

CRDS line shape study of the (7 – 0) band of CO

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Abstract: We present the results of the spectral line shape study of the first measurement of the extremely weak (7 – 0) band of the $^{12}\text{C}^{16}\text{O}$ molecule. Measurements were done with a highly sensitive cavity ring-down spectrometer. Collisional narrowing, analyzed in terms of speed-dependent effects, was observed for the first time for transitions with line intensities below $2 \cdot 10^{-29}$ cm/molecule at 296 K. We provide a full set of line-shape parameters of the speed-dependent and regular Voigt profile analysis for 14 transitions from P and R branches. Experimental verification of a strong vibrational dependence of the pressure shifting described by the Hartmann model [J.-M. Hartmann, JQSRT 110, 2019 (2009)] is extended up to the sixth overtone highly sensitive to the model parameter.

I. INTRODUCTION

Throughout the long history of molecular spectroscopy, carbon monoxide has emerged as a fundamental model system for investigating rotational and ro-vibrational transitions. Given its prevalence as the second-most abundant diatomic molecule following the molecular hydrogen in the interstellar medium, carbon monoxide holds substantial importance in the exploration of astrophysical environments. Carbon monoxide, in addition to satellite measurements, allows ground-based observations providing information about the molecular clouds^{1,2} in which most stars are formed. CO is also present in the atmospheres of Venus^{3,4}, Mars^{5,6} and exoplanets^{7,8}. It is one of the gases used in human breath analysis for disease diagnostics⁹.

Carbon monoxide is one of the major trace gases for biomass burning and fossil fuel combustion in the Earth's atmosphere^{10,11}. With a lifetime of several weeks, it allows tracking of seasonal changes in air pollution^{12,13}. It does not directly affect the global temperature¹⁴ but plays an important role in atmospheric chemistry and controls the oxidative ability of the atmosphere^{15,16}. The reaction of CO with the OH radical, which is the main sink of CO, affects the distribution and the amount of OH, which in turn significantly impacts the concentration of a variety of other trace gases (e.g. methane and other hydrocarbons as well as ozone)^{17,18}. Many different satellite remote-sensing spectrometers such as MOPITT¹⁹, ACE²⁰, and TROPOMI²¹ and ground-based observatories like NDACC²², TCOON²³ and COCCON²⁴ routinely monitor the concentration of CO in Earth's atmosphere.

Many experimental^{25–44} and theoretical^{45–49} works have been devoted to the spectroscopy of CO in the last decades. Significant progress in theoretical calculations of the line intensities has been shown on the example of the CO molecule⁴³. However, purely quantum *ab initio* calculations are infeasible for systems larger than hydrogen, given current computational capabilities, despite their potential to accurately describe observed spectra.

Highly excited vibrational overtones of CO find applications in fundamental research as they are sensitive to the proton-to-electron mass ratio⁵⁰. Hot bands of high vibronic states of CO were observed in stellar spectra^{51–56}, which helps to study the star formation processes. High-order overtones are challenging for laboratory studies due to the rapid decrease of their intensity with the increase of the vibrational quantum number of the upper level. It took more than four decades from the first measurements of CO emission hot bands up to (6 – 4) and (7 – 5) in an acetylene flame⁵⁷ in 1974 until the first measurement of the (6 – 0) overtone band³⁸.

The calculated rotational distributions of intensities in the fundamental (1 – 0) and low-overtone ((2 – 0) and (3 – 0)) vibrational bands of carbon monoxide are nearly immune to the changes of the form of the potential-energy curves (PECs) and dipole-moment curves (DMCs). On the contrary, for high- Δv overtones (where v is a vibrational quantum number) Medvedev et al.⁵⁸ showed that line intensities are very sensitive to different approaches to calculating DMC. This situation indicated the need for experimental study of the sixth overtone unequivocally indicated by Meshkov et al.⁴⁸.

The sixth overtone of CO is located at the 690 nm wavelength region. Prior to this study, no measurements of (7 – 0) band transitions were done. The line intensities measured in this work were reported in Ref.⁴⁹ together with the new *ab initio* calculations. The present paper reports all accompanying line-shape parameters: collisional broadening and shifting, and their speed-dependence parameters, which were out of the scope of the previous paper.

II. EXPERIMENTAL SETUP

Measurements are done with the optical frequency comb (OFC) assisted, Pound-Drever-Hall (PDH) locked, frequency-stabilized cavity ring-down spectrometer (FS-CRDS) in a similar configuration as the one used for the oxygen B-band study⁵⁹. The principal scheme of our setup is shown in Fig. 1.

An external cavity diode laser (ECDL) from Toptica Pho-

tion:

$$\begin{aligned}\Gamma(x) &= \Gamma_0 \left(1 + a_W \left(x^2 - \frac{3}{2} \right) \right), \\ \Delta(x) &= \Delta_0 \left(1 + a_S \left(x^2 - \frac{3}{2} \right) \right),\end{aligned}\quad (1)$$

where x is reduced absorber velocity $x = v/v_0$, v_0 is the most probable absorber velocity, $a_W = \Gamma_2/\Gamma_0$ and $a_S = \Delta_2/\Delta_0$ are dimensionless parameters describing the speed dependence of Γ and Δ , respectively. Other line-shape parameters use the same notation as in Ref.⁷¹.

To minimize the cross-correlation between the fitted line-shape parameters, the multispectrum fitting procedure^{74,75} was used. All baseline parameters were fitted as individual parameters for different pressures, while unperturbed line position, v_0 , the speed dependence of pressure broadening, a_W , and shifting, a_S , were common. Pressure-independent Doppler width was fixed at the value calculated from the temperature measurement. Γ_0 and Δ_0 were assumed to linearly depend on pressure for the given temperature, thus pressure independent coefficients, Γ_0/p and Δ_0/p , were fitted. Two approaches were used with respect to the line intensity S . First, which in this paper we will refer to as the individual line area (ILA) approach, where the line area, A , was fitted in the multfit procedure as an individual parameter for each pressure. The dependence of the line area on concentration was later fitted with a linear function, i.e. $S \propto A/p$, to determine the line intensity. In the second approach, referred to as the linear line area (LLA) approach, the line area was fitted as a coefficient proportional to the concentration, common for all pressures instead. The ideal gas approximation was adopted both in the ILA and LLA approaches, and the line intensity was calculated from the fitted A/p coefficient. The latter approach is considered to be more robust as it reduces the number of fitted parameters in the model, thus the correlation between parameters, while the ILA approach provides a sensitive test to the possible non-linearity of the determined line area on the pressure.

