimization methods and the discrete Fourier transform. Both common procedures, namely the one-by-one spectrum analysis and the multi-spectrum fitting were used to retrieve line-shape parameters. The maximum optical thickness of the sample was 0.041. Nevertheless, its influence on the line shape was noticeable, hence, the Beer–Lambert law was taken into account.

3. Line-shape models

It is well known that the Voigt profile (VP) is a convolution of the Lorentz profile (LP) related to collisions of molecules and the Gauss profile related to the Doppler effect which results from motion of molecules. The half-width of the Lorentz profile determines the rate Γ of collisional relaxation, which characterizes the coherence decay time $\tau=1/\Gamma$ in the considered ensemble of molecules. The wind effect is, basically, the dependence of the collisional relaxation on the absolute speed of the active (radiation-absorbing) molecule. Several models were proposed to allow for this fundamental effect, which received the common name of “the speed dependent Voigt model (SDV)”.

In this work, we used the quadratic Speed-Dependent Voigt Profile (qSDVP) model [9], where the dependence of the collisional relaxation on the velocity of the absorbing molecule is approximated by

$$\Gamma(V_a)=\Gamma_0+\Gamma_2\left[\left(\frac{V_a}{V_{a0}}\right)^2-\frac{3}{2}\right]. \quad (1)$$

Here V_{a0} is the most probable speed of the absorbing molecules, and Γ_2 is the parameter responsible for the speed dependence of the collisional relaxation. The shape of the line is calculated as the Fourier transform of the polarization correlation function, where Γ_0 and Γ_2 enter as adjustable parameters [5,9]. The qSDVP model can be used relatively easily for fitting to the experimental recordings of the lines. Moreover, the parameter Γ_2 should increase linearly with increasing gas pressure, which allows one to test the obtained values easily.

The Dicke effect is based on the fact that the intermolecular collisions, which do not affect the internal state of the active molecule, lead to velocity changes. The corresponding confinement of the diffusion process results in reduction of the Doppler width of the line. The effect is usually described by the Galatry profile [8] or by the Rautian profile [23].

[1] Measured line frequencies from Ref. [17] are given.

Table 1
Details of experimental recordings.

Perturber	Transition $J+1 \leftarrow J$	Pressure absorber/perturber (Torr)	Gas temperature (K)	Optical thickness	Mean QF[a] (VP, one-by-one-spectrum fitting)	Mean QF (SDVP multi-spectrum fitting)
Ne	2←1	0.26/1.2–3.7	298.9–299.6	< 0.0084	672 (32)	833 (9)
Kr	2←1	0.30/1.2–3.7	296.0–296.3	< 0.0084	432 (22)	1079 (11)
Xe	2←1	0.32/1.1–3.6	296.7–297.2	< 0.0084	299 (15)	883 (9)
CO	1←0	0.2–1.9	295.9–296.4	0.001	475 (20)	526 (7)
CO	2←1	0.3–3.3	297.7–300.0	0.0084	438 (22)	445 (5)
CO	3←2	0.2–3.2	297.9–298.7	0.0083	687 (36)	1040 (13)
CO	4←3	0.7–3.7	297.0–297.7	0.0096	264 (13)	282 (3)
CO	5←4	0.5–3.5	297.2–297.6	0.017	600 (31)	689 (9)
CO	7←6	0.5–3.1	296.8–297.9	0.041	235 (13)	258 (3)

[a] Quality-of-the-fit (QF) is defined as the ratio of the difference between maximal and minimal absorption in the recorded spectrum to the standard deviation of experimental points from the model function (see Section 4.1).

Within the Rautian model, the profile was constructed by using the method of the kinetic Boltzmann equation. It was assumed that a molecule "forgets" about its initial velocity (while preserving the internal state and optical coherence) after each collision, i.e., it is the model of strong collisions.

The Galatry absorption profile was derived in the framework of the Brownian motion model [24]. This approach supposes that in order to lose the memory of its initial velocity, a particle should undergo many collisions, i.e., the model of weak collisions is used.

