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Broadening and shifting of the carbon monoxide rotational lines in a wide temperature range: calculations in the framework of the classical impact theory for CO-He

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The classical impact theory of Gordon is used to calculate half-widths and shifts of spectral lines of the pure rotational band of $^{12}C^{16}O$ isotopologue broadened by He. Two rotational transitions are examined: $J = 0 \rightarrow J = 1$ and $J = 1 \rightarrow J = 2$ in the wide temperature range from 1.3 to 600 K. The main purpose of this work is the study of the validity limits of classical impact theory at low temperatures. Dynamical calculations were performed on the accurate CO-He ab initio potential energy surface. The results of calculations are in good agreement with experimental data with the exception of very low temperatures. The contributions of collisions of different types (elastic, inelastic, quasibound complexes) are clearly examined in the classical picture frame. It is shown that the mismatches between classical theory and measurements are caused by the too high contribution of elastic collisions into broadening and shift in the present variant of theoretical model. The idea in the spirit of the Weisskopf theory is applied to try to diminish this contribution. The classical results are also compared with the results of fully quantum close coupling calculations made with using four CO-He interaction potentials. The roots of discrepancies at low temperatures as well as the virtues and the shortcomings of a classical approach are discussed.

Keywords: collisional line broadening and shift, intermolecular interactions, classical impact theory, classical trajectory method, quasibound complexes.

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1. Introduction

Information about the parameters of the contours of spectral lines of molecules in various gas-phase conditions is key for numerous modern optical tasks, for example, in astrophysics (planetary and exoplanet atmospheres, interstellar clouds, etc.), laser sensing of various media, including control of combustion processes, medical applications, etc. [1–4].

Collisional line broadening and shift of vibrational-rotational spectral lines arise as a result of intermolecular interactions in the process of collisions, the dynamics of which is determined by the intermolecular potential energy surface (PES). At pressures below ~ 1 atm, the following reasonable simplifications are often used: (i) approximation of binary collisions (only two particles collide at once), (ii) impact approximation (the duration of binary collisions is much shorter than the free path time), (iii) approximation of isolated lines (there is no collision coupling of lines, or collision interference).

The most accurate in the impact theory of line broadening are fully quantum calculations within the framework of the close coupling (CC) method or in the approximation of coupled states (CS) [1]. Currently, only combined CC/CS quantum calculations using non-empirical (*ab initio*) intermolecular interaction potentials can provide high accuracy and provide reference data for verification of other methods (as well as, in some cases, experimental results). Unfortunately, both of these schemes are not visual, in many cases they cannot clearly explain the physics of collision processes. Moreover, the CC/CS scheme becomes extremely computationally time-consuming and impracticable when many rotational states need to be taken into account, for example, at small rotational constants and/or elevated temperatures. In such a situation, alternative approaches and appropriate computational schemes are needed.

Semi-classical approaches in impact broadening theory are less cumbersome, since they consider translational motion (trajectory) classically, but internal motions (vibration and rotation) are modeled within the framework of quantum mechanics. A serious and main drawback of all semi-classical approaches is the lack of connection between the translational and internal motions of colliding molecules. Other simplifications of these methods are mainly related to the quantum description of rotation, trajectories and PES. Semi-classical schemes are numerous, most of them use perturbation theory and their validity is often difficult to assess (an overview of these schemes and their applications can be found in [1,5]).

The classical impact theory of broadening and shifting of vibrational-rotational spectral lines was proposed in 1966 by Roy G. Gordon [6,7]. This formalism does not use perturbation theory and provides an accurate three-dimensional (3D) self-consistent classical description of rotational and translational molecular motions (naturally, using the principle of correspondence with quantum mechanics). Revived 17 years ago [8] this method (later called C3D, i.e. the classical 3D approach) has now gained a reputation as a very effective, visual and accurate tool for predicting the pressure broadening coefficients of lines of a number of diatomic and linear polyatomic molecules in various mixtures over a fairly wide temperature range [8–21]. At the same time, the lower temperature limit was 77 K [13–15], and the upper — 2400 K [11,15]. Also, no serious attempts were made to calculate the shift of the lines due to problems with proper consideration of the vibrational dephasing for fundamental and overtone vibrational bands.

In this paper, the classical 3D approach is used to calculate collisional half-widths and shifts of purely rotational CO lines in collisions with He atoms. Simple and elegant formulas of the classical Gordon impact theory are used along with Hamilton's exact 3D equations that determine the rotational and translational motions of a CO−He pair during collisions. The calculations use Monte Carlo averaging over collision parameters and a fairly accurate *ab initio* PES of the CO−He interaction in the form of a series expansion by Legendre polynomials. The half-widths and shifts of the lines of the main isotope ^{12} C^{16}O are investigated for two rotational transitions: $J = 0 \to J = 1$ (centered at 115.271204 GHz) and $J = 1 \to J = 2$ (at a frequency of 230.538000 GHz) as a function of temperature in the range $T = 1.3{-}600$ K with an emphasis on the low temperature region, which we have not considered before. The classical 3D results are compared with the available experimental data and fully quantum CC calculations using four different PES of the CO−He interaction.

The grounds for carrying out this work were as follows.

1) In the interstellar medium, the CO−He system plays an important role (for example, observations of CO to estimate the mass of gas in our and other galaxies).

2) CO gas was observed in the chromosphere of the Sun, the atmospheres of planets (including Earth's), as well as in large quantities in combustion products.