Fig. 2 shows averaged spectra of one of the strongest lines – P8, measured at the pressure of 225 Torr together with fit residuals from the VP (red line) and qSDVP (black line) fits shown on bottom panel. The analysis of the spectra with a simple Voigt profile (neglecting speed-dependent effects: a_W and $a_S = 0$) resulted in a characteristic W-shape of the fit residuals indicating that VP cannot accurately model the spectrum. The insufficiency of VP was not so pronounced for all the lines and pressures as it gets masked by the experimental noise. However, we noticed the nonlinear dependence of the area on the pressure for the VP fits with the ILA approach, which is not expected at this level in this pressure range. It was observed for some of the lines, presented in Fig. 3. Other transitions for which this effect was not observed have relatively low intensity with one exception – the R6 transition. Similar nonlinear behavior of line intensities determined with VP was previously observed for H₂O lines⁷⁶. Simulating the spectra for the conditions of the experiment with qSDV and qSDNG profiles, accounting for the speed dependence of collisional width and shift, and comparing the results of analysis

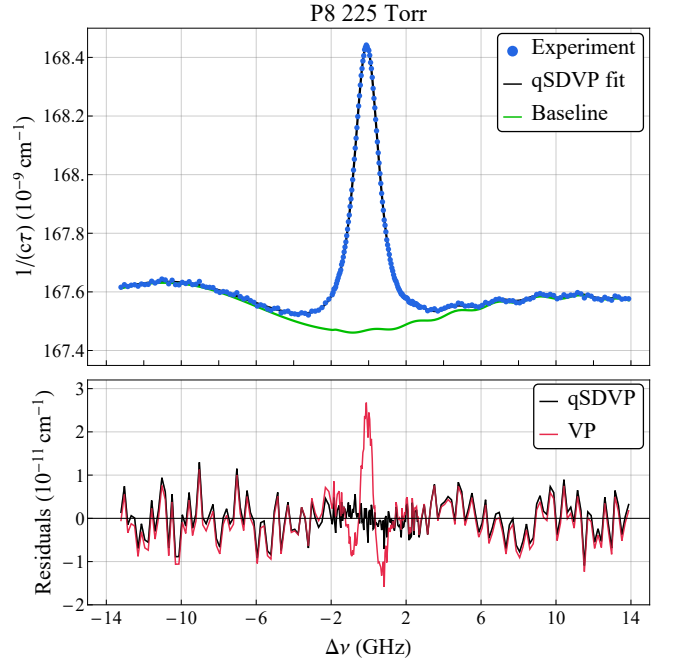


FIG. 2. Top panel: averaged spectra of the P8 line at 225 Torr shown with blue dots (•), black line - fitted qSDVP profile, green line - fitted baseline. Bottom panel: fit residuals for the VP (red line) and qSDVP (black line) analysis.

of simulated data with different profiles with and without the speed dependence in the ILA approach confirmed that such nonlinear behavior of the line area on the pressure is the artifact of an incorrectly chosen line profile. Such behavior means that the determined line intensity would depend on the pressure range of the measurements if VP with LLA had been used and, for the case of experimental data, leads to the underestimation of the line intensities by 1.2% on average compared to the qSDVP LLA results. Systematic nonlinear behavior of the line area over pressure for VP fits suggested that the use of a more advanced line profile is necessary for this data, regardless of the relatively low signal-to-noise (SNR) ratio for the single pressure spectra, which was only up to about 300 for the strongest transitions at the highest pressures.

Comparison of fit results of qSDNGP and qSDVP analysis showed that qSDVP sufficiently well models experimental data. The use of a more advanced qSDNG profile, that takes into account the frequency of the velocity-changing collisions described by the hard collisions model⁷⁷ and resulting Dicke narrowing effect⁷⁸, led to larger uncertainties of line parameters. This was caused by the increased number of fitted parameters and higher cross-correlation between them, especially between a_W , responsible for the line narrowing due to the speed dependence, and v_{VC}/p , responsible for the line narrowing due to the velocity-changing collisions^{79,80}. The effect of the correlation is visually demonstrated in Fig. 4, where there are shown values of v_{VC}/p coefficient from the results of qSDNGP LLA fits of the P8 line with the a_W parameter being fixed to different values together with a corre-

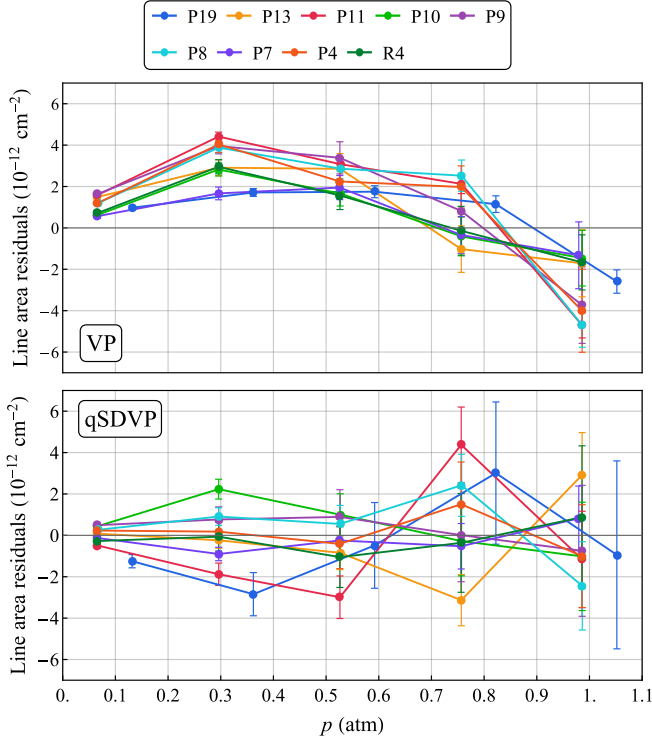


FIG. 3. Residuals of the linear fit of the dependence of area on the pressure for VP ILA (top panel) and qSDVP ILA (bottom panel), for lines indicated with different colors as in the legend. Uncertainty intervals show only type A standard uncertainty. Details in Section III A.

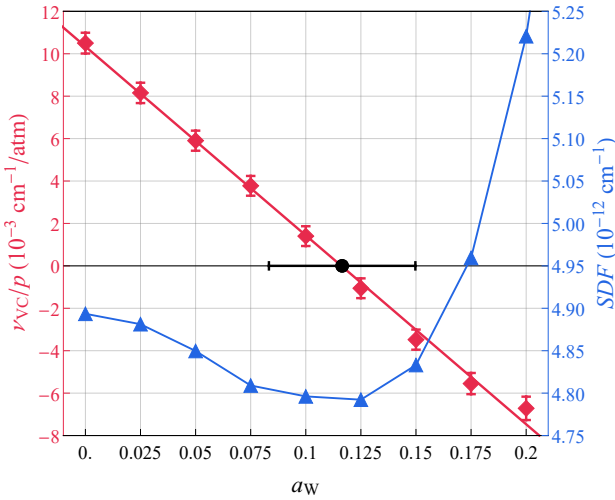


FIG. 4. Overlaid plots of v_{VC}/p (◆) and SDF (▲) (Eq. (2)) against a_W illustrate the correlation between a_W and v_{VC}/p . The results obtained from qSDNGP LLA fit of the P8 line with fixed values of a_W , plotted along the horizontal axis. The red line is a linear fit of the v_{VC}/p data. Uncertainty bars for qSDNGP results show only type A standard uncertainty. The fitted value of a_W from qSDVP LLA fit is shown with a black dot (●) with an uncertainty bar representing total experimental standard uncertainty. Details in Section III A.