Despite the fact that the Rautian and Galatry profiles were obtained on the different initial assumptions about the character of the collisions, they yield highly similar results and are equivalent from the viewpoint of fitting to the experimental data [25]. In both models, the parameter β is introduced to allow for the narrowing effect. This parameter is called the optical diffusion rate. It characterizes the efficiency of velocity changing collision. It determines the time $\tau_v = 1/\beta$ during which a particle "forgets" about its initial velocity, while "preserving the memory" about the coherence. Many studies (see, e.g., Refs. [2,7,25]) have shown that β should be smaller than the kinetic diffusion rate β_{kin}

$$\beta_{kin} = \beta^0_{kin} P, \tag{2}$$

where P is the pressure, $\beta^0_{kin} = k_B T/m_a D_{ab}$, and D_{ab} is the diffusion coefficient of the active molecules in the buffer gas [24]. Herein, for taking the Dicke effect into consideration, we used the correlation function corresponding to the Galatry profile (GP) presented in Ref. [7].

In order to allow for both the aforementioned effects, in Ref. [27] the Galatry profile was modified to take the wind effect into account. The corresponding model is called the Speed-Dependent Galatry Profile or SDGP. The authors of Ref. [28] proceeded in a similar way, generalizing the Speed-Dependent Rautian Profile (SDRP). Both models assume that the wind effect and the Dicke effect act independently. However, it was noted (see, e.g., Refs. [29,30]) that the "partial loss of memory" about the initial velocity and the partial loss of optical coherence is a result of the same collisions and, consequently, the narrowing mechanisms can influence one another, which means that one should introduce additional parameter responsible for this correlation. One of the known models that allow for the simultaneous influence of the Dicke effect and the wind effect, as well the correlation between them, is the so-called "partially-Correlated quadratic-Speed-Dependent Hard-Collision Profile" (pCqSDHCP), which is also called the Hartmann-Tran profile (HTP) for brevity [10,11]. This profile comprises the qSDVP model and the Rautian profile (RP). The HTP model has an analytical form in the frequency domain, which includes β, Γ_0, Γ_2 as parameters, as well as the parameter η that is responsible for the correlation of the wind effect and the Dicke effect. The advantage of the HTP model is its flexibility. If necessary, the model reduces to simpler (qSDRP, SDVP, RP and VP) models just by setting to zero higher order line shape correction parameters.

4. Analysis of experimental data

4.1. General notes on the spectra processing

All spectral recordings were analyzed by using two commonly-used procedures. The first one is the most traditional. It can be called one-by-one-spectrum fitting. In this case line profile parameters are determined from the result of the best fit of model function to each spectrum recording and then the obtained set of parameters is analyzed to retrieve corresponding pressure dependences. Specific features of this approach in application to the RAD spectrometer data were discussed in detail in Ref. [19]. The spectrometer produces an uncontrolled baseline that is rather weak but becomes essential for the high accuracy analysis. The baseline is usually approximated by a function linear with frequency. To take the baseline into account, both the additive and the multiplicative terms should be added to the line-shape model. This entails four additional variable parameters which could be pressure dependent [19].

The second procedure is called multi-spectrum fitting [20]. In this case the additional bounds are applied to line-shape parameters (linear dependence of collisional line width of gas pressure, etc.) and all spectral recordings are fitted simultaneously. It considerably reduces correlation between variable parameters and automatically takes into account different quality of spectral recordings thus giving an advantage in comparison with the one-by-one

spectrum fitting procedure [10,20–22]. To employ this approach we need to "clean" our spectra from the pressure dependent baseline. By analogy with the work of Ref. [31], we determined parameters of the baseline from the single spectrum fits using the VP model and removed the baseline from experimental recordings.