3) The CO−He system is one of the most studied molecular pairs and is used as a test for various computational schemes in scattering dynamics.

4) The CO molecule has strong and well-resolved electrodipole absorption lines in the microwave region. The lower J transitions fall into the micro-windows of water vapor transparency, which is convenient for atmospheric applications.

5) Since it is generally assumed that classical dynamics does not work at low temperatures, we tried to verify this widely held opinion by considering temperatures up to 1.3 K, and thereby clarify the range of applicability of the classical impact theory of broadening of rotational lines.

The article is organized as follows: in Section 2 the basic equations of the classical impact theory of isolated spectral lines are given. In Section 3 the reference PES for CO−He interactions used in calculations is presented. Some details of calculations and improvements of the classical trajectory method are described in Section 4. The Section 5 is devoted to the results and their discussion. In Section 6 the conclusions are given and the directions of further development and application of the classical impact theory are outlined.

2. Main equations

In classical impact theory half-width γ and shift δ of the rotational electric dipole absorption line are described in [7] by the following general formulas:

$$\gamma = \frac{n_b\bar{v}}{2\pi c}\,\mathrm{Re}\sigma,\quad \delta = \frac{n_b\bar{v}}{2\pi c}\,\mathrm{Im}\sigma,\quad \bar{v} = \sqrt{8k_BT/\pi\mu}, \qquad (1)$$

$$\sigma = \left\langle v\left\{1 - P_{el}\exp(+i\eta)\cos^2\frac{\alpha}{2}\right\}\right\rangle_{b,v,O}\bar{v}^{-1}. \qquad (2)$$

Or in a more visual form, convenient for further analysis [6],

$$\gamma = \frac{n_b}{2\pi c}\left\langle v[1 - P_{el}\cos\eta\cos^2(\alpha/2)]\right\rangle_{b,v,O},$$

$$\delta = \frac{n_b}{2\pi c}\left\langle vP_{el}\sin\eta\cos^2(\alpha/2)\right\rangle_{b,v,O}. \qquad (3)$$

In these equations n_b — number density of perturbing particles (here — He atoms, CO molecules are considered as a small impurity in the buffer gas He), μ — reduced mass of the colliding pair, T — temperature, c — speed of light, k_B — Boltzmann constant, P_{el} — probability (index) that this collision is elastic/inelastic. The best results are achieved if P_{el} is calculated using the box quantization procedure (see, for example, [11]; $P_{el} = 1$ for elastic collisions and $P_{el} = 0$ for inelastic ones). Averaging $\langle\ldots\rangle$ is carried out by the impact parameter b, the relative velocity of the pair v and by the initial orientations (denoted as O) of the vectors of the molecular axis $\mathbf{r}$ CO and the angular velocity $\boldsymbol{\omega}$. The angle η characterizes „rotation dephasing", α — the angle between the initial and final orientations of ω („rotation deorientation"). The values η and α are calculated from the classical dynamics of each particular collision by a modified method described in the Appendix [17]. We note that in the present calculations (and in the formulas (1)−(3) above) the vibrational phase shift (i.e., the so-called „vibrational dephasing" [7]) is not taken into account, since a purely rotational band of CO (R-lines) is considered and the molecule is considered rigid (for $J = 01$ and $J = 1$ this assumption is quite justified).

3. Intermolecular potential for CO−He interaction

The surface of the potential energy of the atom-rigid linear rotator interaction was expressed in terms of Legendre

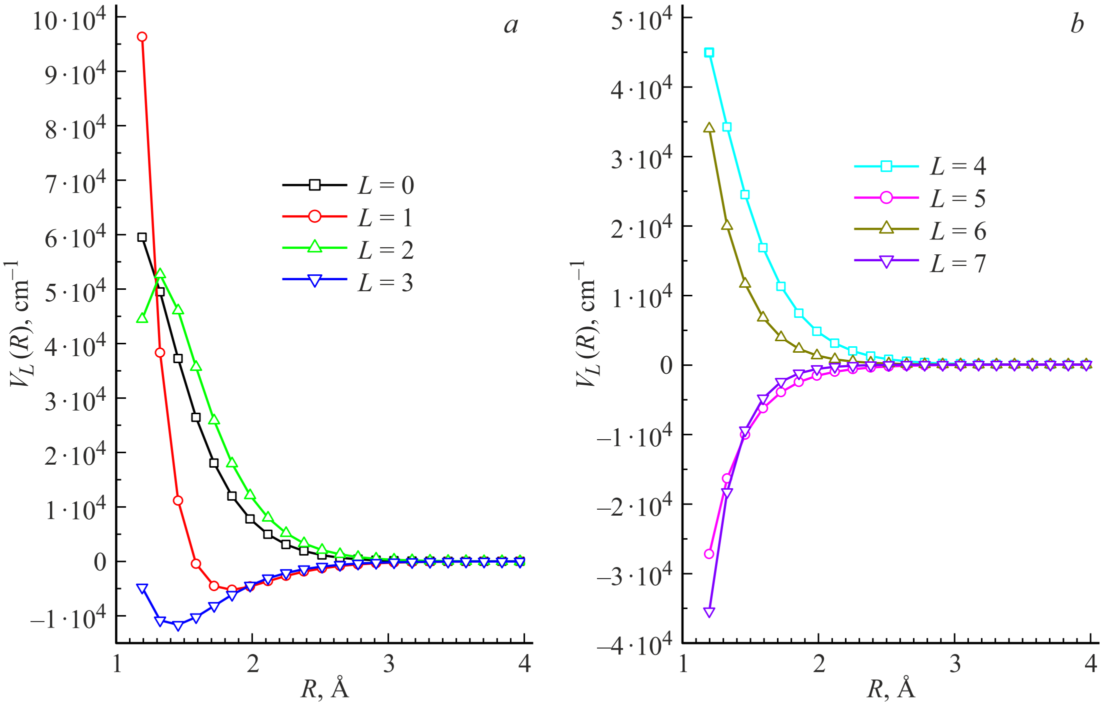

Figure 1. Some radial functions $V_l(R)$ in the equation (4) for the CO−He interaction in the ground vibrational state of the CO molecule.

