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Comparative Studies of $J' \leftarrow J = 1 \leftarrow 0$ CO Line Parameters in Frequency and Time Domains

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The pressure broadening of the CO $J' \leftarrow J = 1 \leftarrow 0$ line has been studied by two different techniques. Analysing coherent transients by the time-domain technique yields a broadening parameter $C_w = 3.43(2)$ MHz/Torr, whereas the analysis of the absorption spectrum by the frequency-domain technique results in $C_w = 3.45(3)$ MHz/Torr. 1996 Academic Press, Inc.

I. INTRODUCTION

A growing interest in measurements of molecular line parameters—such as pressure broadening, pressure shift, and lineshape—makes simultaneous joint studies of the same line parameters using different methods of measurements very desirable. Thus, possible sources of errors may be revealed and more reliable values for lineshape parameters will eventually be obtained. The present paper is concerned with such studies on the $J' \leftarrow J = 1 \leftarrow 0$ rotational line in the vibrational ground state of carbon monoxide ($^{12}C^{16}O$), carried out jointly by Kiel University and Nizhnii Novgorod Applied Physics Institute.

Early stages of Kiel studies of CO $1 \leftarrow 0$ line self-broadening in time domain were described in (*1*). With the improved sensitivity of the Kiel millimeter-wave (mmW) Fourier transform (FT) spectrometer it becomes now possible to study the self-broadening of this line at room temperature. The collaboration between Kiel and Nizhnii Novgorod laboratories made it possible to perform comparative measurements of self-broadening in both time and frequency domains.

Also of interest in this work was the possibility of comparing our frequency-domain data, obtained by acoustic detection, with results from previous measurements (*2*), (*3*) which employed millimeter-wave radiation detection. In the work of Nerf and Sonnenberg (*2*) bolometric power detection was used, whereas Colmont and Monnanteuil (*3*) employed a Schottky barrier diode as power detector. These detectors contrast to acoustic detection, which has the advantage that the minimum detecable absorption is determined by the incident radiation power; i.e., the signal-to-noise ratio increases with increasing power. In view of further applications of both techniques in the frequency- and time domain, comparing the data as well with previous results gives valuable information on their reliability and accuracy.

The subject of this paper is measurements of the CO $1 \leftarrow 0$ line self-broadening at room temperature in the time domain with an improved mmW spectrometer and in the frequency domain with acoustic detection. We will discuss our results and compare them to other existing data.

II. EXPERIMENTAL

A general description of the experimental technique and the procedure for time-domain measurements was given in (*1*). Due to improvements in the experiment, the sensitivity of the spectrometer was increased by about one order of magnitude. Now we are able to measure the $1 \leftarrow 0$ rotational line of CO even at room temperature in a pressure range from 1 to about 300 mTorr. Here we will give only brief information about the main differences of the experimental setup with respect to (*1*).

As the source of the fundamental microwave radiation we used 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 modulation) to the biphase modulator. The modulated signal was amplified (HP 83554A) up to 20 dBm and fed into a multiplier optimized on the third harmonic, which used a varactor diode as nonlinear device.

In our experiment we used the upper sidebands of 160.00012 MHz and 137.00012 MHz for polarizing and local oscillator radiation, respectively. The sidebands have to fulfill only the following condition: the difference between them must be a multiple of the synchronization frequency (500 kHz) of the pulse generator. The use of modulation