Typical results of the single CO line recording processing are shown in Fig. 1 that corresponds to the $J=2\leftarrow1$ transition broadened by Ne. Differences in the approximation of the experimental data using different models are seen only in the residuals. The use of the traditional Voigt profile yields a characteristic W-shaped residual. Under a minimal pressure of 0.26 Torr, all the considered higher-level models (GP, qSDVP, and HTP) fit the experimental line to the experimental noise level. Under a total pressure of the mixture of 1.2 Torr, the GP model residual is better than the one for the VP model, but worse than those for the other models. However, the obtained values of β significantly exceed the maximum possible value corresponding to the rate of the gas-kinetic diffusion (for example, the residual for 0.94 Torr of Ne presented in Fig. 1 corresponds to the enormous narrowing rate of 169 (24) MHz (sic), whereas the kinetic value is only 0.527 MHz [26]). In the case of an even greater pressure increase, the GP model fails to fit the line recording. This indicates that under the conditions of our experiments, the contribution of the Dicke effect to the shape of the observed line is insignificant for the considered gas mixture. Fitting the qSDVP and HTP models to the experimental recordings at all pressures yields noise-like residuals. A similar pattern was observed for all the other lines studied at different pressures under the conditions of self-broadening and Kr- and Xe-pressure broadening.

Along with the parameters of collisional broadening and narrowing, the values of collisional shifts of the central frequencies of the considered lines were determined. The obtained values are not presented here, since they are small (from several kHz to tens of kHz) and actually comparable with the uncertainty of the measurements, which is in agreement with the previous studies [5,13–15,32].

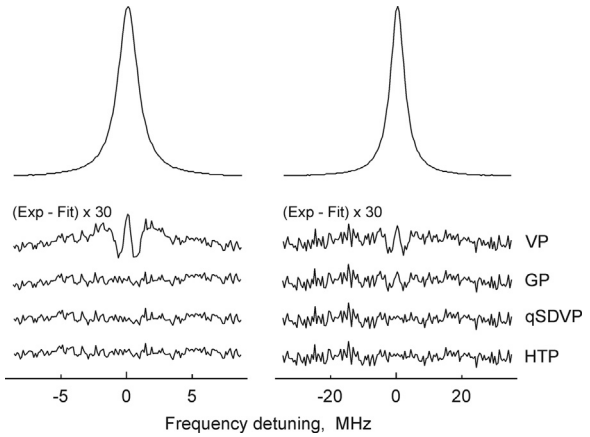

Fig. 1. Experimental recordings for CO molecule $J=2$-1 line under the conditions of Ne broadening. Left column is for 0.26 Torr of pure CO. Right column is for the mixture of 0.26 Torr of CO and 0.94 Torr of Ne. (Exp–Fit) residuals obtained using different models (designations of the models are shown on the right) are given below the recordings. The frequency detuning from 230,500 MHz is plotted along the *X* axis.

There are two dominating sources of uncertainties of the obtained line-shape parameters. The first one is inaccuracy of the baseline approximation by linear functions and the second one is signal-to-noise ratio of experimental recordings. The uncertainty of pressure (0.12%) and temperature (0.5%) measurements make negligible contribution to the resulting uncertainties of the obtained data. The reported parameter uncertainties in the case of the one-by-one-spectrum fitting correspond to one standard deviation of the line-shape parameter points from the fitted straight line, and in the case of the multi-spectrum fitting to the one standard deviation of parameter value determined from the global fit. In both cases this is, in fact, the statistical uncertainty only.

In the case of foreign gas broadening, the first pressure point corresponding to the pure CO case was excluded from the fits. The reason of this was possible influence of adsorption/desorption processes. Adding inert gas to the cell saturated by pure CO slightly changes the adsorption/desorption equilibrium leading to the CO partial pressure uncontrolled increase, which could systematically affect the retrieved line-shape parameters.

For the sake of comparison of the obtained results with the data from other works, the values of the broadening coefficient measured at room temperatures varying within 296–300 K, were recalculated to 296 K using the simplest empirical dependence $\gamma(296)/\gamma(T)=(T/296)^m$, where $m=0.8$ [33] (possible inaccuracy of the parameter m introduces a negligibly small error to the recalculation result).

4.2. Foreign gas collisional broadening

As a typical example of a result of the one-by-one-spectrum fitting procedure, Fig. 2 shows the pressure dependence of the collisional width of the Ne-broadened $J=2\leftarrow1$ CO line, by using different models. All models yield, as expected, a good linear dependence of the parameter on gas pressure. Deviation of the experimental points from the result of their linear regression does not exceed 50 kHz. The collisional broadening coefficients ($\gamma_0=\Gamma_0/2\pi P$) resulting from the qSDVP and HTP models coincide with each other within the measurement accuracy and, as expected, exceed noticeably the value of Γ resulting from the Voigt profile (Table 2).