polynomials, $P_l(\cos\theta)$, in the form of decomposition

$$V(R,\theta) = \sum_{l=0}^{l_{\max}} V_l(R)P_l(\cos\theta), \tag{4}$$

where θ — is the angle between the vector $\mathbf{r}$ of the C−O bond and the vector $\mathbf{R}$ between the centers of mass of CO and He. In the case of an asymmetric molecule (such as CO) all Legendre polynomials, i.e. $l = 0, 1, 2, \ldots, l_{\max}$, must be included in the expansion (4). For calculations of CO−He, a fairly accurate Heijmen potential with co-authors [22] was used. The radial functions $V_l(R)(l \le l_{\max} = 13)$ were calculated from the original *ab initio* PES $V(R,\theta)$ in the following standard way:

$$V_l(R) = \frac{2l+1}{2}\int_0^{\pi} V(R,\theta)P_l(\cos\theta)\sin\theta d\theta. \tag{5}$$

The analysis showed that $l_{\max} = 13$ is quite a sufficient value to reproduce the original *ab initio* PES. Some radial functions $V_l(R)$ are shown in Fig. 1.

4. Details of calculations and modifications of the classical trajectory method

Eleven classical Hamilton equations in body-fixed coordinates (given in the Appendix to Pattengill's paper [23]) were numerically integrated using the standard IMSL procedure (implicit BDF-Gear method [24]). All calculations were performed using double precision with a typical tolerance parameter TOL $= 10^{-9}$ and a variable integration step within fixed intervals Δt of the grid in time (in most cases $\Delta t = 0.05$ ps). The trajectories started and finished at $R_{\max} = 15$ Å. Bond length ^{12} C−^{16} O was assumed to be equal to $r = 1.128$ Å [25].

The Monte Carlo method was used to select the initial orientations of the vectors $\mathbf{r}$ and $\boldsymbol{\omega}$, uniformly distributed in 3D space, provided they are orthogonal. Maxwell's averaging over the initial relative velocity $v = (0.01-3)v_p$ was used in all calculations, where $v_p = (2k_BT/\mu)^{1/2}$ — the most probable relative speed of the colliding pair ($\mu = 3.5$ amu for ^{12} C−^{4} He). This range covers the vast majority of speeds.

The statistical error of calculating line widths (the root-mean-square error of averaging by the Monte Carlo method) in all cases was maintained at less than 0.5% (calculations continue until the result of averaging begins to change by less than $\sim 0.5\%$.). The accuracy of the shift in these conditions was different and was not strictly maintained. Let us pay attention to the fact that the line shifts in the considered cases are much smaller than the half-widths. The root-mean-square errors for the shifts were as follows: for the transition $J = 0 \to J = 1 \sim 5\%$ (3−10 K), $\sim 19\%$ (200 K) and for the transition $J = 1 \to J = 2 \sim 5\%$ (3−15 K), $\sim 90\%$ (500 K).

In all calculations, an efficient algorithm [26] was used to select the impact parameter b. The convergence of the Monte Carlo method in this case turns out to be about twice as fast as with the traditional uniform drawing of b^2.

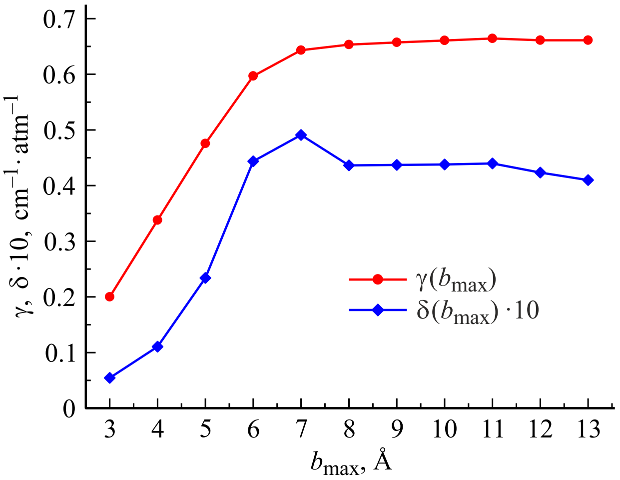

Figure 2. The dependence of the half-width and shift of the transition line CO $J = 0 \rightarrow J = 1$ at $T = 10$ K on the maximum impact parameter $b_{\max}$ at $R_{\max} = 15$ Å.

An auxiliary study showed that the range of the impact parameter $b \leq b_{\max} = 8$ Å is optimal for calculating the broadening and shift of CO lines in He (Fig. 2).