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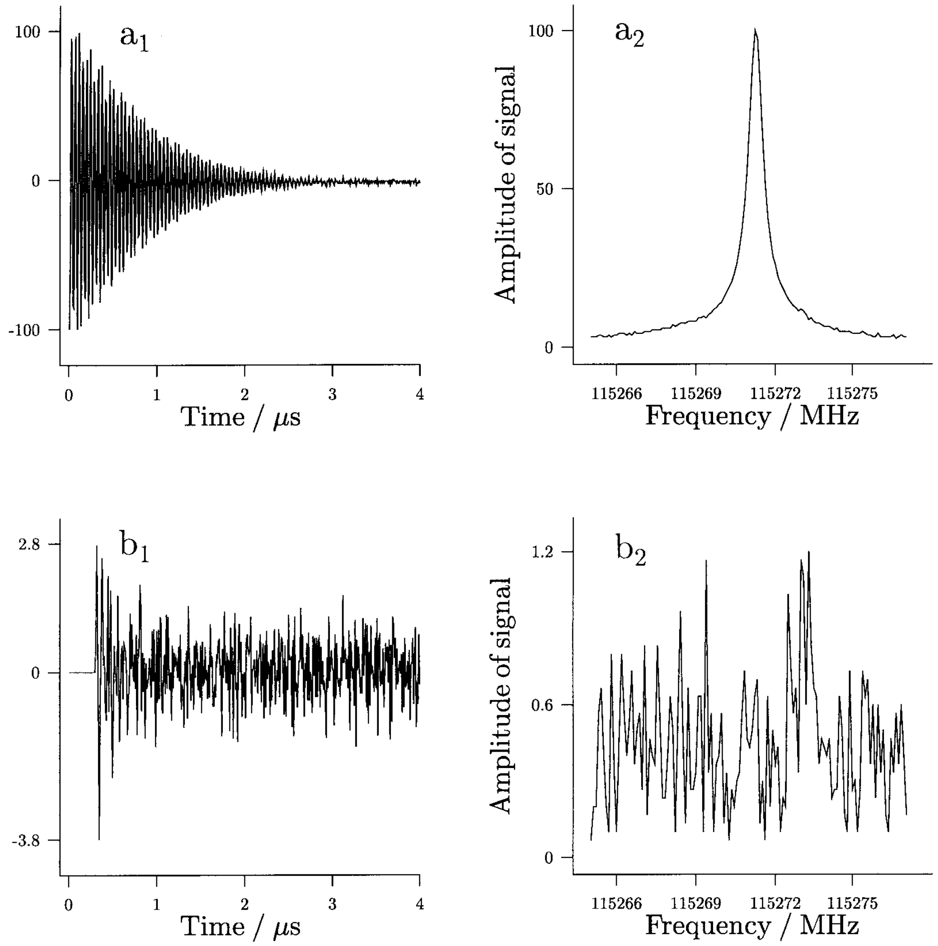

FIG. 1. (a) Transient emission signal (a_1) for the $^{12}C^{16}O$ $J' \leftarrow J = 1 \leftarrow 0$ line at 296.8 K and 32.6 mTorr, together with the corresponding power spectrum (a_2). Start of the recording ($t = 0$): 200 ns after the end of the excitation pulse. Line center frequency: 115 271.205(1) MHz, HWHM: 0.121(2) MHz. (b) Residue of the fit of the time-domain signal (b_1) to a Voigt-profile, together with the corresponding power spectrum (b_2). The first 30 data points were omitted in the fit analysis.

frequencies which are not multiples of this synchronization frequency gives some advantages since distortions from the radiofrequency (RF) synthesizers disappear in the averaged signal because they are not phase synchronous.

The RF switch in (*1*), which controls the change in the modulation frequency, is replaced by a system of four RF switches. Two of them are mounted in series for each of the two radiofrequencies. This gives more than 60 dB suppression of the sideband which is currently not in use. We were using a delay of about 100 ns between the switching off of the polarizing and the switching on of the local sideband. This procedure minimizes distortions which might be produced by reflections of the TTL signals in our system.

The mmW radiation in the range 105—120 GHz was fed either into a free space cell by a horn antenna, or into an oversized waveguide cell by a taper. The brass waveguide cell allows measurements in a temperature range between 220 K and room temperature.

Instead of the software averaging system in (*1*) we now use a fast hardware averager (Strauss 100 MHz transient recorder TR-AV 100-8/32). The repetition rate of the experiment is about 50 kHz. The sample interval of 10 ns implies a Nyquist frequency of 50 MHz.

For suppression of coherent noise we employed a phase alternating pulse sequence (PAPS) for phase switching only during the excitation period (*6*).