sponding standard deviation of the fit residuals (SDF):

$$SDF = \sqrt{\frac{\sum_i^W (\alpha_{\text{exp}}(v_i) - \alpha_{\text{fit}}(v_i))^2}{W - r}}, \quad (2)$$

where α_{exp} and α_{fit} are values of the absorption coefficients measured in the experiment and calculated with the fitted profile, respectively, W is the total number of experimental points, and r is the number of fitted parameters in the model. Fig. 4 shows a strong correlation between v_{VC}/p and a_W . It also shows that the best fit (corresponding to the minimal SDF value) is obtained for the values of v_{VC}/p close to zero. Fitting qSDNGP, with both v_{VC}/p and a_W as floating parameters for most of the lines, resulted in v_{VC}/p values equal to zero within their standard deviations. Nonetheless, taking into account a very strong correlation between parameters characterizing the speed dependence of collisional broadening and Dicke narrowing, as well as a relatively low signal-to-noise ratio, we opted not to ascertain the relative importance of both effects. Consequently, for the conclusive analysis, we selected the qSDVP model, employing the LLA approach for multi-spectrum fitting. This model describes all narrowing using solely the a_W parameter, even if its origin in part can be due to the Dicke narrowing effect.

Derived qSDVP LLA line-shape parameters are listed in Table I. Because the Voigt profile is used in many applications, we provide an additional set of parameters (see Table II) arising from the VP LLA fits, for which etalon parameters (See section III B for the details) were fixed to the values from qSDVP fits to minimize the effect of the baseline on the line shape. The VP has fewer floating parameters, and only line-shape parameters together with constant offset and linear slope of the baseline were optimized for VP analysis. This makes a significant difference in the total number of floating parameters in the case of the multispectrum fit compared to the qSDVP case, which explains the fact that for some of the weaker lines, their quality-of-the-fit factors (QFs)^{81,82} are higher for VP than for qSDVP.

In addition to the 14 explicitly stated transitions, we identified the R22 line, which was only partially recorded because it was situated on the edge of the spectra of the R6 line. Attempting to derive meaningful values for a_W and a_S under these circumstances proved unfeasible, resulting in excessively large uncertainties. To address this, we constrained their values to the corresponding averages derived from other recorded lines (from P19 to R4). Line parameters for R22 are provided in Tables I and II but are excluded from all figures for visual clarity as well as from the discussion and conclusions. The positive pressure shifting observed in the R22 line is likely an artifact arising from its incomplete recording. It is highly improbable that the actual value of pressure shifting coefficient is inherently positive.

B. Spectra baseline

Raw spectra consist of CO absorption lines (whose absorption in the line center was 0.07% – 0.6% of the total losses)

TABLE I. Line-shape parameters from qSDVP LLA fit. Unperturbed line position, ν_0 , is given in cm^{-1} , line intensity, S , is in units 10^{-30} cm/molecule, collisional broadening, Γ_0/p , half width at half-maximum (HWHM), and shifting, Δ_0/p , coefficients are in $\text{cm}^{-1}/\text{atm}$ at reference temperature $T_{\text{ref}} = 296$ K. Speed-dependence parameters a_W and a_S are dimensionless. Uncertainties given in parentheses are total experimental standard uncertainties (1σ) in units of the last digit quoted. QF is the quality-of-the-fit factor.

Line	ν_0	S	Γ_0/p	Δ_0/p	a_W	a_S	QF
P19	14334.40122(84)	1.81(38)	0.0616(107)	-0.0193(28)	0.065(44)	0.08(15)	36
P16	14358.36237(42)	3.65(27)	0.0624(26)	-0.0168(14)	0.124(36)	0.17(12)	76
P13	14380.14082(29)	6.70(27)	0.0653(19)	-0.0173(10)	0.087(35)	0.33(12)	124
P12	14386.91468(23)	7.53(31)	0.0656(19)	-0.0164(9)	0.080(35)	0.08(12)	136
P11	14393.44482(35)	9.07(37)	0.0683(22)	-0.0190(9)	0.103(35)	0.34(12)	138
P10	14399.73166(19)	9.59(35)	0.0677(18)	-0.0165(8)	0.102(34)	0.12(12)	190
P9	14405.77460(18)	10.65(36)	0.0698(17)	-0.0163(8)	0.098(34)	0.13(12)	184
P8	14411.57391(15)	10.99(37)	0.0714(17)	-0.0151(7)	0.117(34)	0.10(12)	249
P7	14417.12981(16)	11.03(37)	0.0728(17)	-0.0152(7)	0.131(34)	0.12(12)	248
P4	14432.33271(22)	8.45(32)	0.0778(20)	-0.0132(9)	0.086(34)	0.14(12)	157
P1	14445.33617(63)	2.54(27)	0.0939(57)	-0.0128(18)	0.092(46)	0.31(23)	37
R0	14452.78145(69)	2.46(28)	0.0899(65)	-0.0110(19)	0.064(44)	0.50(24)	42
R4	14464.72911(21)	9.12(32)	0.0746(17)	-0.0144(7)	0.115(34)	0.23(12)	183
R6	14469.22876(18)	9.99(34)	0.0689(16)	-0.0144(7)	0.078(34)	0.14(12)	168
R22	14469.70244(423)	0.89(32)	0.0876(131)	0.0119(97)	0.100 ^a	0.18 ^a	12

^a a_W and a_S for the R22 line fitting were fixed to the weighted average values, with the weights inversely proportional to the variance of the value, from the results of the other lines (from P19 to R4). Details in the Section III A.

TABLE II. Line-shape parameters from the VP LLA fit. Unperturbed line position, ν_0 , is given in cm^{-1} , line intensity, S , is in units 10^{-30} cm/molecule, collisional broadening, Γ_0/p (HWHM), and shifting, Δ_0/p , coefficients are in $\text{cm}^{-1}/\text{atm}$ at reference temperature $T_{\text{ref}} = 296$ K. Uncertainties given in parentheses are total experimental standard uncertainties (1σ) in units of the last digit quoted. QF is the quality-of-the-fit factor.