In all our previous studies of classical collision dynamics, the initial angular rotation frequency of the molecule ω was determined through the initial rotational quantum number J in two ways. In the first works, the rotation frequency ω was calculated from the traditional quantum mechanical formula of angular momentum quantization $I\omega = \hbar\sqrt{J(J+1)}$ (I — the moment of inertia of the rotator, $\hbar$ — Planck's constant). Later, Langer's correction („prescription") [26,27] $I\omega = \hbar(J_{\text{average}} + 1/2)$ was applied using the average value J for the optical transition in question. In the case of a purely rotational absorption spectrum (only R-lines, $\Delta J = +1$) we have

$$J_{\text{average}} = \frac{J+(J+1)}{2} \text{ and } \hbar\left[\frac{J+(J+1)}{2} + \frac{1}{2}\right] = \hbar(J+1). \tag{6}$$

In [20], it was shown that the Langer correction in the form (6) provides better broadening coefficients for small values of J (especially for $J = 0$) compared to the traditional formula. With the growth of J, the effect of the correction is quickly leveled.

5. Results and discussion

The results of calculations and their analysis are presented in Fig. 3–7. We have tried to compare our calculations with the experimental data of Beaky with co-authors [28] obtained in a wide temperature range. For the transition $J = 0 \rightarrow J = 1$, the broadening was measured at $T = 1.249{-}482$ K, the shift — at $T = 1.249{-}41.330$ K. For the transition $J = 1 \rightarrow J = 2$, the broadening was measured in the range $T = 1.298{-}638$ K, shift — at $T = 1.298{-}37.552$ K. According to the authors of [28], the errors of their measurements were: ± 0.01 K for temperature at $T < 50$ K and ± 1 K at $T > 50$ K; for half-widths $\pm 10\%$. For line shifts, the estimated experimental inaccuracies at temperatures in the region of 2 K were ~ 2 MHz/Torr (which corresponds to ~ 2 Å^2 for cross sections).

The figures below demonstrate fairly good C3D results for medium and high temperatures, but unsatisfactory for very low temperatures. As will be shown below, this disadvantage of the classical model is caused by the overestimated contribution of elastic collisions to broadening and shift. For this reason, some attempts have been made (in the spirit of Weisskopf's old ideas) to reduce the role of elastic collisions in the classical picture.

5.1. Limiting the influence of elastic collisions in the spirit of Weisskopf's idea and investigating the role of collisions of various types

The idea was proposed by Weisskopf in 1932 [29,30] in order to explain the broadening and shifting of electronic transitions of atoms in the framework of the classical impact approach. This approach took into account only elastic collisions through the change of the electron phase η during the collision. Since integration by the impact parameter b to infinity is impossible in the classical picture, „clipping " by η at a certain value of $\eta_{\min}$ turns out to be inevitable, and all trajectories with $\eta < \eta_{\min}$ are not considered at all as collisions. Weisskopf suggested setting $\eta_{\min} = 1$ rad, but this method is clearly „arbitrary" (why exactly $\eta_{\min} = 1$ rad, and not other values ? [30]). Thus, the main question remains —„what is a collision " in the classical sense? Indeed, in the classical picture, the particles „feel" each other at any distances up to infinity. However, it is impossible to overcome such a difficulty by simply setting the value $b_{\max}$ very large, since interparticle interactions in this case will no longer be binary, and the impact approximation will fail. Some useful visual information can

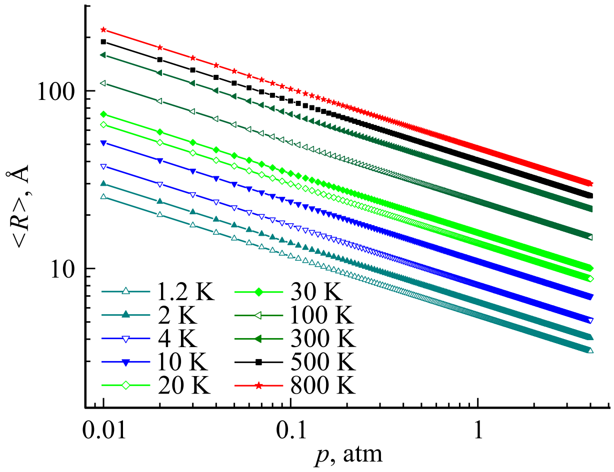

Figure 3. The average distance between the particles of an ideal gas depending on the pressure at different temperatures.

