

## SPECTRAL LINE SHAPE AND SHIFT IN THE $3\nu_3$ BAND OF $\text{CO}_2$

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*The  $\text{CO}_2$  absorption near the  $3\nu_3$  band edge was measured for  $\text{N}_2$ , He- and self-broadening. A absorption calculations were arrived out using Lorentzian line profiles. The experimental and calculated data agree fairly well in the case of  $\text{N}_2$ - and self-broadening. For He-broadening, the theoretical predictions tend to underestimate the experimental measurements. The self-broadening line shifts were found to range from  $-0.005$  to  $-0.010 \text{ cm}^{-1}\text{atm}^{-1}$ .*

The spectral line shape problem has been studied extensively for a long time because of its practical importance for atmospheric optics. A number of significant results have been obtained lately for the most important minor constituents of the atmosphere, such as water vapor and carbon dioxide. Areas et.al.<sup>1</sup> discovered and measured the line pressure shift in the  $3\nu_3$  band of  $\text{CO}_2$ . Tarabukhin and Tonkov<sup>2</sup> showed that the measured  $\text{CO}_2$  absorption with  $\text{N}_2$ - and He-broadening was essentially non-Lorentzian not only outside the band, but also within it, near its edge. The authors attribute this to the spectral line mixing effect; however, theoretical estimates<sup>3</sup> for self-broadened  $\text{CO}_2$  in the  $\nu_3$  and  $\nu_3 - \nu_1$  bands show that the shape of the line center does not seem to be significantly affected. Since the results obtained in Ref. 2  $|K_{\text{exp}} - K_{\text{cal}}^L| \leq 17\%$  are important for solving a variety of applied problems, it appears useful to make further absorption

measurements in the centers of lines lying near the edge of the  $3\nu_3$  band of  $\text{CO}_2$ . To this end, absorption was measured in the region of interest for the cases of  $\text{CO}_2$ - $\text{CO}_2$ - $\text{N}_2$ - and He-broadening, and pressure shift was estimated for a number of lines in the band.

The experimental computer-controlled setup included a conventional 5 m-focal length diffraction spectrometer described elsewhere<sup>4</sup>, and an automated 15 VUMS 28-025 recording system based on an Elektronika-60 minicomputer. The monochromator slit width ranged from 0.07 to 0.12  $\text{cm}^{-1}$  in the experiments, and was well in excess of the maximum attainable spectral resolution, resulting in increased signal-to-noise ratio and improved instrumental function approximation accuracy and stability. The absorption measurements near the band edge were made under conditions approaching those reported in Ref. 2. The gas mixture and spectral system parameters recorded during the experiments are given in Table 1.

Table 1.

No of experiment	Temperature K	Path length m	$P_{\text{CO}_2}$ atm	$P_{\text{N}_2}$ atm	$P_{\text{He}}$ atm	Instrument function width $\text{cm}^{-1}$	spectral range $\text{cm}^{-1}$
1	295.5	4.45	0.516	-	-	0.072	6886 - 6989
2	295.5	8.90	0.516	-	-	0.072	6986 - 6989
3	296.0	40.00	0.0328	0.936	-	0.072	6986 - 6988
4	296.0	60.00	0.0328	0.936	-	0.072	6986 - 6989
5	296.5	60.00	0.0335	0.955	-	0.072	6986 - 6989
6	297.0	100.00	0.0343	0.966	-	0.072	6986 - 6989
7	296.0	4.45	0.528	-	-	0.072	6969 - 6976
8	296.8	40.00	0.0412	-	0.990	0.12	6986 - 6989
9	297.2	60.00	0.0419	-	1.000	0.12	6986 - 6989
10	296.7	40.00	0.0411	-	0.986	0.08	6969 - 6977
11	296.9	40.00	0.0414	-	0.946	0.08	6986 - 6989

The validity of the Lorentzian profile in describing the line absorption near the band edge was

determined from by comparing the experimental and calculated spectra. (The experimental data in Ref. 2

for the absorption coefficients may be inaccurate due to spectrum reduction errors.) Such an approach obviously requires that the effect of possible uncertainties in the input data on the discrepancy between the spectra to estimated.