Line	ν_0	S	Γ_0/p	Δ_0/p	QF
P19	14334.40136(84)	1.78(38)	0.0597(107)	-0.0191(28)	41
P16	14358.36250(42)	3.59(27)	0.0599(26)	-0.0161(14)	77
P13	14380.14098(29)	6.64(27)	0.0639(19)	-0.0161(10)	124
P12	14386.91475(23)	7.45(31)	0.0640(19)	-0.0162(9)	144
P11	14393.44512(35)	8.97(37)	0.0666(22)	-0.0177(9)	130
P10	14399.73176(19)	9.47(35)	0.0656(18)	-0.0162(8)	178
P9	14405.77470(18)	10.52(36)	0.0678(17)	-0.0159(8)	178
P8	14411.57398(15)	10.82(37)	0.0688(17)	-0.0148(7)	204
P7	14417.12989(16)	10.83(37)	0.0696(17)	-0.0147(7)	194
P4	14432.33278(22)	8.36(32)	0.0760(20)	-0.0128(9)	160
P1	14445.33632(63)	2.51(27)	0.0916(57)	-0.0119(18)	43
R0	14452.78171(69)	2.45(28)	0.0889(65)	-0.0103(19)	48
R4	14464.72924(21)	8.99(32)	0.0721(17)	-0.0137(7)	164
R6	14469.22885(18)	9.88(35)	0.0672(17)	-0.0140(7)	173
R22	14469.70255(415)	0.85(37)	0.0833(131)	0.011(10)	12

and the baseline that represents losses not related to absorption in the gas. The baseline was modeled with a linear function comprising two parameters: a constant offset and a slope, accounting for possible changes in mirrors reflectivity and sine functions, accounting for the etalons (See next paragraph). The amplitude of the baseline function observed on the spectra was comparable to the amplitude of the line. This required a detailed investigation of the influence of the baseline model on determined line parameters. Averaged spectra at different pressures with corresponding etalons in the baseline and fit residuals on the example of the P10 line are shown in Fig. 5.

Interference between light oscillating inside the ring-down cavity (formed by the internal reflective surfaces of cavity mir-

rors) and the light reflected back from weakly reflective surfaces outside the main cavity caused sinusoidal modulation of the spectra baseline. This effect is known as an etaloning effect^{83,84}. We observed at least two etalons in our spectra with periods of about 26 GHz and 17 GHz corresponding to the reflection from the external surfaces of cavity mirrors and from the cell windows, respectively. Those etalons were modeled with a simple sine function with parameters fitted individually for each pressure. Additionally, we noticed a quasi-periodical signal, which will be referred to in this paper as the third etalon, with a period of 2.5 GHz covering only part of a spectrum (see Fig. 5). Half-period of 1.3 GHz is close to the line width at low pressures as the Doppler width is about

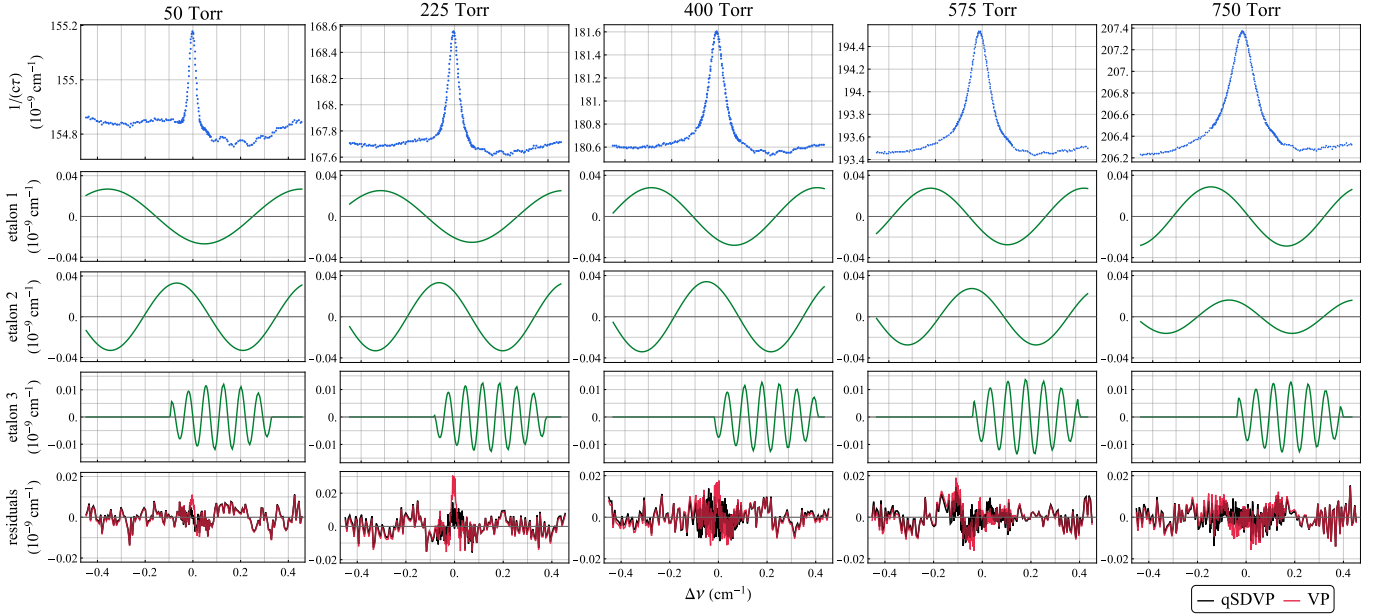


FIG. 5. P10 line of (7 – 0) band of CO measured at five different pressures at temperature of 296 K. Top row shows raw averaged spectra with nominal pressures indicated above. Fitted etalons are shown in rows No 2, 3, and 4. The bottom row shows fit residuals from LLA fit for qSDVP in black and for VP in red. The horizontal axis shows the frequency detuning $\Delta\nu$ from the unperturbed line position. Details in Section III B.

1 GHz, and the collisional width for the experimental conditions varied between 0.25 GHz and 6 GHz. This made the third etalon a potential source of significant systematic uncertainty. Such quasi-etalon spectrum may be a consequence of several interfering etalons with different periods. Contrary to the first two etalons, formed by parasitic reflections from surfaces located inside the temperature-stabilized enclosure, the third etalon is partially formed by elements outside of the thermal enclosure, which leads to changes in its parameters (mainly the phase) during measurements. To model the third etalon, its approximating function was modified by a smooth envelope made from a half-period-part of cosine function between zeros and equal to zero elsewhere and characterized by its effective width and position. This form was chosen from considerations of possible beat note of two etalons with equal amplitudes and the difference between periods of about 2.5 GHz. While regular cosine envelope function could potentially account for the observed 2.5 GHz etalon's amplitude modulation, it would create similar increasing and decreasing oscillations after the envelope crossed the zero level. However, this was not in accordance with the patterns observed in the spectra. To address this inconsistency, we made the decision to utilize only one half-period segment of the envelope function and set it to zero elsewhere. It is important to note that this peculiar behavior may be attributed to an artifact of temporal variations of the frequency and the phase of the third etalon and the consequent averaging of numerous scans conducted over an extended time span for a single pressure measurement (lasted on average nine hours) rather than being intrinsic characteristics of the etalon itself.

C. Uncertainties estimation

Parameters uncertainties presented in Tables I and II are the total experimental standard uncertainty (1σ) determined by accounting for all considered contributions according to Table III where a detailed breakdown of the corresponding contributions to the uncertainty budget for LLA qSDVP parameters is shown on the example of the P10 line.