The line-shape parameters obtained from the multi-spectrum fitting are also given in Table 2. These parameters coincide with the results of the one-by-one-spectrum fitting procedure within $1-\sigma$ statistical uncertainty except for the Xe-broadening case where the difference is somewhat larger for some unknown reason. Typical residuals of the fitting corresponding to the Ne-broadened $J=2\leftarrow1$ CO line is shown in Fig. 3.

The foreign gas pressure broadening parameters of the $J=2\leftarrow1$ line can be compared qualitatively with the results from Ref. [34], where a similar study of the $J=3\leftarrow2$, $5\leftarrow4$ lines is presented. It is known (see, e.g., Ref. [5]) that the broadening coefficient decreases as the rotational quantum number increases. Accordingly, all foreign gas

broadening parameters of the $J=2\leftarrow1$ transition (Table 2) exceed regularly (by 6–11%) the corresponding values obtained in Ref. [34] for the $J=3\leftarrow2$ transition. Note that the values of the Xe-broadening parameters for the $J=3\leftarrow2$ and $J=5\leftarrow4$ transitions obtained in Ref. [34] differ in a similar way by 22%.

4.3. Self broadening

Many works dealing with experimental studies of collisional-broadening and shifting of CO rotational lines [12–15,32–35] have been published. Table 3 presents comparison of the self-broadening parameters obtained in this work with other known data.

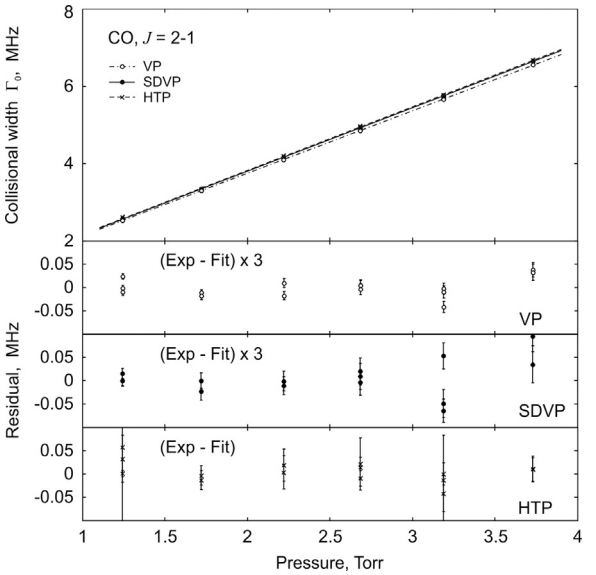

Fig. 2. Pressure dependence of collisional half-width ($\Gamma/2\pi$ for VP and $\Gamma_0/2\pi$ for qSDVP and HTP) for Ne-broadened CO, $J=2$-1 line obtained by data processing using different models. Here and in what follows, the pressure means the total pressure of the gas mixture (CO partial pressure is 0.26 Torr.) Error bars correspond to uncertainty of the parameter value estimated from the treatment of several (usually $2-3$) repeated recordings. Solid lines are results of linear regression of experimental points. The residuals of the regression are shown below. Note different multiplication factors.

The comparison of γ and γ_0 parameters reveals, on the one hand, disagreement within the reported uncertainties practically for all data. On the other hand, deviation of our VP-based γ values from HITRAN's data does not exceed 4.5%, which can be regarded to be a very reasonable agreement. Moreover, it is well known (see, e.g., Refs. [5–7] and Fig. 2) that the same data treated by VP yield systematically smaller collisional broadening parameter than treated by qSDVP. This is confirmed by our data, but the data from Ref. [14] are systematically larger than the ones from HITRAN at small J, but become systematically smaller at high J.

It is shown in Ref. [5] with an example of the self-broadened OCS lines that the narrowing coefficient γ_2 is weakly dependent on the rotational quantum number J. One can see from Table 3 that a similar conclusion can be made in the case of the lines of the rotational CO spectrum as well.

