

# Foreign Gas Broadening Studies of the $J' \leftarrow J = 1 \leftarrow 0$ Rotational Line of CO by Frequency and Time Domain Techniques

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The collisional broadening of the  $J' \leftarrow J = 1 \leftarrow 0$  rotational line of carbon monoxide by the buffer gases He, Ne, Ar, Kr, CO, N<sub>2</sub>, O<sub>2</sub>, and air has been studied at room temperature. Two different experimental techniques in time- and frequency-domain, respectively, were used. The obtained data are in good agreement. Time-domain investigations on the temperature dependence of the foreign gas broadening parameters are also presented.

**Key words:** CO; Line Broadening; Buffer Gases; Temperature Dependence.

## I. Introduction

Line shape studies for the investigation of the collisional broadening and shift of the spectral lines of molecules in foreign gases is of interest in astrophysics, studies of planetary atmospheres, the propagation of radiation in our atmosphere, quantum chemistry, etc. The employment of complementary experimental techniques for such studies is very desirable since it may reveal possible sources of errors and can yield very reliable lineshape parameters. Such a comparative investigation of the influence of foreign gases on the  $J' \leftarrow J = 1 \leftarrow 0$  rotational line broadening of carbon monoxide (<sup>12</sup>C<sup>16</sup>O) in the ground vibrational state was carried out jointly at the Kiel University and the Institute of Applied Physics of the Russian Academy in Nizhny Novgorod, employing two different experimental techniques in the time- and frequency domain, respectively. Early time-domain studies of the CO  $J' \leftarrow J = 1 \leftarrow 0$  line self-broadening at Kiel were described in [1]. This paper continues a collaboration of the two laboratories on the comparative investigation of the pressure self-broadening of this line [2], which showed good agreement of the results obtained with the different types of spectrometers.

The choice of the rare gases He, Ne, Ar, and Kr as buffer gases was motivated by the development of theories describing collisional line broadening phenomena, and the mixtures of CO with N<sub>2</sub>, O<sub>2</sub> and air were investigated in view of the Earth's atmosphere. We compared the CO  $J' \leftarrow J = 1 \leftarrow 0$  line broadening by foreign gases at room temperature, obtained from time-domain data with use of an improved Fourier Transform spectrometer in the millimeter wave (MMW) region, with that obtained from frequency-domain data, employing a computer controlled radio acoustical detection (RAD) spectrometer. Results from time-domain investigations on the temperature dependence of the line broadening due to foreign gas collisions are also presented.

## II. Experimental

A general description of the experimental technique and the procedure of time-domain measurements was given in [1]. Due to the improvements of the experiment, the sensitivity of the spectrometer was increased by about one order of magnitude. Thus we were able to detect also the  $1 \leftarrow 0$  rotational line of the isotopomers <sup>13</sup>CO, C<sup>18</sup>O and C<sup>17</sup>O in natural abundance, the latter one with resolved <sup>17</sup>O nuclear quadrupole hyperfine structure [3]. Here we will only report the main differences between the present experimental setup and that of [1], Figure 1.