For the estimation of systematic uncertainties due to the fitting procedure, the maximal difference of parameters from ILA and LLA multispectrum fit approaches of qSDVP was divided by $\sqrt{3}$ as it is advised⁸⁵ to consider a rectangular distribution as an alternative assumption, given that systematic deviations are unlikely to follow a normal distribution. The resulting relative systematic uncertainty contributed from 0.11% to 16% to the total relative standard uncertainty of line intensity, depending on the transition, and up to $1.7 \cdot 10^{-4} \text{ cm}^{-1}$ (5.2 MHz) to the uncertainty of the unperturbed line position.

To determine the impact of the baseline on the uncertainty of the fitted line parameters, a set of simulations was made with over one hundred configurations of observed etalons and line profiles. We estimated how using different line profiles together with different phases of etalons relative to the line center would affect retrieved parameters values for the conditions of the experiment. All simulations were done for two levels of SNR corresponding to the strongest and the weakest measured transitions, giving us the ability to linearly scale corresponding uncertainties for all measured spectra. Baseline-related uncertainty contributed from 2.2% up to 13% to the total relative standard uncertainty of the line intensity. It contributed

TABLE III. Detailed uncertainty budget of the qSDVP parameters for the P10 line. Contributions to the standard uncertainty of the unperturbed line position, ν_0 , are given in 10^{-3} cm^{-1} , contributions to the standard uncertainties of all other parameters are given as relative values except for the a_W and a_S , for which it is absolute and dimensionless.

Parameter	ν_0	S	Γ_0/p	Δ_0/p	a_W	a_S
Type A uncertainty	0.067	0.003	0.0038	0.0095	0.0062	0.022
Contribution to B type uncertainty:						
frequency reference accuracy	0.000015	0.00008	0.00015	0.00071	—	—
temperature measurement accuracy	—	0.00012	0.00012	0.00012	—	—
temperature dependence	—	0.00032	0.00006	0.00006	—	—
pressure measurement accuracy	—	0.00013	0.00013	0.00013	—	—
approach to multisppectrum fitting (ILA or LLA)	0.033	0.016	0.016	0.012	0.021	0.0003
repeatability	0.029	0.018	0.019	0.037	0.0075	0.075
baseline model	0.14	0.025	0.012	0.025	0.025	0.082
Total uncertainty	0.17	0.034	0.027	0.05	0.034	0.12

from $1.3 \cdot 10^{-4} \text{ cm}^{-1}$ to $8 \cdot 10^{-4} \text{ cm}^{-1}$ (3.7 to 23 MHz) of line position, depending on the transition. Uncertainty related to the baseline model was the main uncertainty component for the line intensity, the unperturbed line position, and the speed dependence of the pressure broadening coefficient.

Additionally, in order to not underestimate the total uncertainty, we include the contribution from the comparison of repeated measurements for the P8 line as an example. Subsequent measurement was done in the same way for all pressures more than one month after the first one.

The line mixing effect should not affect the line intensity of CO on a level higher than 0.26%. This was calculated by fitting qSDVP to the spectra simulated with qSDVP with line mixing. Spectra were simulated using the maximal absolute value of the first order⁸⁶ line mixing coefficient $Y = 0.02 \text{ atm}^{-1}$ from the HITRAN2020 database⁸⁷ for the CO (7 – 0) band, and maximal values of pressure broadening and shifting coefficients observed in the experiment with the noise level typical for the experiment. This error is safely below the stated total standard uncertainty.

For pressure shifting and its speed-dependence parameter most of the uncertainty came from the measurement repeatability and the influence of the baseline. Pressure-broadening uncertainty originated evenly from the systematic uncertainty, repeatability, and the impact of the baseline.

For the VP LLA results presented in Table II the total experimental uncertainty (in parentheses) for unperturbed line position and line intensity, include also uncertainty associated with the choice of the line profile. It was estimated by comparing the results of the qSDVP LLA fit and the VP LLA, for which the etalons parameters were fixed to the values from qSDVP spectra analysis. The choice of the line profile contributed from 0.6% up to 1.8% to the total relative standard uncertainty of the line intensity and from $0.7 \cdot 10^{-4} \text{ cm}^{-1}$ to $3 \cdot 10^{-4} \text{ cm}^{-1}$ (2 to 9 MHz) of the line position, depending on the transition. Other parameters are not directly comparable for considered profiles.

Type A uncertainty was always smaller than type B for all transitions and parameters. We acknowledge that some components of the uncertainty are not completely independent and thus partially account for the same source of uncertainty.

Nonetheless, we prefer to overestimate the uncertainty rather than underestimate it by neglecting any of the components.

IV. RESULTS AND DISCUSSION

A. Comparison with available theoretical data

All determined line-shape parameters are presented in Tables I and II, resulting from the qSDVP fits with the LLA approach and from the VP LLA fits, respectively. Fig. 6 displays all the results, where values determined with the qSDVP LLA approach, indicated with black dots (●), and VP LLA, indicated with red triangles (▲), are compared with data from the HITRAN2020 database^{87,88} for qSDVP, marked with empty rectangles (□), and for VP, marked with green rectangles (■), plotted against the line index m . Line index m is defined as follows: $m = -J''$ for the P branch and $J'' + 1$ for the R branch, where J'' is the rotational quantum number of the lower state of the CO molecule. Note that the line intensities and unperturbed line positions for VP and qSDVP in HITRAN2020 are exactly the same data. The experimental results for the qSDVP and VP analysis agree with each other within their total standard uncertainty.

Line positions and intensities given in HITRAN2020 are taken from the semi-empirical calculation of Li et al.⁴⁷. This calculation is based on the PEC of Coxon and Hajigeorgiou⁴⁵ and the DMC combined from a fit of the best available at that time, experimental data of transitions from (0 – 0) up to (6 – 0) bands and spline-interpolation of their *ab initio* DMC.

Panel a) of Fig. 6 shows absolute values of the line intensities of measured transitions. Comparison with HITRAN2020 data shows that calculations significantly underestimate intensities, and the experimental values are approximately two times higher.

The difference between measured values of unperturbed line positions and values from HITRAN2020 is shown in panel b) of Fig. 6. Experimental values agree with the calculation within one standard uncertainty for most of the lines and within two standard uncertainties for all of the measured lines.