In Fig. 1 the transient emission signal (a_1) for the CO $1 \leftarrow 0$ line is shown for times $t > 0$ referring to the offset of the excitation pulse. The power spectrum of the line (a_2) is also depicted, and was obtained by Fourier transformation of the time-domain signal. The figure also shows the residue of the time-domain signal (b_1) after fitting to a Voigt-profile model, and the corresponding power spectrum (b_2). In this fit the first 30 datapoints ($\equiv$300 ns) were omitted to suppress distortions of the switching transients.

A general description of the technique of frequency-do-

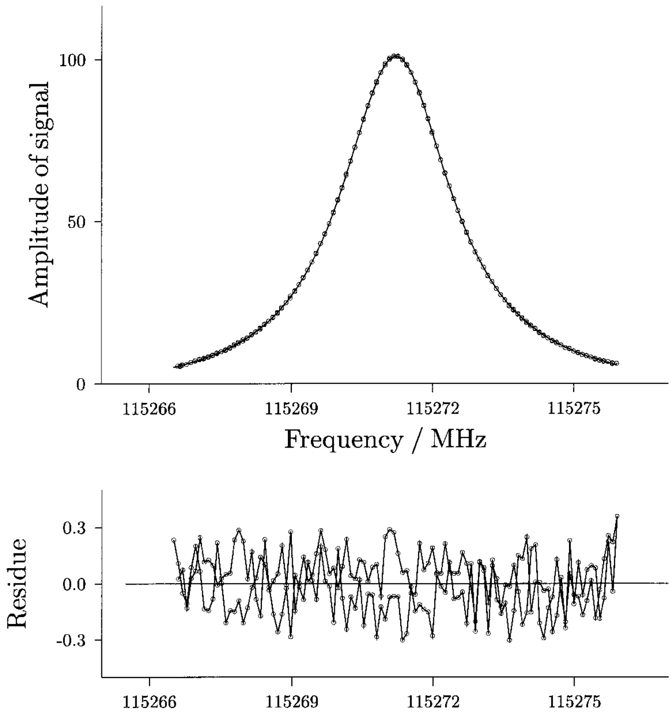

FIG. 2. CO 1 ← 0 line in frequency domain obtained with the RAD spectrometer at 296 K and 0.39 Torr. Line center frequency: 115 271.200(2) MHz, HWHM: 1.435(3) MHz. The fit to a Lorentzian lineshape model and the residue of the fit are also shown.

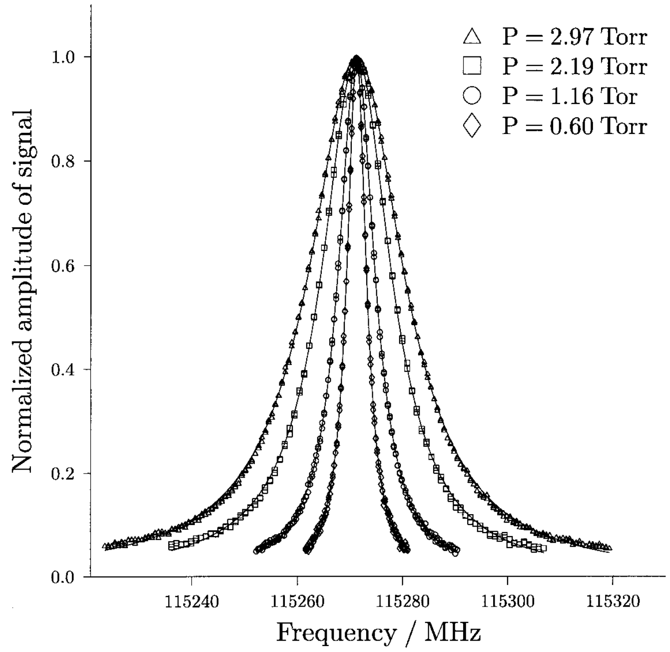

FIG. 3. CO 1 ← 0 line in frequency domain at room temperature for different pressures.

main measurement with acoustic detection (RAD spectrometer) was given in (*4*).