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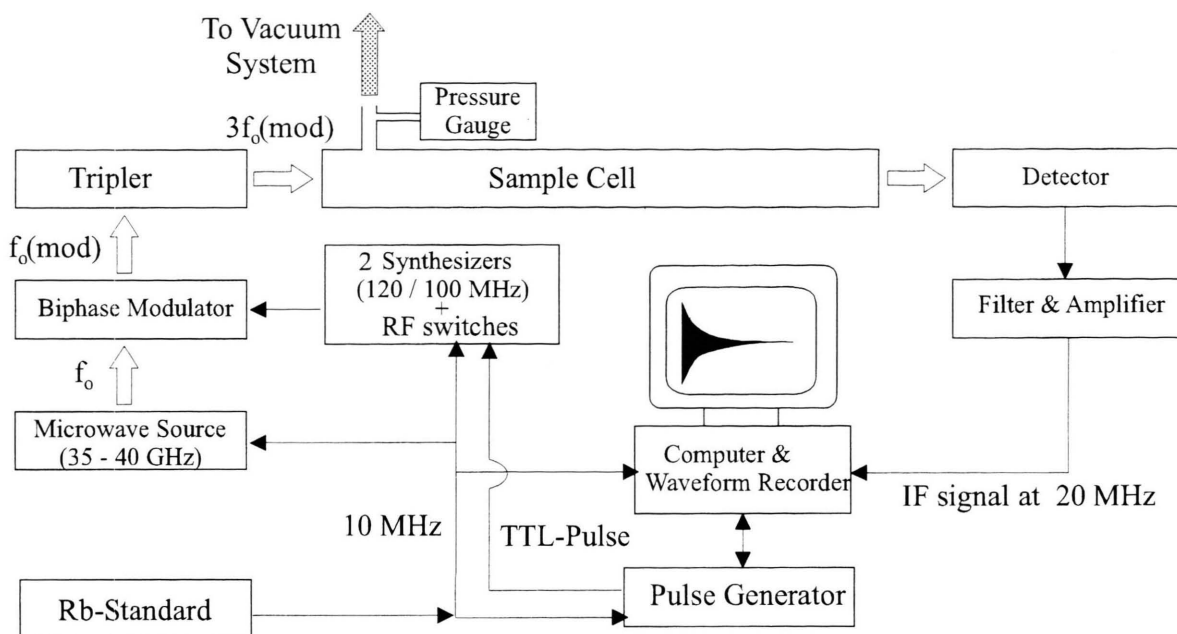


Fig. 1. Scheme of experimental setup of MMWFT spectrometer.

The fundamental microwave radiation was produced by a homemade, phase stabilized Gunn oscillator with a Thompson AH 655-00 diode (frequency range 35 - 40 GHz). The output of the Gunn oscillator was coupled through three unilines (to avoid feedback modulations) to the biphase modulator. The modulated signal was amplified (HP 83554A) up to 20 dBm and fed into a tripler with conventional losses (-13 dB) developed in "Kvarz" Co., N.Novgorod. The new tripler allowed to increase the output MW-power from 10  $\mu$ W to about 100  $\mu$ W.

The RF switch in [1], which controls the change in the modulation frequency, was replaced by a system of four RF switches. Two of them were mounted in series for each of the two radiofrequencies. This gave more than 60 dB suppression of the sideband which is not used. The delay between the switch off of the polarizing and the switch on of the local sideband was about 160 ns. This procedure minimized distortions produced by reflections of the TTL signals.

The MMW radiation in the range 105 - 120 GHz was fed into an oversized waveguide cell by a taper. The brass waveguide cell allowed measurements at 230 - 300 K. Cell cooling was achieved by circulating refrigerated methanol around the cell. The cell temperature was determined with three Pt resistors to an accuracy of about 1 K. The pressure was measured

with an accuracy of about 0.1% by a MKS Baratron Type 390HA-00001 gauge.

The partial pressure of CO, first filled into the sample cell, was fixed to about 36 mTorr, and the buffer gases were added to partial pressures of 10 - 100 mTorr.

For signal averaging, a fast hardware averager (Strauss 100 MHz transient recorder TR-AV 100-8/32) was used, which allowed data sampling at 10 ns intervals. The repetition rate of the experiment was about 50 kHz. For suppression of coherent noise we employed a phase alternating pulse sequence (PAPS) for phase switching only during the excitation period [4].

For determination of the pressure-broadened half-width  $\Delta\nu$  of the line, the signal was analysed by a least squares program according to the expression

$$S(t) = S_0 \cdot e^{-t^2/4q^2} e^{-t/T_2} \cdot \cos(2\pi\nu \cdot t + \Phi) \quad (1)$$

with  $S_0$ ,  $T_2$ ,  $\nu$ , and  $\Phi$  as fitting parameters.  $S_0$  is the value of the signal at the end of the microwave pulse,  $1/T_2 = 2\pi\Delta\nu$  the decay rate due to collisions either with other molecules or with the walls of the sample cell,  $\nu$  corresponds to the frequency of the oscillating signal and  $q$  is related to the Doppler halfwidth ( $\Delta\nu_D = (\ln 2)^{1/2}/2\pi q$ ) of the line.