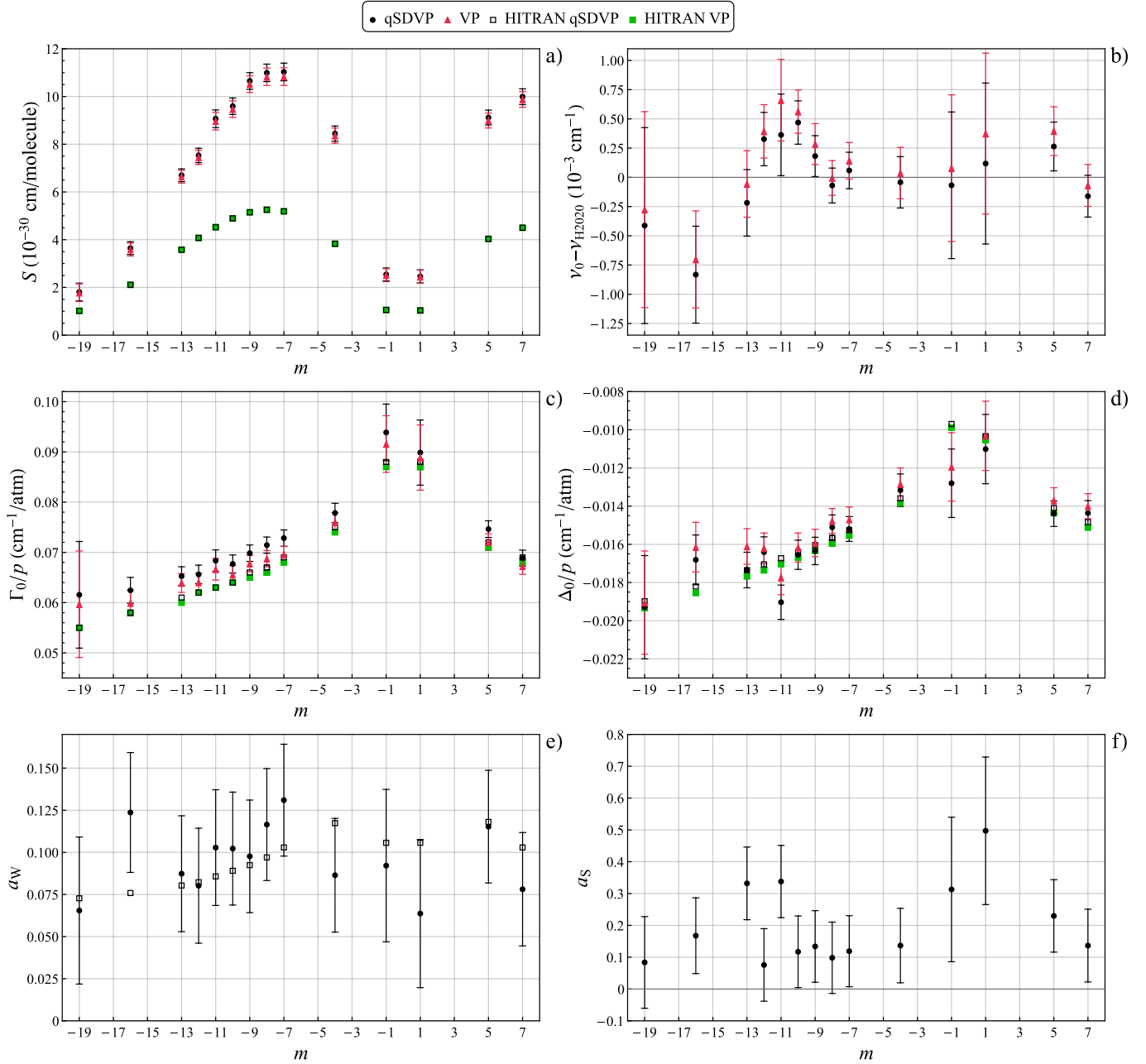


FIG. 6. Comparison of experimental values from the qSDVP LLA (●) and VP LLA (▲) analysis of all determined line parameters with data from HITRAN2020 database^{87,88} for qSDVP (□) and VP (■) against line index m . Panel a) shows absolute values of line intensities, and panel b) shows the difference between determined line positions and corresponding values v_{H2020} from the HITRAN2020 database. Comparisons of absolute values of pressure broadening (HWHM) and shifting are shown in panels c) and d), respectively. Panel e) shows a comparison of the speed dependence of pressure broadening parameter, a_W , for qSDVP fit and data available in the HITRAN2020 database. For the speed dependence of pressure shifting, a_S , only qSDVP data from this work is available and shown in panel f). Uncertainty bars on the experimental data points correspond to the total standard uncertainty. Details in Section IV A.

We should mention that no direct calculations for the line-shape parameters (other than line position and intensity) nor measurements are available for considered transitions of (7–0) band. The comparison of pressure broadening with HITRAN2020 would show only consistency across different bands. This is because the HITRAN2020 VP data is a Padé approximation of the best available at that moment measure-

ments of the lower bands⁸⁸ (only up to the (4–0)), while qSDVP data is an approximation of measurement of (2–0) band by Devi et al.³⁴. Although it has been observed that pressure broadening for those transitions remains relatively independent of the branch and the band⁸⁸, it should not be automatically assumed that the same holds true for higher overtone

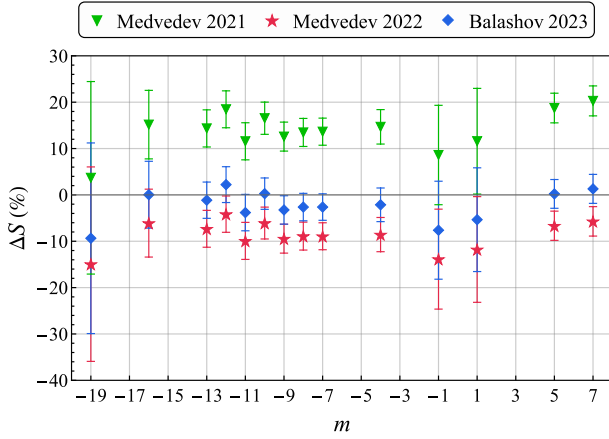


FIG. 7. The relative differences of the theoretical line intensities from the experimental data, determined with Eq. (3). The calculations of Medvedev and Ushakov from 2021⁵⁸ and 2022⁸⁹ are indicated with green (▼), and red (★)⁸⁹ symbols, respectively. The calculations of the UCL group⁴⁹ are shown in blue (◆).

transitions. The self-induced pressure shifting coefficients in HITRAN2020 are based on measurements of the fundamental band and the first two overtones⁸⁸ for the VP case and on the measurement of (2 – 0) band by Devi et al.³⁴ for the qSDVP case, see details in Section IV B.

Our measured values of the collisional self-induced pressure broadening coefficient, Γ_0/p , show good repeatability of the shape of its dependence on the line index m in comparison with HITRAN data, but calculations seem to underestimate the absolute values by about 5% on average, see panel c) of Fig. 6. Also, Γ_0/p values of the R branch seem to agree better with predicted values than for the P branch. Panel d) of Fig. 6 shows the pressure shifting coefficient, Δ_0/p . Its values are in agreement with HITRAN2020 data within total standard uncertainty for most of the transitions. The results for a_W (panel e) of Fig. 6 are in agreement within the total standard uncertainty with calculations and are able to reflect the general shape of its m dependence. This fact additionally supports the use of the qSDVP for the final analysis. The qSDVP implementation in HITRAN2020 assumes only speed dependence of pressure broadening and no speed dependence of pressure shifting. Therefore, in the panel f) of Fig. 6 only results of this work are shown.

