

Line Broadening and Shifting Studies of the $J = 5 \leftarrow 4$ Transition of Carbon Monoxide Perturbed by CO, N₂, and O₂

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The collisional relaxation of the $J = 5 \leftarrow 4$ rotational transition of CO induced by carbon monoxide, nitrogen, and oxygen has been studied at room temperature. Pressure-broadening parameters were determined as 3.29(2), 2.61(2), and 2.30(2) MHz/Torr for CO, N₂, and O₂ buffer gases, respectively. Experimental deviations from the Voigt line shape profile have been observed which are mostly the effect of a narrowing in the spectral line core. The difference between the model profile and the experimental profile is less than 0.5% of the maximum line amplitude in the investigated pressure range 0.2–5 Torr. In addition, a small positive collision-induced shift of the line center frequency was observed for the pure gas, corresponding to a pressure self-shift parameter of 6(3) kHz/Torr. © 2002 Elsevier Science (USA)

I. INTRODUCTION

Studies of the effect of collisional relaxation phenomena of gas-phase molecular spectral lines are usually done by observation of the pressure dependence of absorption line profiles. An accurate modeling of such experimental line shapes is particularly important with respect to the interpretation of spectra from Earth's and other planetary atmospheres in order to better understand their composition and their dynamical behavior (1, 2). Precise lineshape parameters for description of collision-induced effects are required not only to interpret atmospheric absorption, but also to better understand intermolecular interactions and to develop more advanced theories describing their effect on the lineshapes of rotational or rovibrational transitions (3).

For these reasons, the CO molecule is of special interest. Carbon monoxide is a trace gas molecule in Earth's as well as other planetary atmospheres and is also rather abundant in the interstellar medium (4, 5). Detection of emission lines of CO from some galaxies could also help to clarify the star formation processes, see for example (6). Thus, there is a necessity to investigate rotational lineshapes of CO in many respects, as particularly pointed out in a recent investigation of the $J = 3 \leftarrow 2$ transition in the submillimeter wavelength range (7). Moreover, carbon monoxide is an often-studied diatomic molecule with well-known parameters of intermolecular interaction, and therefore it is very interesting to compare the experimental results with a prediction of the theoretical models (8).

The frequency of the CO $J = 5 \leftarrow 4$ transition in the ground vibrational state was determined previously (9–12) but, to our knowledge, collisional relaxation effects for this rotational

line have not been investigated before. A few papers on line-shape investigations were concerned with the study of the $R(4) (m = 5)$ line in the fundamental vibrational band of CO (13–19). In this paper we report on the results of an experimental investigation of the collisional relaxation of the $J = 5 \leftarrow 4$ rotational line of CO induced by carbon monoxide, nitrogen, and oxygen. The description of the experimental setup is also presented.

II. EXPERIMENT AND ANALYSIS

The study was carried out by using a RAD spectrometer (20) with acoustic detection based on a broadband submm Backward Wave Oscillator (BWO) (21), stabilized against the reference signal of a mm-wave synthesizer, "Kvarz" (Nizhnii Novgorod, Russia) (22).

A block diagram of the RAD spectrometer with the BWO phase stabilization circuit is shown in Fig. 1. A tube (526–714 GHz) placed in an electromagnet with a magnetic field of about 1.0 T and driven by a high-voltage power supply (voltage ripples <10 mV on high-voltage output \approx 4000 V, voltage drift <0.1 V/h, overcurrent protection circuit with switch off time \leq 10 μ s) with a highly stable filament current output is used as radiation source. High spectral purity and low phase noise (below –25 dBc at 10 kHz in the 600-GHz range) was obtained by means of a phase-lock loop (PLL) circuit.

The PLL-circuit consists of a home-made PLL synchronizer, a quasioptical harmonic mixer with a planar Schottky-barrier diode, a beam splitter (mica plate, thickness 50 μ m), and the "Kvarz" mm-wave synthesizer (78–118 GHz, output

the slope and amplitude of the baseline are strongly reduced what is extremely important for lineshape studies.

III. RESULTS AND DISCUSSION

The results of the present investigation on pressure broadening and shift of line center of the carbon monoxide $J = 5 \leftarrow 4$ transition in the ground vibrational state at room temperature are presented in Table 1. The broadening and shift parameters given in the table are the coefficients which describe the linear dependence of $\Delta\nu_L$ (HWHM) and ν_0 (see Eq. [1]) on the pure gas pressure or the foreign gas partial pressures, respectively. The pressure dependence of $\Delta\nu_L$ is depicted in Fig. 3 for broadening by CO, N₂, and O₂ together with linear regression lines from least squares analysis.