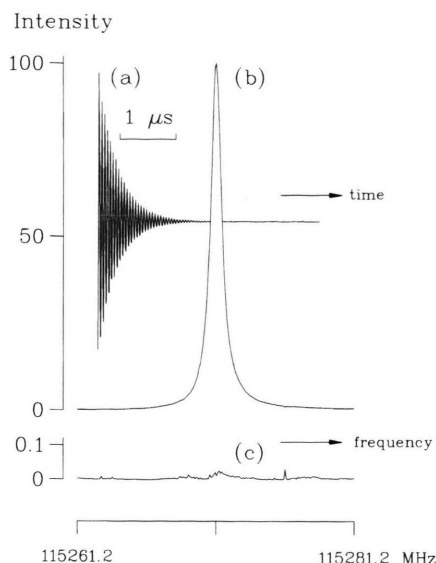


Fig. 2. Example for a time-domain record of the  $J' \leftarrow J = 1 \leftarrow 0$  line of  $^{12}\text{C}^{16}\text{O}$  in a mixture with Ar at  $P_{\text{CO}} = 36.0$  mTorr and  $P_{\text{Ar}} = 85.9$  mTorr, at  $T = 244.7$  K. (a) transient emission signal recorded at 10 ns sample interval; (b) power spectrum in arbitrary intensity units; (c) power spectrum of residuum of time domain data fitted to a time-domain Voigt-profile. Intensity with respect to (b) enlarged by a factor of 100.

As an example, Fig. 2 shows the transient emission signal of the investigated transition of CO in a mixture with Ar together with the corresponding power spectrum and its residuum.

For the frequency domain studies on foreign gas broadening of the  $J' \leftarrow J = 1 \leftarrow 0$  rotational line of CO we employed the RAD spectrometer, a general description of which is given in [5]. The experimental setup includes the following parts and components, Figure 3:

- a commercial synthesizer of the “Kvarz” Company [6]. Frequency range 78.33 -118.1 GHz, mean output power level about 10 mW;
- a rubidium frequency standard as reference for the synthesizer;
- an amplitude modulator (synchronous mechanical chopper);
- an absorption cell with acoustic detector (RAD cell), as described in [2];
- a homemade digital synchronous detector (DSD) board with two integrated channels providing ampli-

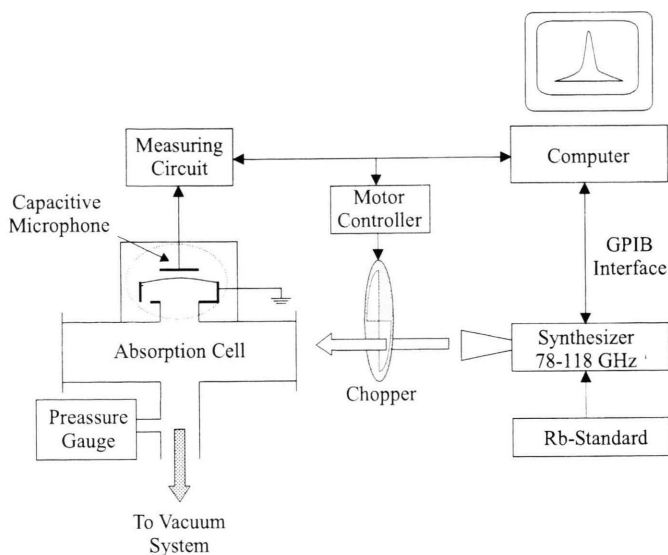


Fig. 3. Scheme of the experimental setup of the computer controlled RAD spectrometer with MW synthesizer.

fication, synchronous averaging and digitizing of the signals received by the microphone based sensor, as well as the internal square wave reference signal for the motor controller of the chopper;

- an IBM PC/AT compatible computer with the software developed for the spectrometer system control described above, collects and processes digitally the recorded data;

- an absolute pressure gauge (MKS Baratron Type 122AAX-00010ADS) with an accuracy of 0.15%.