In Fig. 7 we compare our measured line intensities with more recent calculations. The relative differences of line intensities of different theoretical calculations from the experimental values are calculated according to the formula:

$$\Delta S = \frac{S_{\text{Theoretical}} - S_{\text{Experimental}}}{S_{\text{Experimental}}} \cdot 100\%. \quad (3)$$

Calculations of Medvedev and Ushakov using DMF constructed with irregular functions and 16 adjustable parameters⁵⁸, shown with green triangles (▼), predicted roughly two times higher values of line intensities of (7 – 0) band transitions than the HITRAN2020. They are higher by 14% on average from the experimental ones. Refined calculations of

the same authors with irregular DMF and 13 adjustable parameters⁸⁹, shown with red star symbols (★), predicted line intensities even closer to the experimental values, only 9% on average smaller than the measured ones. However, the new calculations from the theoretical group in University College London⁴⁹, shown with blue diamond symbols (◆), yield the best agreement with the experiment. It matched experimental values of almost all line intensities within one standard experimental uncertainty. Calculated intensities are smaller than the experimental ones by 2.4% on average. The calculations are based on a similar approach that gave sub-promille accuracy in determining line intensities of (3 – 0) band⁴³. For a detailed discussion of the results on line intensities and issues that accompanied the new theoretical calculations, we send the reader to our recent paper⁴⁹.

B. Comparison of (7 – 0) broadening and shifting coefficients with other CO bands

Fig. 8 shows a comparison of our values of self-induced pressure broadening coefficients from the VP LLA fit (top panel) and the qSDVP LLA fit (bottom panel) with available experimental data for the pure rotational band (0 – 0), fundamental ro-vibrational band (1 – 0) and overtones of CO up to (6 – 0). The results of measurements of the (2 – 0) band by Predoi-Cross et al.⁹⁰ and Devi et al.³⁴ are not shown on the top panel of Fig. 8, as they are in perfect agreement with more recent measurement by Esteki et al.³⁹(△). The results of the (3 – 0) band by Swann et al.³⁰, not shown on the top panel of Fig. 8, agree within the margin of uncertainty with the results of Predoi-Cross et al.³²(×). Our values (●) of pressure broadening coefficients obtained with the VP fit are within the scatter of experimental values for fundamental and lower overtone bands. However, our qSDVP results (bottom panel of Fig. 8) are slightly higher on average than the results for other bands. For certain values of m , they diverge by more than one experimental uncertainty from other measurements. However, it is worth noting that, for the results of Tretyakov et al.⁴⁴(☆), Wójtewicz et al.³⁵(×), (4 – 0) band results of Borkov et al.⁴⁰(○) and for this work (●), uncertainty bars on the bottom panel of Fig. 8 show total standard experimental uncertainties (1σ) while for all the others only statistical (1σ) uncertainty from the fit, as the rest of the authors did not provide estimation of their type B uncertainties.

Fig. 9 shows our qSDVP LLA values (●) of self-induced pressure shifting coefficients, Δ_0/p , together with measurements for lower overtones, fundamental and pure rotational bands from the literature in comparison with theoretical values of Δ_0/p for qSDVP and VP, shown with solid lines and dashed lines respectively. Experimental data from Tretyakov et al.⁴⁴, Devi et al.²⁶ and from this study results from analysis assuming speed dependence while other not, except for the data from Bordet et al.⁴², where the data were analyzed differently depending on the conditions of the experiment. The theoretical values are calculated according to the semiempir-

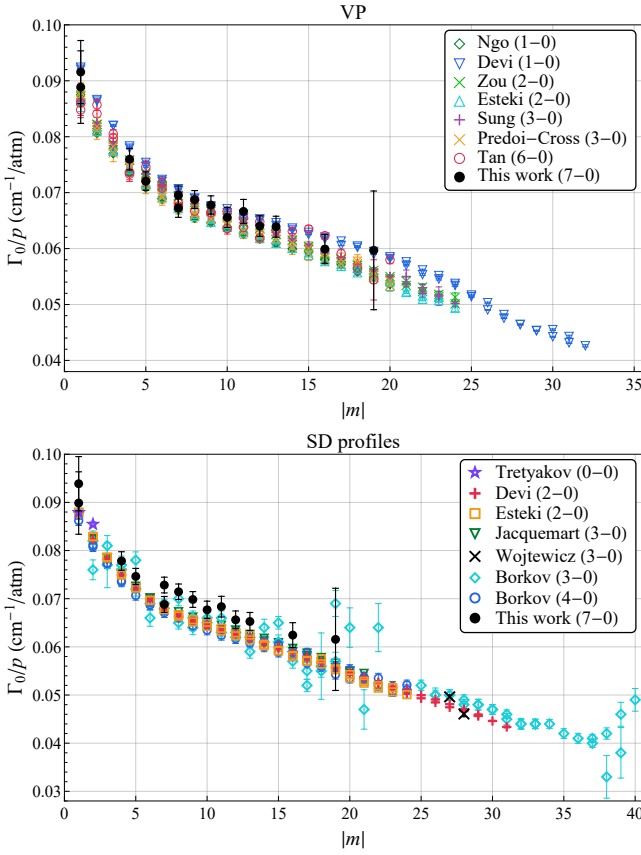


FIG. 8. Top panel: The measured self-induced pressure broadening coefficients versus absolute values of the line index m from the VP analysis. The values from this work for the (7-0) band (●) are compared to the values for (1-0) band by Ngo et al.³⁶ (◇) and Devi et al.²⁶ (▽), (2-0) band by Zou and Varanasi²⁹ (×) and Esteki et al.³⁹ (△), (3-0) band by Sung and Varanasi³¹ (+) and Predoi-Cross et al.³² (×), and (6-0) band by Tan et al.³⁸ (○). Bottom panel: The measured self-induced pressure broadening coefficients versus absolute values of the line index m from the analysis with profiles accounting for the speed dependence of pressure broadening. The values from this work for the (7-0) band (●) are compared to the values for pure rotational (0-0) band by Tretyakov et al.⁴⁴ (☆), (2-0) band by Devi et al.³⁴ (+) and Esteki et al.³⁹ (□), (3-0) band by Jacquemart et al.²⁸ (▽), Wójtewicz et al.³⁵ (×) and Borkov et al.⁴¹ (◇), and (4-0) band by Borkov et al.⁴⁰ (○).

ical model proposed by Hartmann for the CO₂ line shift⁹¹. This model, adapted for the CO molecule, takes the following form:

$$\Delta_0[(v + \Delta v, J') \leftarrow (v, J'')] = (J'' - J') \Delta_0^R(|m|) + a \Delta v \Delta_0^V(|m|) \quad (4)$$

where J' is the rotational quantum number of the upper state. Functions $\Delta_0^R(|m|)$ and $\Delta_0^V(|m|)$ represent two contributions to the line shift. The first one is purely rotational. The second one is scaled by a factor depending on the vibrational mode, which for a diatomic molecule is simply proportional to Δv .