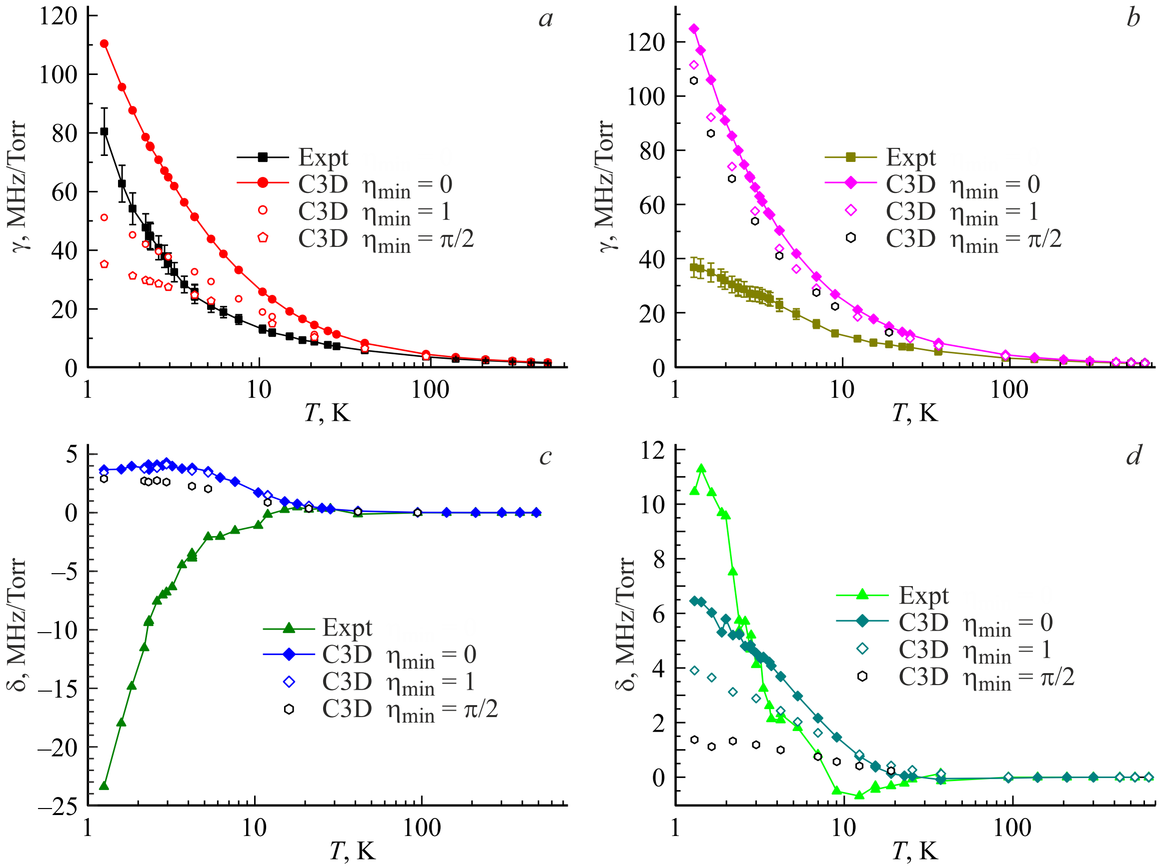

Figure 4. Influence of η — Weisskopf constraints („clipping“ by η) on half-width (a, b) and shift (c, d) transition lines CO $J = 0 \rightarrow J = 1$ (a, c) and $J = 1 \rightarrow J = 2$ (b, d). Experimental data of Beaky with co-authors [28]; classical C3D calculations without η-constraint ($\eta_{\min} = 0$) and with η-constraint ($\eta_{\min} = 1$, $\eta_{\min} = \pi/2$).

be extracted from the auxiliary Fig. 3, where the average distance $\langle R \rangle = (k_B T/p)^{1/3}$ between ideal gas particles is given as a function of pressure p at different temperatures T.

From this figure, we can conclude that the choice of $R_{\max} = 15\,\text{Å}$, $b_{\max} = 8\,\text{Å}$ for CO−He collisions is justified only at $T > 20\,\text{K}$ at any pressure below $\sim 3\,\text{atm}$, but problems arise if $T < 20\,\text{K}$ at pressures $p > 0.1\,\text{atm}$.

As a result of the analysis of the results of C3D calculations, it was found that the main discrepancy between the classical theory and the measurements of Beaky with co-authors [28] stems from the overestimated contribution of elastic collisions to the width and shift in the present version of the C3D model. In this paper, we tried to apply Weisskopf's idea to the rotational motion of molecules by limiting the elastic rotational phase shift (2), (3). The limit values are $\eta_{\min} = 1$ and $\eta_{\min} = \pi/2$. Some results of such modeling are presented in Fig. 4.

For both transitions, one can observe a fairly good agreement of the classical impact theory with the broadening and shift measurements at T above $\sim 20{-}30\,\text{K}$ (while the values of γ and δ are small, especially δ), but poor below this temperature. For broadening of the transition $J = 0 \rightarrow J = 1$,the Weisskopf „cutting“ procedure is very effective at $T < 20\,\text{K}$ (and its influence increases sharply with decreasing temperature, making the predictions of the theory inadequate, especially at $T < 2{-}3\,\text{K}$). For $J = 1 \rightarrow J = 2$, the situation is the opposite — Weisskopf „cutting“ has little effect on broadening at almost any temperature. The reverse pattern is observed for line shifting — the „clipping“ procedure is ineffective for $J = 0 \rightarrow J = 1$, but for $J = 1 \rightarrow J = 2$ greatly reduces the shift, making the classical results even worse for $T < 3\,\text{K}$.