The following procedure for the study of collisional broadening by foreign gases was used. The RAD cell was first filled with pure carbon monoxide to a fixed pressure of about 0.4 Torr and the self-broadened halfwidth of the line was determined. After that, a controlled amount of foreign gas was added and the line halfwidth was again determined. This procedure was continued by further adding a foreign gas up to a partial pressure of about 3 Torr. The self-broadening parameter of carbon monoxide was also remeasured with higher accuracy than before [2] using the Baratron pressure gauge.

For the detailed lineshape investigation, a computer program makes a step-by-step frequency scan controlling the synthesizer via an NI GPIB interface. During the scan the program stores experimental data from the DSD board onto a hard disk. A scan frequency range of about six or ten line halfwidths was used.

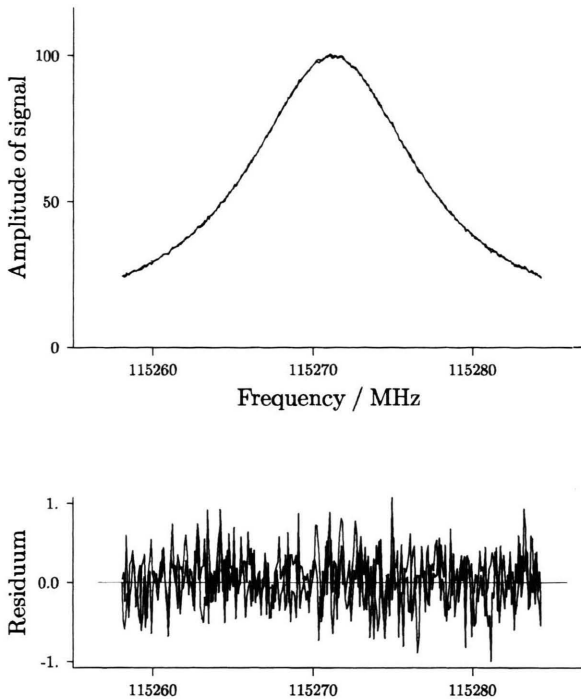


Fig. 4. Frequency-domain record of the  $J' \leftarrow J = 1 \leftarrow 0$  line of  $^{12}\text{C}^{16}\text{O}$  in a mixture with Ar at  $P_{\text{CO}} = 0.405$  Torr and  $P_{\text{Ar}} = 1.794$  Torr, at 296 K. The residuum resulting from a fit of 600 data points to a Lorentzian model is also shown.

All lines were recorded twice in order to avoid any amplitude instability by performing a forward and a backward frequency scan. Two integral channels of the DSD board were used to solve the problem with indefinite signal phase (quadrature detection).

In order to determine the pressure-broadened halfwidth of the investigated line, the experimental data set was fitted by a least squares analysis to the following model function describing a Lorentzian line-shape with inclusion of a linear frequency dependence of the MW power and a constant level of baseline

$$I(\nu_n) = A_0 \cdot (1 + k \cdot (\nu_n - \nu_0)) \cdot \frac{\Delta\nu}{(\nu_n - \nu_0)^2 + (\Delta\nu)^2} + b \quad (2)$$

where  $A_0$  is an amplitude factor,  $\Delta\nu$  the half-width at half-maximum (HWHM) of the Lorentzian lineshape,  $\nu_n$  the MW frequency,  $\nu_0$  the frequency of line center,  $k$  the linear trend coefficient of MW power, and  $b$  the constant level of baseline.

As an example a recording of a portion of six halfwidths of the CO line broadened by argon is pre-

Table 1. Self- and foreign gas pressure broadening parameter  $Cw$  for the  $J' \leftarrow J = 1 \leftarrow 0$  line of  $^{12}\text{C}^{16}\text{O}$  obtained with frequency(RAD)- and time(FTMMW)-domain technique, respectively.