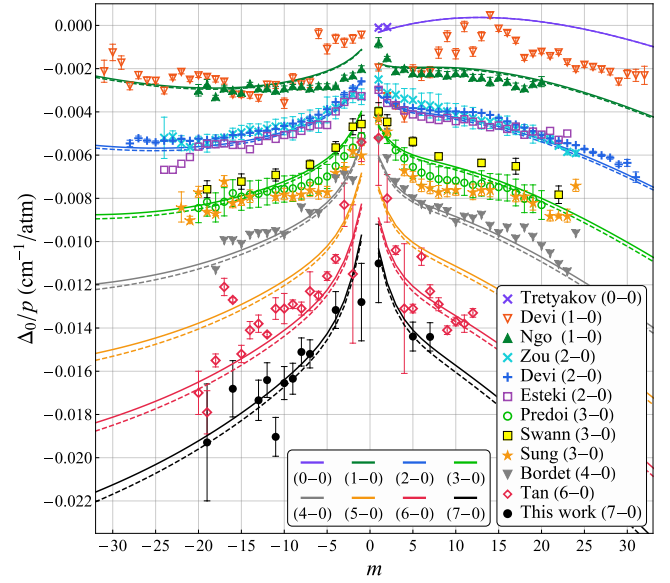


FIG. 9. The experimental and theoretical self-induced pressure shifting coefficients Δ_0/p versus line index m . The values from this work for (7-0) band from the qSDVP LLA analysis (●) are compared to the values for (0-0) band by Tretyakov et al.⁴⁴ (×); (1-0) band by Devi et al.²⁶ (▽) and Ngo et al.³⁶ (△); (2-0) band by Zou and Varanasi²⁹ (×), Devi et al.³⁴ (+) and Esteki et al.³⁹ (□), (3-0) band by Predoi-Cross et al.³² (○), Swann and Gilbert³⁰ (■) and Sung and Varanasi³¹ (★); (4-0) band by Bordet et al.⁴² (▽); (6-0) band by Tan et al.³⁸ (◇). Solid lines show Δ_0/p values calculated from Eq. (4) and corresponding to the qSDVP while dashed ones correspond to the VP. Details in Section IV B.

They may be modeled by five-parameter functions:

$$\begin{aligned} \Delta_0^R(|m|) &= \alpha_1^R + \alpha_2^R e^{-|m|\beta_1^R} + \alpha_3^R e^{-|m|\beta_2^R}, \\ \Delta_0^V(|m|) &= \alpha_1^V + \alpha_2^V e^{-|m|\beta_1^V} + \alpha_3^V e^{-|m|\beta_2^V}. \end{aligned} \quad (5)$$

Values of parameters $\alpha_i^{V,R}$ and $\beta_i^{V,R}$ are given in Table IV. These parameters were determined by Hashemi et al.⁸⁸ based on experimental data for (1-0)^{29,36}, (2-0)^{29,92}, and (3-0)³² bands and have the same values for the line shifting determined with the VP and speed-dependent profiles. Only the a coefficient in Eq. (4) was determined separately for the case of VP and speed-dependent profiles. For the VP, $a = 0.54$ was determined using (2-0) data²⁹, and for speed-dependent profiles $a = 0.5$ was retrieved from the fit to the data of the same band measured by Devi et al.³⁴. However, the latter value does not reproduce pressure shifting values given in the supplementary material of Ref.⁸⁸ and in the HITRAN2020 database⁸⁷. The value of a fitted to the SDV pressure shifting values in HITRAN2020 is $a = 0.529471(23)$. This value agrees with the one determined on the basis of our (7-0) measurements: $a = 0.530(8)$.

The results of measurements of (3-0) band by Picque et al.⁹³ are not shown in the Fig. 9 as they are in agreement within the margins of uncertainty with more recent results

TABLE IV. Parameters from Ref.⁸⁸ used in functions $\Delta_0^R(|m|)$ and $\Delta_0^V(|m|)$ given by Eq. (5).

$\Delta_0^R(m)$	$\Delta_0^V(m)$
$\alpha_1^R = 2.413 \times 10^{-2}$	$\alpha_1^V = -2.476 \times 10^{-2}$
$\alpha_2^R = -8.608 \times 10^{-2}$	$\alpha_2^V = 1.520 \times 10^{-3}$
$\alpha_3^R = 6.240 \times 10^{-2}$	$\alpha_3^V = 2.125 \times 10^{-2}$
$\beta_1^R = 1.507 \times 10^{-2}$	$\beta_1^V = 5.363 \times 10^{-1}$
$\beta_2^R = 2.301 \times 10^{-2}$	$\beta_2^V = 3.993 \times 10^{-3}$

of Swann and Gilbert³⁰ (■). The data for (4–0) band (▼) is acquired in private communication with authors of Bordet et al.⁴² and does not have estimation of uncertainty. Uncertainty bars for the data by Tretyakov et al.⁴⁴ (×) and from this study (●) show total standard uncertainty (1 σ) and one standard statistical uncertainty for the other data. Retrieved in this study Δ_0/p values agree with calculated values for most of the lines within the experimental uncertainty, reflecting the expected shape of its m -dependence, and show good scaling with the vibrational quantum number of the upper level.

V. CONCLUSIONS

We present the first experimental line shape study of (7–0) band of carbon monoxide, located near the 690 nm wavelength range. For 9 transitions the line positions are determined with an accuracy of $3 \cdot 10^{-4} \text{ cm}^{-1}$. Self-pressure broadening and shifting coefficients are determined with a relative uncertainty of about 5%. Collisional narrowing of the spectral line is observed for the first time for such weak transitions and analyzed in terms of speed-dependent effects. Comparison of collisional broadening and shifting coefficients with values extrapolated from prior measurements of lower overtone bands demonstrates good agreement. However, for the (7–0) band we note slightly higher pressure broadening than for the lower overtone bands if SDV profile is used. We verified experimentally a strong dependence of the pressure shifting on the vibrational quantum number. The Hartmann model⁹¹, describing this dependence, was confirmed up to the sixth overtone, which is highly sensitive to the model parameter.

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AUTHOR DECLARATIONS

Conflict of interest

The authors have no conflicts to disclose.

Author contributions

Aleksandr A. Balashov: Data curation (equal); Formal analysis (lead); Investigation (equal); Software; Visualization; Writing - original draft. Szymon Wójtewicz: Funding acquisition (equal); Investigation (equal); Validation (equal); Writing - review & editing (equal). Jolanta Domysławska: Formal analysis (supporting); Funding acquisition (equal); Investigation (equal); Validation (equal); Writing - review & editing (equal). Roman Ciuryło: Methodology (equal); Validation (equal); Writing - review & editing (equal). Daniel Lisak: Conceptualization (equal); Funding acquisition (equal); Methodology (equal); Supervision (equal); Validation (equal); Writing - review & editing (equal). Katarzyna Bielska: Conceptualization (equal); Data curation (equal); Funding acquisition (equal); Investigation (equal); Supervision (equal); Writing - review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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