Fig. 5 illustrates the effect of collisions of various types on the half-width and shift of the lines CO $J = 0 \rightarrow J = 1$ and $J = 1 \rightarrow J = 2$. Fig. 5, a, b demonstrates that the neglect of elastic collisions at $T < 10\,\text{K}$ fatally underestimates the half-width and manifests itself in the incorrect temperature dependence of $\gamma(T)$. Thus, it can be concluded that for $T < 10\,\text{K}$, the broadening in the framework of classical impact theory is mainly caused by elastic collisions. It can also be argued that in the current version of the C3D model, the contribution of elastic collisions to broadening is modeled incorrectly, noticeably overestimating their role (especially at $T < 30\,\text{K}$.). As for the line shift (Fig. 5, c, d), the contribution of elastic collisions for the transition $J = 0 \rightarrow J = 1$ at $T < 10\,\text{K}$ is also greatly overestimated. Moreover, the calculated shift has a different sign compared to the measured one. For the line $J = 1 \rightarrow J = 2$, on the

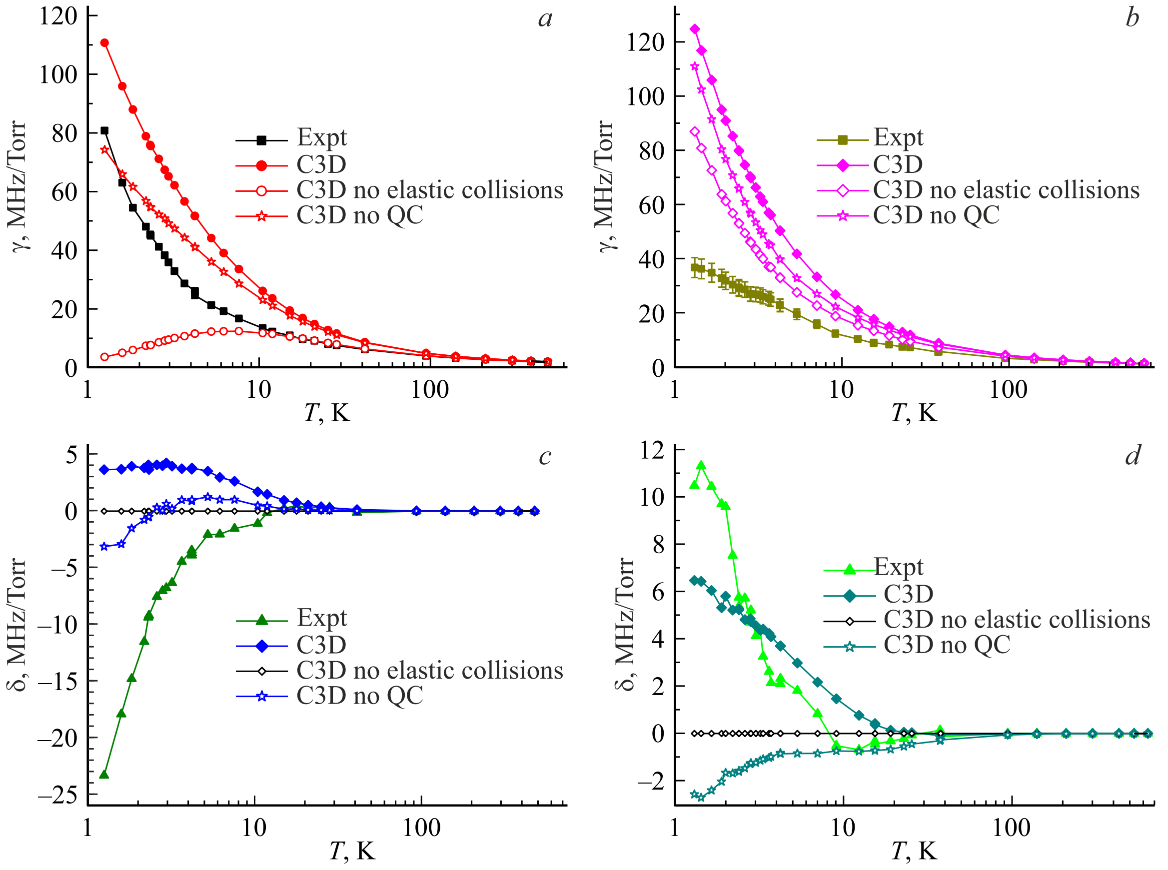

Figure 5. The effect of collisions of various types on the half-width (a, b) and the shift (c, d) of the transition lines CO$J = 0 \rightarrow J = 1$ (a, c) and $J = 1 \rightarrow J = 2$ (b, d). Classical C3D calculations without „clipping“ Weisskopf $(\eta_{\min} = 0)$.

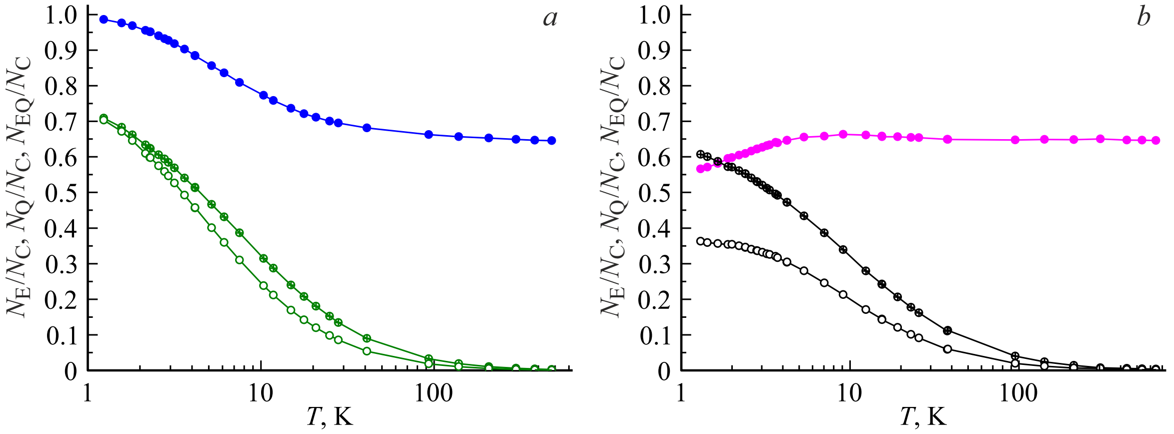

Figure 6. The shares of CO−He collisions of different types for transitions $J = 0 \rightarrow J = 1$ (a) and $J = 1 \rightarrow J = 2$ (b): N_E/N_C — elastic collisions (blue and purple circles), N_Q/N_C — all QC (crossed out circles), N_{EQ}/N_C — elastic QC (light circles), N_C — total number of collisions in calculations, N_E — number of elastic collisions, N_Q — total number of QC, N_{EQ} — number of elastic QC.