4.4. Collisional narrowing due to the wind effect

Values of the $\gamma_2=\Gamma_2/2\pi P$ coefficients responsible for line narrowing due to the wind effect for the case of self-broadening are presented in Table 3, and for the foreign gas broadening in Table 2. Contrary to the collisional broadening, practically all our γ_2 coefficients agree with the data from Ref. [14] within the $3-\sigma$ statistical uncertainty. The exception is the parameter of the $7\leftarrow6$ transition which was recorded with the smallest signal-to-noise ratio (Table 1).

Fig. 4 presents the pressure dependence of the parameter $\Gamma_2/2\pi$. It is seen that within the measurement accuracy, this parameter depends linearly on the pressure for all collisional partners. The narrowing coefficient γ_2, which determines the slope of the dependence, increases with an increase in the mass of the foreign-gas molecules. This confirms the known conclusion about the greater contribution of the wind effect to the line shape in the case of a great ratio of masses of the buffer molecule and the absorbing molecule. The figure demonstrates that both procedures of the spectra fitting yield very similar results.

Fig. 5 shows the γ_2/γ_0 ratio as a function of the buffer-to-absorbing molecule mass ratio in the case of broadening of two CO lines by pressure of noble gases. It is seen that the obtained dependence of the parameters agrees

Table 2
Coefficients of collisional line shape of CO, $J=2$-1 line broadened by pressure of different buffer gases at 296 K obtained using different models. All values except for η (that is in relative units) are in the units of MHz/Torr. The value of one standard-deviation of the parameter is shown in parenthesis.

	Fitting procedure[a]	VP	qSDVP		HTP			
		γ	γ_0	γ_2	γ_0	γ_2	β_0	η
CO–Ne	OS	1.613 (2)	1.635 (3)	0.162 (7)	1.645 (4)	0.25 (7)	1.90 (44)	0.59 (30)
	MS	1.613 (1)	1.635 (1)	0.158 (5)	1.643 (3)	0.14 (4)	−3.0 (4.7)	−2.5 (2.9)
CO–Kr	OS	2.705 (2)	2.823 (3)	0.484 (5)	2.800 (6)	0.79 (14)	8 (2)	0.92 (22)
	MS	2.705 (1)	2.815 (2)	0.472 (5)	2.799 (4)	0.43 (24)	−1.1 (1.5)	−0.12 (52)
CO–Xe	OS	2.821 (3)	3.044 (3)	0.706 (9)	3.026 (7)	0.501 (38)	0.7 (1.5)	−0.3 (0.9)
	MS	2.824 (3)	3.035 (1)	0.704 (2)	2.972 (4)	0.44 (3)	−1.78 (46)	−0.29 (16)

[a] OS corresponds to the one-by-one-spectrum fitting and MS to the multi-spectrum fitting.

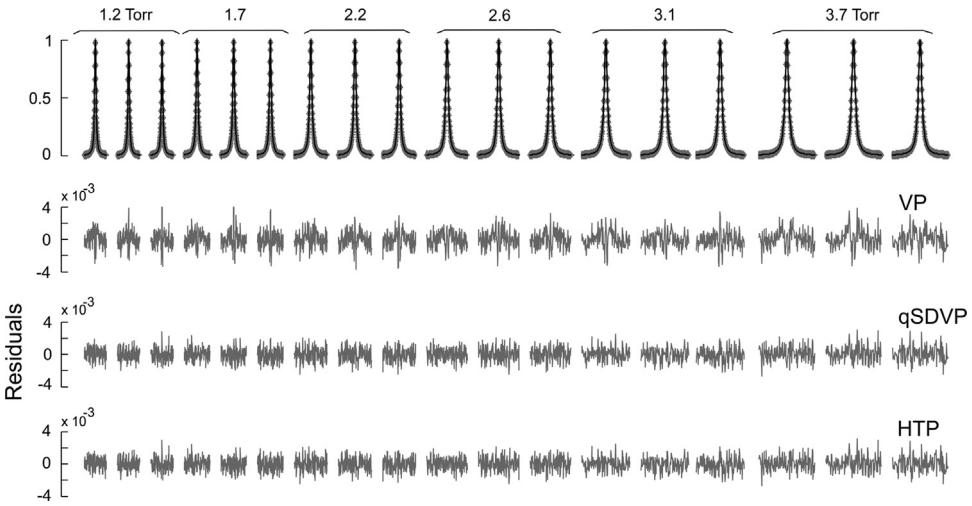

Fig. 3. Result of the multi-specrum fitting procedure in the case of the Ne-broadening of the $J=2-1$ CO line.