CO and Perturber	$Cw(T)/\text{MHz Torr}^{-1}$		$T/\text{K}$
	RAD	FTMMW	
CO	3.43(1)	3.42(2)	296(2)
N <sub>2</sub>	3.22(2)	3.16(3)	296(2)
O <sub>2</sub>	2.83(2)	2.83(3)	296(2)
Air	3.09(2)	3.07(3)	298(1)
He	1.94(1)	1.97(2)	299(1)
Ne	1.66(1)	1.69(3)	301(1)
Ar	2.77(1)	2.75(9)	296(1)
Kr	2.84(1)	2.77(5)	301(1)

Table 2. Self- and foreign gas pressure broadening parameter  $Cw(300)$  and temperature dependence exponent  $n$  for the  $J' \leftarrow J = 1 \leftarrow 0$  line of  $^{12}\text{C}^{16}\text{O}$  obtained from time-domain studies (this work) and investigations of absorption spectra (literature data).

CO and Perturber	$Cw(300 \text{ K})$ MHz/Torr	$n$	Reference
CO	3.38(1)	0.80(1)	this work
	3.39(26) <sup>a</sup>	0.75(10) <sup>a</sup>	[7]
	3.36(2) <sup>b</sup>	0.93(3)	[8]
	3.45(6) <sup>c</sup>	—	[9]
N <sub>2</sub>	3.13(1)	0.74(2)	this work
	3.26(10) <sup>b</sup>	0.86(12)	[8]
	2.99(14)	0.74(10)	[10]
O <sub>2</sub>	2.80(1)	0.76(2)	this work
	2.58(10) <sup>b</sup>	1.09(13)	[8]
Air	3.05(1)	0.76(2)	this work
	2.92(14)	0.74(10)	[10]
He	1.97(1)	0.55(2)	this work
	1.86(20) <sup>a</sup>	0.54(11) <sup>a</sup>	[7]
	1.97(9) <sup>d</sup>	0.55(7) <sup>c</sup>	[11]
Ne	1.69(1)	0.72(3)	this work
	1.62(17) <sup>a</sup>	0.80(12) <sup>a</sup>	[7]
Ar	2.73(3)	0.72(6)	this work
	2.70(26) <sup>a</sup>	0.73(11) <sup>a</sup>	[7]
Kr	2.78(2)	0.71(13)	this work

<sup>a</sup> obtained from the fit of the data at 294 K, 195 K, and 77 K; <sup>b</sup> calculated value for  $Cw(300)$  from given  $Cw(293)$  and  $n$  values; <sup>c</sup> at 295.7(10) K; <sup>d</sup> obtained from the fit of the data at temperature region 90 - 500 K.

sented in Fig. 4 together with the residuum of the fit to the model function (2).

### III. Results and Discussion

The results of the comparative study for foreign gas pressure broadening of the  $J' \leftarrow J = 1 \leftarrow 0$  rotational line of carbon monoxide( $^{12}\text{C}^{16}\text{O}$ ) in the ground

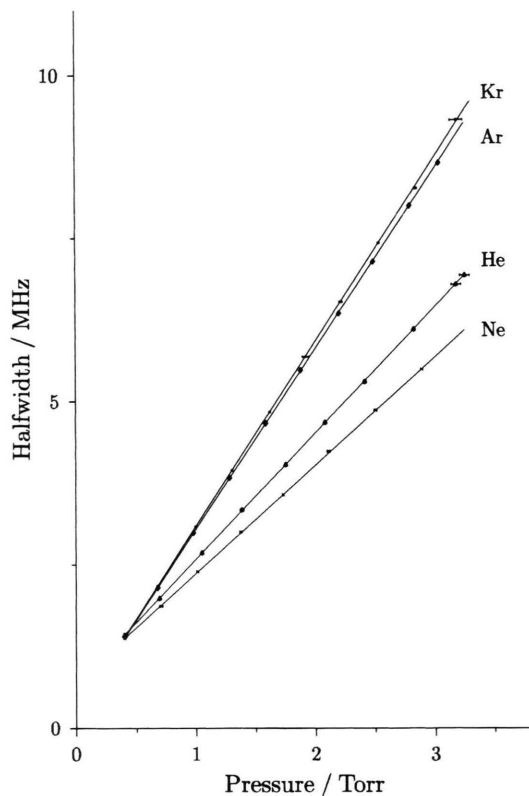


Fig. 5. Pressure dependence of HWHM of the CO  $J' \leftarrow J = 1 \leftarrow 0$  line for mixtures of carbon monoxide with rare gases obtained with the technique of frequency-domain at room temperature. Pressure gives total pressure of mixtures with  $P_{\text{CO}} = 0.4$  Torr.