contrary, at $T < 3$ K the contribution of elastic collisions is underestimated, at $T > 3$ K is overestimated, and in the range $\sim 7{-}20$ K has a different sign.

We emphasize that the shift of the line in the present classical description is caused exclusively by elastic collisions (3), where, according to box quantization, for a nonzero shift there should be $P_{el} = 1$. Neglecting elastic collisions leads to zero shift (horizontal line $\delta = 0$ in Fig. 5, c, d). In calculations, the contribution of reorientation α and rotation phase shift η into elastic effects (3) were separately controlled. It was found that the deorientation of rotation (angle α) has little effect on the broadening and

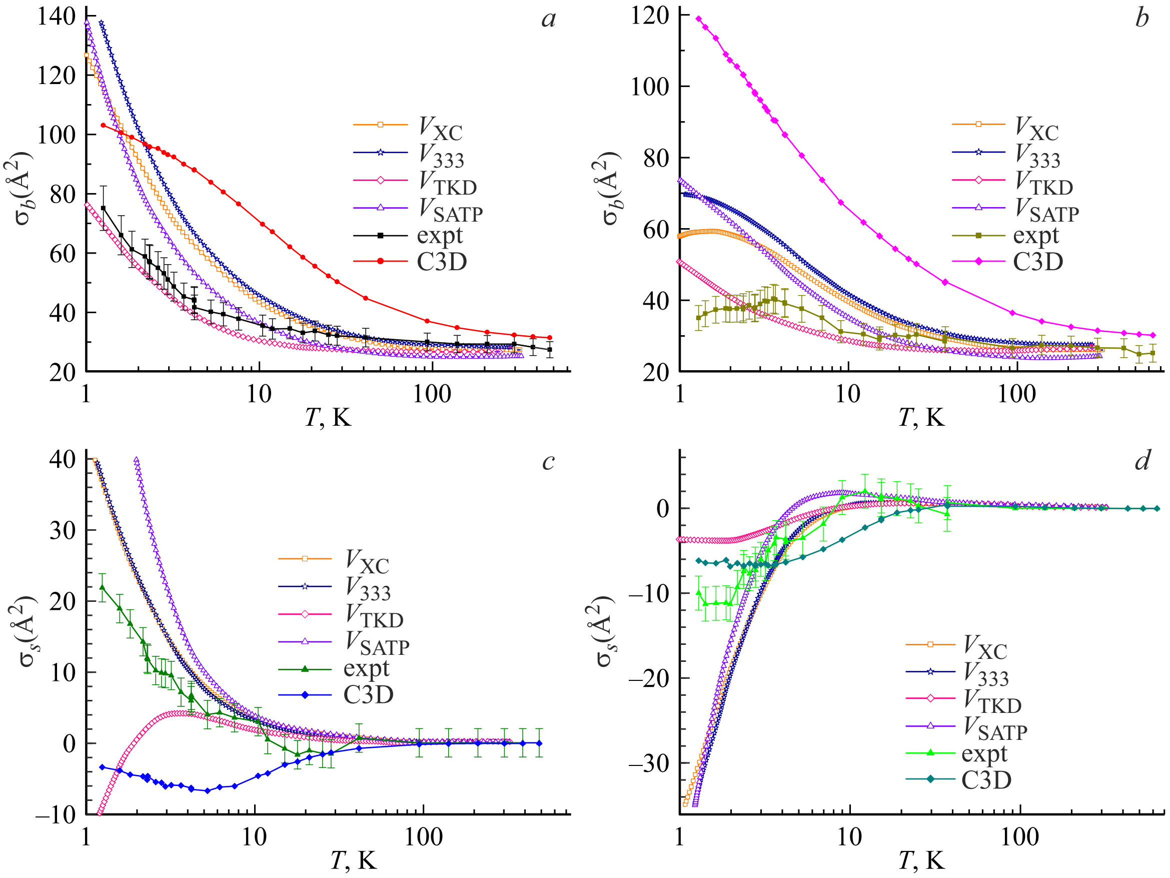

Figure 7. Comparison of calculated classical and quantum cross sections of broadening (a, b) and shift (c, d) of transition lines CO$J = 0 \to J = 1$ (a, c) and $J = 1 \to J = 2$ (b, d) with experiment [28]. V_{XC}, V_{333}, V_{TKD}, V_{SATP} — fully quantum calculations by CC [33] with various PES (see text); C3D — present classical calculation with PES [22] without η — „clipping“ Weisskopf ($\eta_{\min} = 0$). The errors of the measured shift cross sections are set in the figure $\pm 2\,\text{Å}^2$ for all T (as in [33] at $T < 40\,\text{K}$).

shift of the line, and the main contribution is made by the phase shift of rotation η.