Table 3
The collisional self-broadening and narrowing coefficients of $J+1\leftarrow J$ transitions of CO at 296 K obtained in this work using different models in comparison with previously known data. All values are in the units of MHz/Torr. One standard deviation is shown in parenthesis.

J	Fitting procedure[a]	This work VP	HITRAN	This work qSDVP		Ref. [14] qSDVP	
		γ	γ	γ_0	γ_2	γ_0	γ_2
0	OS	3.499 (8)	3.392	3.53 (1)	0.25 (6)	3.4681 (7)	0.367 (1)
	MS	3.499 (3)		3.546 (9)	0.30 (3)		
1	OS	3.350 (3)	3.235	3.420 (8)	0.39 (3)	3.2507 (3)	0.341 (1)
	MS	3.351 (2)		3.412 (6)	0.37 (2)		
2	OS	3.126 (3)	3.077	3.182 (6)	0.343 (15)	3.0918 (3)	0.343 (1)
	MS	3.126 (1)		3.179 (3)	0.334 (9)		
3	OS	2.998 (7)	2.958	3.06 (1)	0.35 (4)	2.9588 (3)	0.346 (1)
	MS	2.999 (3)		3.061 (8)	0.37 (2)		
4	OS	2.869 (2)	2.880	2.905 (7)	0.27 (2)	2.8429 (2)	0.330 (1)
	MS	2.869 (2)		2.901 (4)	0.26 (2)		
6	OS	2.752 (4)	2.682	2.83 (1)	0.41 (3)	2.6736 (2)	0.283 (1)
	MS	2.754 (4)		2.826 (7)	0.40 (2)		

[a] OS corresponds to the one-by-one-spectrum fitting and MS to the multi-spectrum fitting.

qualitatively with the results of Ref. [34]. Following the authors of Ref. [34], we derived the exponent for the speed dependence of collisional relaxation in accordance with the model $\Gamma(v_r) \propto (v_r)^n$. The obtained value of $n=0.67$ is slightly smaller than $n=0.79$ obtained in Ref. [34] for the $J=2\leftarrow 1$ line.

4.5. HTP model testing

The HTP model has been developed as "a practical way to go beyond the Voigt profile" [10]. The authors of the model, in addition to the multi-spectrum fitting procedure, require experimental recordings in a very broad range of pressures corresponding to the ratio of the Lorentz to Doppler widths varied from much smaller than 1 to much larger than 1. This is rather difficult to achieve experimentally keeping in mind high signal-to-noise ratio requirement. However, the model was recommended by IUPAC as the "isolated-line profile for representing high-resolution spectroscopic transitions" [11]. Therefore it was interesting to fit the model to our data.

It has been noted already that the HTP model fits all the single spectrum recordings to the experimental noise level in the considered pressure range and in majority of cases yields the value of the collisional line width, which coincides with the one from the qSDVP model within the measurement accuracy. At the first stage, we purposely varied all parameters of the model. It was found that allowing for the correlation parameter η and for the optical diffusion parameter β is totally redundant in our case. These parameters are undeterminable from our spectra. This can be seen from their values reported in Table 2 for the foreign gas broadening case. Statistical uncertainty of the determination of these parameters is close to or even larger than the parameter value. Meaningless negative values of these parameters should be also pointed out.

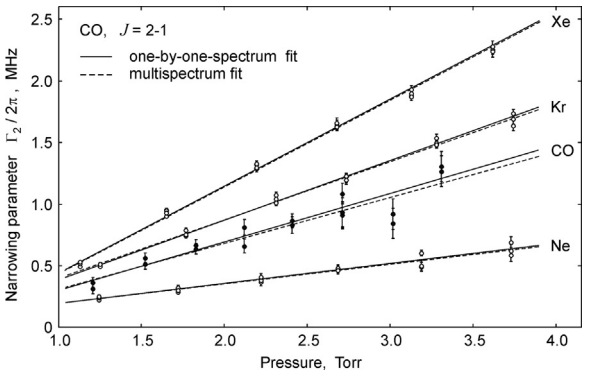

Fig. 4. Pressure dependence of the collisional narrowing parameter $\Gamma_2/2\pi$ (CO, J=2-1) obtained by use of the qSDVP model for different foreign gases. Error bars correspond to one standard deviation of obtained parameter value. Solid lines are results of linear regression of corresponding points obtained from one-by-one-spectrum fitting and dashed lines corresponds to parameters obtained from the multi-spectrum fitting.