The experimental results demonstrate the quite good sensitivity of our spectrometer. The residues which were found from the fitting to a Voigt profile line function (for example, see Fig. 2) show a pattern similar to the ones observed in a recent investigation on the $J = 3 \leftarrow 2$ of CO perturbed by N₂ and O₂ (7), but have somewhat less residuum in our case (about 0.5% of the line peak amplitude for all pressures).

In (7) these significant deviations (typically about 2% at a total gas pressure of 0.18 Torr) were explained by a narrowing of the line due to speed dependence effects of relaxation rate (28) as well as from velocity-changing collisions (collisional Dicke narrowing) (29). In the present study collisional broadening is, for the higher pressures, much more important than Doppler broadening. The effect of Dicke narrowing may be then be neglected, but speed dependence of relaxation rates and effects of velocity averaging may still contribute significantly to distortions on the Voigt (30) or Lorentzian (31) lineshape profiles. However, in view of the fact that pressure-broadening parameters which are derived from a speed-independent model are normally not much affected by an analysis based on more sophisticated lineshape models, no such further analysis was done in the present paper. We did also not measure and consider the behavior in the far wings of absorption lines where non-Lorentzian profiles prevail.

Additionally, it should be pointed out that the observed deviations from Voigt profiles may also result from distortions such as

TABLE 1

Pressure-Broadening and Frequency-Shift Parameters of the $J = 5 \leftarrow 4$ Rotational Line of Carbon Monoxide Due to Collisionally Induced Relaxation by CO, N₂, and O₂ at Room Temperature

CO and Perturber	Broadening parameter* MHz/Torr	Shift parameter* kHz/Torr
CO	3.29(2)	6(3)
N ₂	2.61(2)	5(5)
O ₂	2.30(2)	6(6)

*Error given in parentheses is in units of the last digit quoted.

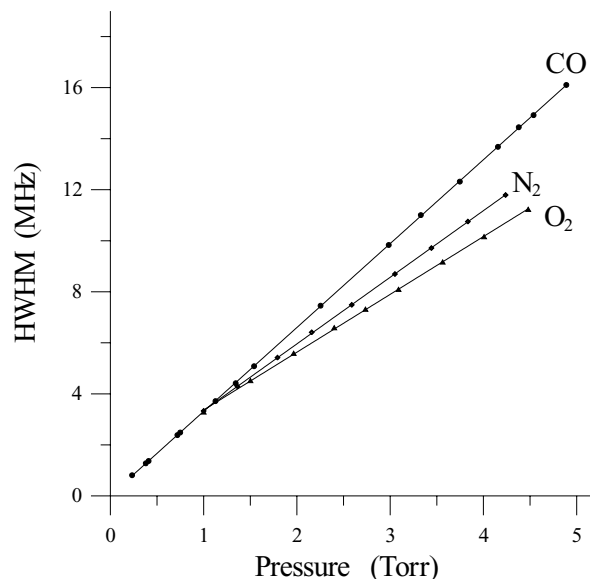


FIG. 3. Pressure dependence of the HWHM of the $J = 5 \leftarrow 4$ rotational line of carbon monoxide, broadened by CO, N₂, and O₂. The error bars retrieved from Voigt profiles for the individual points are for one standard deviation less than the size of the data point symbols.

transit time effects, e.g., collisions with the walls of the sample cell (34).

Apart from pressure broadening of the investigated line, we also observed a small, but significant pressure dependence of the line center frequency of the transition for the pure CO gas. Figure 4 shows the results for this positive selfshift of the

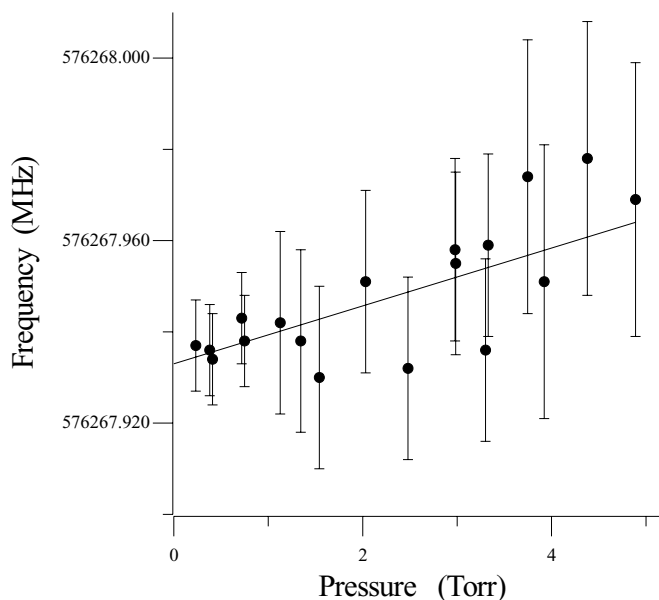


FIG. 4. Pressure dependence of center frequency of the $J = 5 \leftarrow 4$ line of pure carbon monoxide. The fitted straight line with zero pressure intercept $\nu_0 = 576267.933(5)$ MHz and slope (selfshift parameter = 6(3) kHz/Torr) is also shown.