vibrational state at room temperature are presented in Table 1, showing the pressure broadening parameter  $Cw$  for various buffer gases.  $Cw$  is the slope of the linear pressure dependence of the halfwidth of the line ( $Cw = d(\Delta\nu)/dP$ ), and was determined from a linear regression analysis of the observed  $\Delta\nu$ -values for different buffer gas pressures. The data demonstrate a good consistency between the results from the measurements with use of time- and frequency-domain techniques, respectively.

The improvements in the experimental set-up for the frequency-domain technique allowed to increase significantly the accuracy of pressure broadening data as compared to previous results [2]. The pressure dependence of halfwidth of the line are shown in Fig. 5 for broadening by the rare gases He, Ne, Ar, and Kr together with the straight lines from linear least squares analysis. Figure 6 shows the corresponding results for self- and foreign gas broadening by  $\text{N}_2$ ,  $\text{O}_2$  and air.

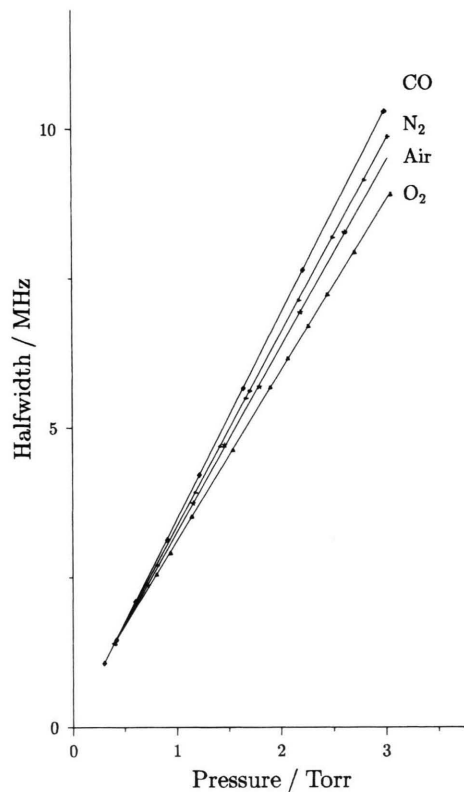


Fig. 6. Pressure dependence of HWHM of the CO  $J' \leftarrow J = 1 \leftarrow 0$  line for the pure gas and mixtures with atmospheric gases obtained with the technique of frequency-domain at room temperature. Pressure gives total pressure, with fixed partial pressure  $P_{\text{CO}} = 0.4$  Torr for the mixtures.

For a study of temperature dependence, the parameters of interest are  $Cw(300)$  and  $n$ , which are used for the determination of a pressure broadening parameter  $Cw(T)$  by the empirical relation

$$Cw(T) = Cw(300) \cdot (300/T)^n \quad (3)$$

Figures 7 and 8 show the temperature dependence of the broadening parameter  $Cw(T)$  for the  $J' \leftarrow J = 1 \leftarrow 0$  line of CO mixed with various buffer gases.

The results for  $Cw(300)$  and  $n$  are given in Table 2 together with the corresponding data from the literature [7 - 11]. Apart from the results for the mixture with  $\text{O}_2$  [8], the broadening parameters  $Cw(300)$  show good consistency. Good agreement for results from different laboratories is also found for the temperature dependence coefficient  $n$  with exception of self- and  $\text{O}_2$ -broadening [8].