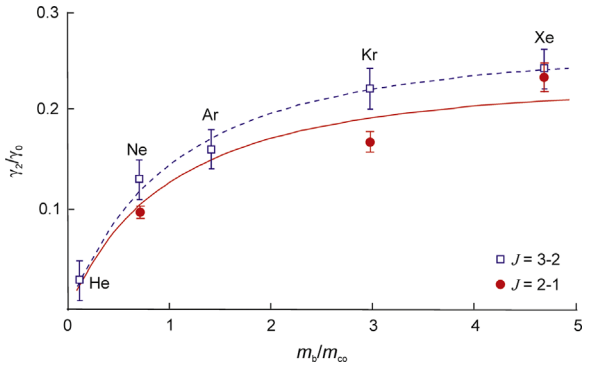

Fig. 5. (based on Fig. 8 from Ref. [34]). Narrowing-to-broadening parameter ratio versus buffer-to-absorber gas mass ratio. The dashed curve (n=0.79, see text) and empty squares show the data for the CO J=3−2 transition obtained in Ref. [34]. Filled circles and solid line (n=0.67) correspond to the values obtained in this work for Ne-, Xe- and Kr-broadening of CO, J=2−1 line. Error bars correspond to three standard deviation of obtained parameter value.

It should be mentioned that processing of the single line recordings under pressures over 1.7–2 Torr using the VP and LP models, yields practically identical residuals. Their difference is several times less than the level of experimental noise (Fig. 6). This means that under these conditions one can neglect not only the collisional Doppler profile narrowing effect (the Dicke effect), but the Doppler broadening of the line as well.

It was interesting, however, to estimate which signal-to-noise ratio is necessary for the meaningful retrieval of line parameters using the HTP model. For such estimation we made the following numerical experiment. The HTP model was used to calculate a series of five line profiles corresponding to the ratio of the collisional to Doppler line width varying from 2 to 10, which approximately corresponds to the conditions of our experiments. Parameters corresponding to the J=2-1 transition of the CO molecule at 296 K in the Ne-broadening case reported in

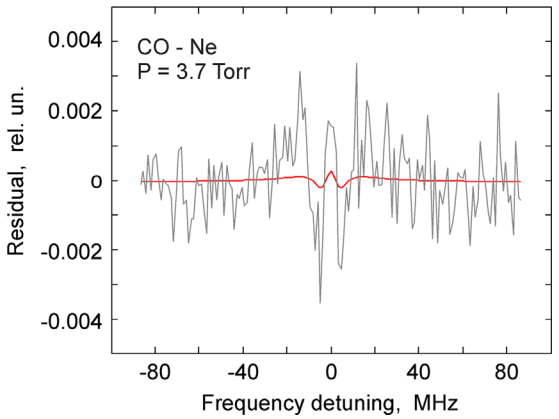

Fig. 6. Residual of fitting of experimental recording for $J=2-1$ line under the conditions of Ne-broadening (0.26 Torr of CO and 3.44 Torr of Ne) by the VP model (black broken line) and difference between this residual and similar residual obtained using the LP model (smooth red line). The frequency detuning from 230,500 MHz is plotted along the X axis. Amplitude of the line maximum is 1.

Table 2 were partly used (γ_0=1.635, γ_2=0.158, $\beta=\beta^0_{kin}$=0.561 MHz/Torr, η=0.5 (arbitrary value)). A numerical equivalent of experimental noise was calculated as a random value normally distributed within the preset interval and added to line profiles. At the next step, the multi-spectrum fitting procedure with the HTP model was used to retrieve the line-shape parameters from this simulated set of spectra using the preset values of parameters as a starting point. Then the procedure was repeated 50 times with different realization of noise. Fig. 7 presents mean values and standard deviations of retrieved line-shape parameters in percentage of its "real" (preset) value plotted as a function of signal-to-noise ratio of simulated set of spectra.