A computer controlled Russian backward wave oscillator (BWO) in the range of 78–118 GHz, based on a frequency synthesizing system, was used as the source of radiation. The reference frequency of the synthesizer was produced by a rubidium frequency standard. The output power level was about 10–20 mW. Amplitude modulation and acoustic detection of the signal from the spectral line (RAD gas cell) were used. In the course of experiments we tried to minimize the reflections of millimeter-wave radiation between cell windows and the BWO output horn antenna, which were the main source of systematic errors of lineshape measurements in this spectral range. The most satisfactory results were obtained when Brewster angle cones were used as cell windows. An acoustic signal from the sample cell was detected by a homemade two-channel digital lock-in amplifier. The pressure of CO in the sample cell was measured by a commercial pressure gauge of VDG-1 type, which had an accuracy of about 5%. Measurements were made at room temperature (296 ± 1 K).

A typical record of the collision-broadened CO line in the frequency domain at a pressure of 0.39 Torr is presented in Fig. 2 together with the fit to the Lorentzian lineshape model and the residue of the fit.

A set of observed profiles of the line at different pressures is presented in Fig. 3 for pressures ranging from 0.60 Torr up to 2.97 Torr. All lines were recorded twice, first by step-

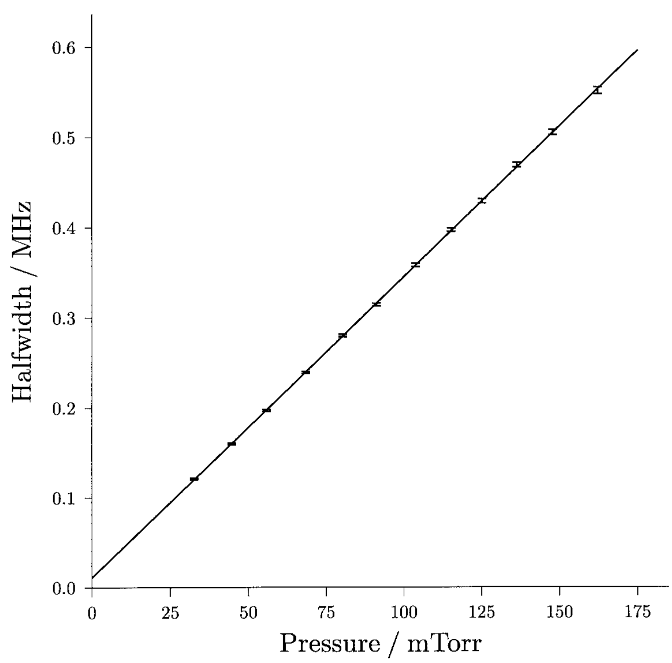

FIG. 4. Experimental results for the pressure dependence of HWHM of the CO 1 ← 0 rotational line obtained in time domain at 296.8 K. The error bars give one standard deviation of the halfwidth, resulting from a fit analysis of the emission signal.

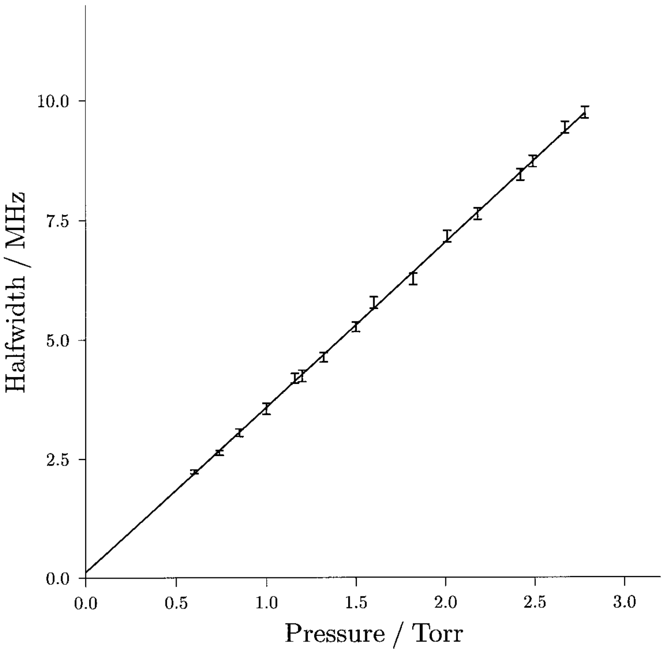

FIG. 5. Pressure dependence of HWHM of CO 1 ← 0 line obtained in frequency domain at 296 K. The error bars give one standard deviation of the halfwidth, resulting from a fit analysis of the absorption signal.

ping the frequency up and second by stepping the frequency down.