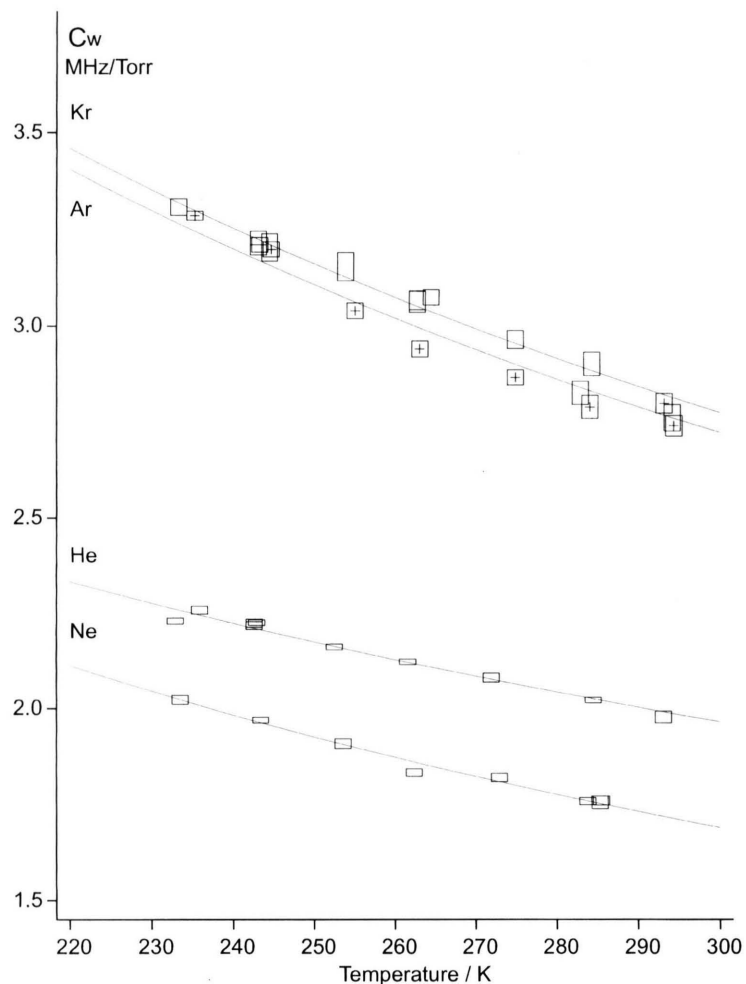


Fig. 7. Temperature dependence of the foreign gas pressure broadening parameter  $C_w(T)$  of the CO  $J' \leftarrow J = 1 \leftarrow 0$  line for the rare gases He, Ne, Ar, and Kr obtained with time-domain technique. Crosses give results for argon.