It follows from such calculations that in our case (corresponding to the signal-to-noise ratio of about 1000) accuracy of γ_0, γ_2, β and η parameter determination cannot be better than about 0.15, 35, 800 and 600% respectively. Similar trial with the qSDVP model yields about 0.1 and 3% for γ_0 and γ_2 respectively. It should be pointed out that such simulation yields the most optimistic estimation of the parameter retrieval accuracy. However it explains the results reported in Tables 2 and 3. The simulation allowed us also to study the correlation between the model parameters fixing one of them, finding the other ones and plotting the result versus the value of the fixed parameter. We will not go into details of this modeling because an interested reader can easily repeat it for any desired conditions. It turned out that all parameters of the model noticeably correlate with each other. This explains, in particular, why the residual corresponding to the HTP model in Fig. 2 is larger than the others.

The trial led us to the conclusion that the HTP model is too excessive for our case. The only meaningful results with the model were obtained when all variable parameters of the model except γ_0 and γ_2 were fixed to 0. Obtained results in this case coincided, as expected, with the use of the qSDVP model.

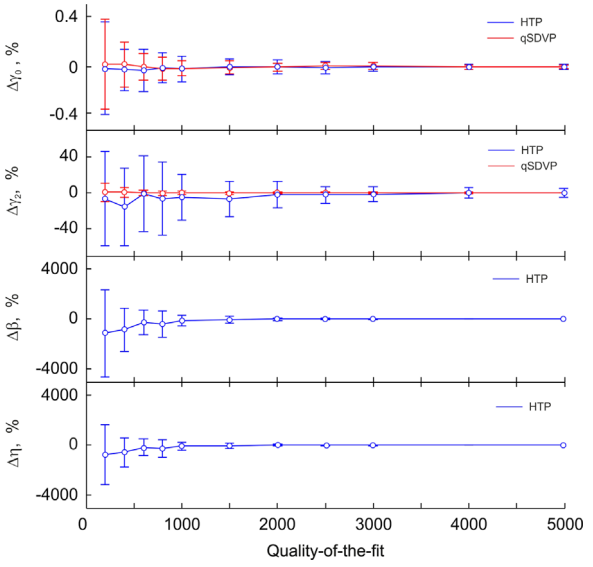

Fig. 7. Results of numerical testing of the HTP model (see text). Relative deviation of the retrieved line shape parameters from its real values ($\Delta z = 100(z_{fit} - z_{real})/z_{real}$, where z is either γ_0, γ_2, β or η) versus signal to noise ratio of considered spectra.

5. Conclusions

The experimental recordings of a series of collision-broadened lines of the rotational spectrum of the CO molecule have been analyzed. The collision broadening and collision narrowing parameters of the CO line profiles obtained from the self- and foreign-gas broadening conditions are valuable data for spectroscopic databases and are of importance for the development of the theory of intermolecular interactions.

The data were analyzed using the known VP, GP, qSDVP, and HTP models. It is shown that the qSDVP and HTP models fit the experimental data to the experimental noise level in the considered pressure range and yield the values of the collisional-relaxation coefficient, which practically coincide with each other within the measurement accuracy, whereas the GP model yields totally redundant optical diffusion rates at lowest pressures and becomes inapplicable for fitting the experimental recordings starting at larger pressure values. This result indicates that for the considered gas mixtures under the conditions of prevailing collisional broadening, the Dicke effect makes no noticeable contribution to the shape of the observed line. The expected stronger manifestation of the wind effect with increasing mass of foreign gas molecules has been demonstrated. It has been shown that the use of the HTP model for obtaining accurate values of the line-shape parameters is not always straight forward. The simple numerical testing is suggested to evaluate the applicability of the model to the obtained experimental data.

Thus, the data analysis performed herein indicates that under the conditions considered, the wind effect has a dominant influence on the shape of the lines in the rotational spectrum of the CO molecule.

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