In addition to the usual collisions having only one distance of closest approach (minimum in time dependence of the intermolecular distance $R(t)$), unstable quasi-bound complexes („quasi-bound complexes“ —QC), otherwise called Feshbach resonances or metastable dimers, may occur during the interaction [21,31,32]. Quasi-bound complexes can be formed provided that at least one of the colliding partners has an internal degree of freedom (for example, rotational). In the classical trajectory method, the number of QC-type collisions was automatically controlled in all calculations. Formulas determining the contribution of QC to the broadening and shifting of lines are given in [21].

Fig.6 shows the temperature dependences of the portion of elastic collisions and collisions of QC-type (all and elastic). In this case, the values $(1 - N_{\mathrm{E}}/N_{\mathrm{C}})$ correspond to inelastic collisions, and $(N_{\mathrm{Q}}/N_{\mathrm{C}} - N_{\mathrm{EQ}}/N_{\mathrm{C}})$ — inelastic QC. Let us pay attention to a noticeable percent of elastic collisions and QC at low temperatures, especially below 10 K.

It can be seen from Fig. 6 that for both rotational transitions $J = 0 \to J = 1$ and $J = 1 \to J = 2$, similar QC fractions are observed, but with slightly different temperature dependences of the elastic collision fraction, including elastic QC. There is also a strong influence of QC, increasing the shift, especially for the transition $J = 1 \to J = 2$.

5.2. Comparison with fully quantum calculations by CC method

An important and necessary point is the comparison of classical calculations with quantum ones. In the work of Thachuk with co-authors [33] to reproduce experimental results [28] the calculations of impact broadening and shift of transitions $J = 0 \to J = 1$ and $J = 1 \to J = 2$ were carried out within the framework of a fully quantum technique of close coupling CC with four different intermolecular PESs: V_{TKD} [34] (1980), V_{333} [35] (1994), V_{XC} [36] (1994), V_{SATP} [37] (1995).

The results of the comparison are shown in Fig. 7. Formulas [28] were used to recalculate half-widths γ and line shifts δ into the corresponding cross sections

$$\sigma_b = 0.447\sqrt{\mu T}\gamma, \quad \sigma_s = -0.447\sqrt{\mu T}\delta, \tag{7}$$

where the cross sections are expressed in Å^2, the reduced mass μ of the pair CO$-$He — in amu, T — in kelvins, γ and δ — in MHz/Torr.

It can be seen from Fig. 7 that at $T \leq 10\,\mathrm{K}$ there is no good correspondence between classical and quantum results. In addition, the results of quantum calculations in many cases are also far from measurements. This suggests that, apparently, the root of the discrepancies between the classical impact theory and the experiment at low temperatures is not the difference between the classical and quantum descriptions of the impact approximation. The good agreement of the quantum results obtained with the TKD potential with the measured half-widths (Fig. $7, a, b$) should probably be considered as accidental, since TKD is the oldest of the used PES (its imperfections are discussed in [28]).

To explain the discrepancy between the impact theory of broadening (both classical and quantum) and the experiment at very low temperatures, it is possible to propose (following [33]) possible other mechanisms for the formation of spectral lines. These are, for example, non-impact effects (violation of the impact approximation), gas non-ideality (the effect of triple collisions, etc.), strong absorption of stable dimers (at low temperatures their number is large), etc. However, the exact source of these discrepancies and ways to overcome them are still unknown.

6. Conclusions

Summing up, the following conclusions can be made.

1. The classical approach (the C3D method) has great possibilities for modeling various manifestations of intermolecular interactions, including spectroscopic ones. The method of classical trajectories makes it very easy to analyze the role of collisions of various types (elastic, inelastic, metastable dimers). In the present version, the C3D method is able to quickly and with satisfactory accuracy calculate the coefficients of broadening and shifting of rotational lines of rigid diatomic and linear polyatomic molecules in a very wide temperature range. This is especially true in situations where other methods require a lot of time (such as the quantum CC/CS method) or the introduction of fitting parameters to agree with the experiment (like many semi-classical methods).

We note that the CO$-$He system may not be a good object for checking the classical description, because helium „is too light", and the CO$-$He system „is too quantum". However, in this paper we deliberately tried to investigate this system in a wide range of temperatures (mainly from the side of very low temperatures) in order to clarify the range of applicability of the classical impact theory. As a result of such a rigorous analysis, it can be stated that this theory works satisfactorily for the coefficients of broadening and shifting of transitions $J = 0 \to J = 1$ and $J = 1 \to J = 2$CO in the system ^{12} CO$-^4$He only at temperatures above 20$-$30 K.

2. The development of the classical approach, apparently, should be carried out in the following directions. Firstly, it is a further increase in accuracy, making the role of elastic collisions and quasi-bound complexes more adequate. However, this problem is not simple, as can be seen from the unsuccessful application of Weisskopf's idea in this work. Secondly, further verification of the impact theory for other linear molecules. Thirdly, taking into account non-rigidity and oscillatory motion when modeling vibrational-rotational spectra (this is especially necessary for calculating the shift in fundamental and overtone bands). Fourthly, further application to the problems of interference of spectral lines. Fifthly, adaptation to other types of molecules (spherical, symmetrical and asymmetric tops). Sixthly, modeling of non-impact effects (i.e. caused by a violation of the impact approximation).

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Conflict of interest

The author declares that he has no conflict of interest.

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