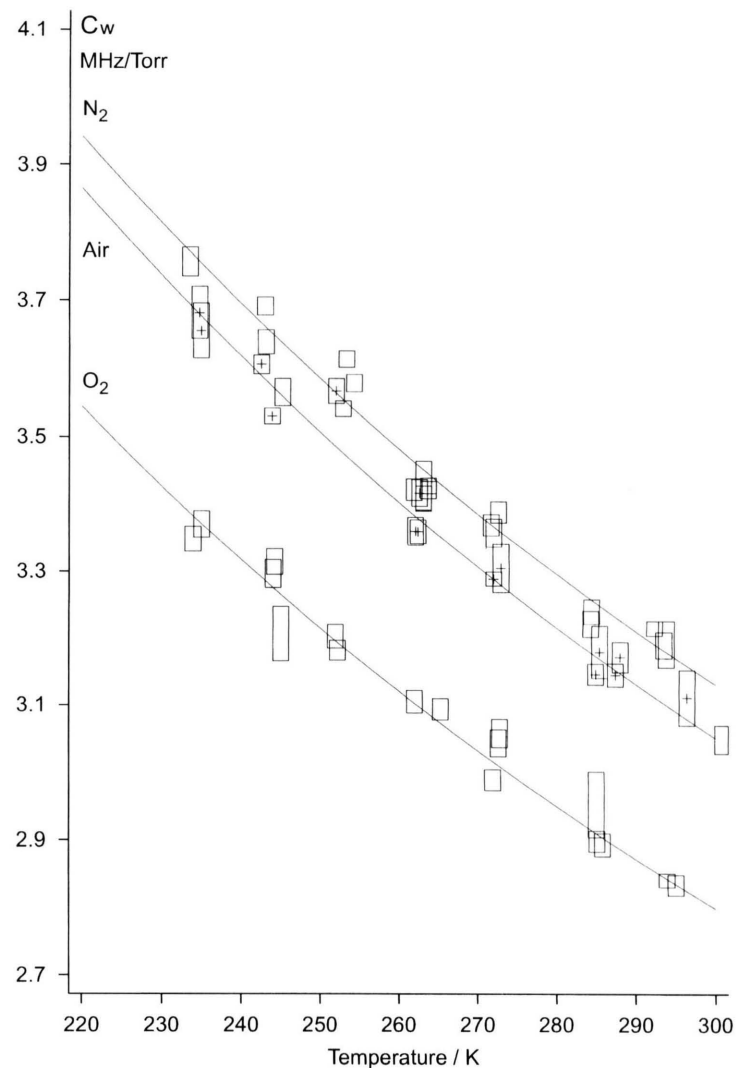


Fig. 8. Temperature dependence of the foreign gas pressure broadening parameter  $C_w(T)$  of the CO  $J' \leftarrow J = 1 \leftarrow 0$  line for the atmospheric gases  $N_2$ ,  $O_2$  and air obtained with time-domain technique. Crosses give results for air.



#### IV. Conclusion

Our results presented in this work demonstrate a good consistency between the data from the time- and frequency-domain experiment, which are approximately of the same accuracy now. This study allowed to increase significantly the accuracy of the pressure broadening parameter  $Cw$  and the temperature exponent  $n$  for the  $J' \leftarrow J = 1 \leftarrow 0$  rotational line of carbon monoxide in the pure gas and mixtures with He, Ne, Ar, Kr, N<sub>2</sub>, O<sub>2</sub>, and air.

In our opinion both techniques have the advantage for line broadening studies that they minimize baseline distortions which may limit the accuracy of line shape data when using conventional MMW absorption spectrometers. In particular, the RAD cell has a broadband receiver, and influences of standing waves are suppressed efficiently using Brewster angle cones as cell windows.

No significant lineshift due to foreign gas pressure was found in our investigations. However the pure gas showed a tendency to negative pressure shift which was estimated to be less than 0.01 MHz/Torr in agreement with a recently reported value within the error limit (−0.027(24) MHz/Torr) [9]. Extrapolation to zero pressure yields a center line frequency  $\nu_0 = 115\,271.202(1)$  MHz which is in excellent agreement with the result from sub-Doppler investigations by Winnewisser *et al.* [16].

Finally we would like to note that the comparison of our data with results from infrared investigations on the  $m = 1$  ( $J' \leftarrow J = 1 \leftarrow 0$ ) line of the fundamental vibrational band gives also a good consistency, see Table 3. This allows the conclusion that line broadening of the rovibrational line is predominantly governed

Table 3. Comparison of pressure broadening parameter  $Cw(300)$  and temperature dependence exponent  $n$  for the  $J' \leftarrow J = 1 \leftarrow 0$  of  $^{12}\text{C}^{16}\text{O}$  line obtained from time-domain studies with literature data for the R-branch,  $m = 1$  transition of fundamental vibrational band.

CO and Perturber	$Cw$ (300 K) MHz/Torr	$n$	Reference
CO	3.38(1)	0.80(1)	this work
	3.42(5) <sup>a</sup>	0.770 <sup>a</sup>	[12, 13]
N <sub>2</sub>	3.13(1)	0.74(2)	this work
	3.15(9) <sup>a</sup>	0.841 <sup>a</sup>	[12, 13]
	3.12(12) <sup>b</sup>	—	[14]
	3.14(16) <sup>c</sup>	—	[15]
O <sub>2</sub>	2.80(1)	0.76(2)	this work
	2.81(10) <sup>a</sup>	0.836 <sup>a</sup>	[12, 13]
Ar	2.73(3)	0.72(6)	this work
	2.70(8) <sup>c</sup>	—	[15]

<sup>a</sup>  $Cw(300)$  was given from [12], exponent  $n$  from [13];

<sup>b</sup>  $T = 298$  K; <sup>c</sup> the value for room temperature is absent.

by rotational relaxation phenomena like collisional-induced transitions between rotational levels.

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