III. RESULTS AND DISCUSSION

Figures 4 and 5 give the results for the pressure dependence of the investigated CO line halfwidth (HWHM) measured at room temperature with the two techniques, respectively. The results for the line center frequency and the line broadening parameter at room temperature are presented and compared with literature values in Table 1. No significant pressure shift of the line was found in our investigations.

It should be noted that the accuracy of line shape measurements by the RAD spectrometer even at pressures up to about 4 Torr is limited by baseline problems.

The experimental values demonstrate good consistency between the three methods of investigation (two used in the present paper and one earlier in the frequency domain).

However, in the present status of the time-domain experiment, we are still facing some problems concerning the reliability of pressure-broadening data for the investigated transition.

First, because of the low power of the radiation field, between 10 and 20 μW, the molecules might not be uniformly polarized over the full Doppler profile. Deviations from a Voigt-profile lineshape, which is assumed in the analysis, are minimized at sufficiently large pressures since then the pressure broadening is large with respect to the Doppler broadening.

Our results at lower pressures also indicate that shorter pulses give better agreement with the frequency domain data. This behavior might be roughly explained by an increase of the excitation bandwidth with decreasing pulse length. On the other hand, shorter pulses lead to a substantial decrease of signal intensities. At present we use polarizing pulse lengths of 140 ns. Polarizing with radiation ± 1 MHz offresonant from the transition frequency, we observed no significant decrease of the signal amplitude. This indicates that the

TABLE 1
Parameters for the $J' \leftarrow J = 1 \leftarrow 0$ $^{12}C^{16}O$ Line Obtained in Frequency and Time Domains

Technique	Line Frequency [MHz]	Reference
Frequency-Domain	115 271.202(2)	this work
	115 271.204(5)	(5)
Time-Domain	115 271.200(5)	this work

Technique	Self - Broadening Parameter [MHz/Torr]	Reference
Frequency-Domain	3.45(3)	this work
	3.4(3)	(2)
	3.43(4)	(3)
Time-Domain	3.43(2)	this work

Note. The given errors for the time-domain results are estimates for systematic errors and do not reflect the smaller statistical errors from the fit analysis.

bandwidth of the pulse is broad enough to yield uniform polarization over the full Doppler range (Doppler halfwidth is about 130 kHz).

Second, the time-domain technique generates switching transients, which are more important for shorter pulses. In order to minimize their influence on the recorded signals, typically the first 20 to 40 data points (corresponding to a time interval of 200 to 400 ns) had to be omitted for the data analysis. Thus at higher pressures with shorter decay times, the sensitivity of the method is strongly reduced. This limits the usable range of pressures to less than 200 mTorr.

Taking into account the limitations of the applicability of the time-domain method, reasonable results on pressure broadening of the $J' \leftarrow J = 1 \leftarrow 0$ line were obtained for intermediate pressure ranges and short pulse lengths, as shown in Fig. 4 and Table 1.

IV. CONCLUSION

Our results presented in this work demonstrate good consistency between the data from time- and frequency-domain experiments, which are of approximately the same accuracy. Within the given error limits they also agree with the data from previous frequency-domain studies on the self-broadening of the CO $1 \leftarrow 0$ rotational line (*2, 3*), which are about an order of magnitude less accurate in one case (*2*) and of comparable accuracy in the other case (*3*).

The problems involved in the present state of the time-domain experiment require further improvements of the experimental setup and theoretical description of the recorded signal in order to make this method applicable to a wider range of rotational relaxation studies.

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