TABLE 2
Zero-Pressure CO Line Center
Frequency of $J = 5 \leftarrow 4$

Frequency (MHz)	Reference
576267.75(10)	(9)
576267.934	(10)
576267.910(72)	(11)
576267.9305(5)	(12)
576267.933(5)	this work

line center. The corresponding slope value (shift parameter) is also given in Table 1 together with our results for the mixtures with the foreign gases nitrogen and oxygen, respectively, which also indicate a small positive but poorly determined pressure shift.

IV. CONCLUSION

The zero-pressure line center frequency of the $J = 5 \leftarrow 4$ transition of carbon monoxide, $\nu_0 = 576267.933(5)$ MHz, determined in this work demonstrates good consistency with values of previous measurements (9–12), especially with the results of Gordy's group (10) and a sub-Doppler investigation by Winnewisser *et al.* (12); see Table 2.

Our results from the pressure-broadening investigation may be compared with broadening coefficients at room temperature reported from IR studies on the $R(4) (m = 5)$ line of the fundamental vibrational band (13–19), which involves the same lower ($J = 4$) and upper ($J = 5$) rotational state as for the line reported here. As shown in Table 3, the results from the two spectroscopic ranges are in fair agreement for self-broadening, and very consistent for foreign gas broadening with N_2 and O_2 . The smaller value reported in (15) for the self-broadening parameter may

TABLE 3

Comparison of the Pressure-Broadening Parameter for the $J = 5 \leftarrow 4$ Line in the Ground Vibrational State of Carbon Monoxide Perturbed by CO , N_2 , and O_2 , with Literature Data for the R -branch, $m = 5$ Transition of the Fundamental Vibrational Band

CO and Perturber	Broadening parameter MHz/Torr	Temperature K	References
CO	3.29(2)	295	this work
	2.84(1)	300	(15)
	2.95(1)	296	(17)
N_2	2.61(2)	295	this work
	2.68	298	(13)
	2.61	300	(14)
	2.67(5)	300	(15)
	2.61	298	(16)
	2.58(3)	301	(18)
O_2	2.57(3)	301	(19)
	2.30(2)	295	this work
	2.22(5)	300	(15)

TABLE 4

Comparison of the Pressure-Broadening Parameter for the $J = 5 \leftarrow 4$ Line of Carbon Monoxide at Room Temperature, Perturbed by CO , N_2 , and O_2 , with Literature Data for Other Rotational Transition of CO in the Ground Vibrational State

Transition $J' \leftarrow J$	CO MHz/Torr	N_2 MHz/Torr	O_2 MHz/Torr	References
$1 \leftarrow 0$	3.43(1)	3.22(2)	2.83(2)	(26)
$2 \leftarrow 1$	3.36(7)	3.01(5)	2.64(5)	(35)
$3 \leftarrow 2$	^a	2.80(2)	2.46(2)	(7)
$5 \leftarrow 4$	3.29(2)	2.61(2)	2.30(2)	this work

^a 3.10(6) from IR measurement on the $R(2) (m = 3)$ line in the fundamental vibrational band [15].

indicate some systematic deviation to smaller values for the results from the measurement in the IR region; see also Table 4 below, which compares with pressure-broadening parameters of other rotational transitions of CO. The observed consistency of linewidth data for pure rotational and rovibrational transitions allows the conclusion that line broadening of the rovibrational line is predominantly governed by rotational relaxation phenomena involving rates due to collision-induced transitions between rotational levels which are not much dependent on the vibrational state. In contrast to this behavior, the lineshift data for the observed pure rotational transition (see Table 1) differ significantly from the corresponding values for the R -branch $m = 5$ transition of the fundamental vibrational band, determined to $-82(10)$ kHz/Torr for CO–CO (17), -72.8 kHz/Torr for CO– N_2 (32), and -84.9 kHz/Torr for CO– O_2 (33), respectively. Such differences are related to the fact that the rovibrational lines are predominantly shifted due to the isotropic part of the shifting cross section which does not contribute to the shifts of pure rotational transitions (36).

Finally, it may be interesting to compare our results with the experimentally determined broadening coefficients for the $J = 1 \leftarrow 0$ (26), $J = 2 \leftarrow 1$ (35), and $J = 3 \leftarrow 2$ (7) pure rotational lines of CO; see Table 4. For the pure gas, as well as for the mixtures with the foreign gases N_2 and O_2 , our results fit very well to the row of J -quantum numbers which show a slight decrease of the broadening parameters for a $J + 1 \leftarrow J$ transition with increasing J .

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