Absorption calculations near the band edge were made in a straightforward manner. The parameters of the CO<sub>2</sub> spectral lines for the Lorentzian absorption calculations were taken from the AFGL compilation<sup>5</sup> except for the line halfwidths. The latter were assigned as in Ref. 6 for self- and N<sub>2</sub>-broadening. As for He-broadening, an R20 line halfwidth of 0.062 cm<sup>-17</sup> was used as the reference. The rotational quantum number dependence for He was assumed to be just the same as for N<sub>2</sub>-broadening.

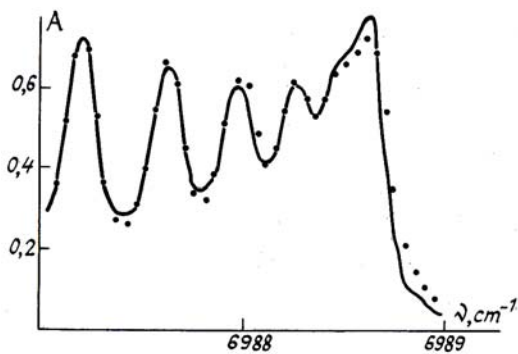


FIG. 1. CO<sub>2</sub>-CO<sub>2</sub> absorption spectrum. Solid curve: experimental data under conditions No. 1 (see Table 1). Points-calculation data.

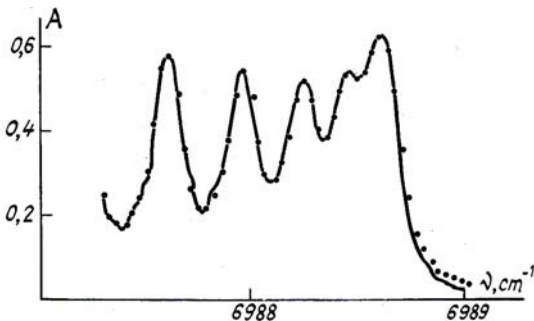


FIG. 2. CO<sub>2</sub>-N<sub>2</sub> absorption spectrum (experiment No. 5).

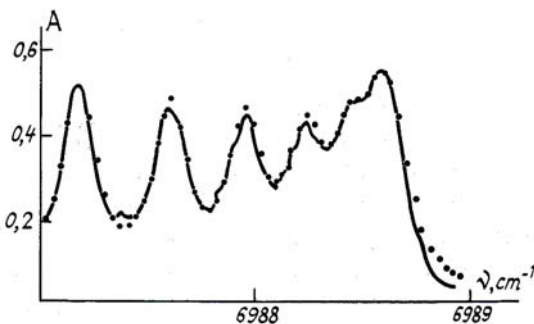


FIG. 3. CO<sub>2</sub>-He absorption spectrum (experiment No. 10).

Samples of the calculated and measured absorption data are shown for comparison in Figures 1–3 for experimental conditions given in Table 1 as Nos. 1, 5 and 10, respectively. An analysis of the data suggests the following conclusions.

First, the absorption of self-broadened CO<sub>2</sub> in a small region around 6988.55 cm<sup>-1</sup> is successfully described by a superposition of Lorentzian profiles. Under the observation conditions ( $P = 0.5$  atm,  $\gamma_{1,f} = 0.072$  cm<sup>-1</sup>), the maximum absorption in the vicinity of the edge is greatly affected by the given accuracy of the instrument function used. In the neighborhood of  $\nu = 6988.55$  cm<sup>-1</sup>, the discrepancy between the experimental and calculated data exhibits random behavior and lies within the experimental error (1±2%). At  $\nu > 6988.7$  cm<sup>-1</sup>, the Lorentzian absorption tends to exceed experimental values, as expected.

Second, in the case of the CO<sub>2</sub>-N<sub>2</sub> absorption, no systematic differences between the experimental and calculated spectra were found. In the vicinity of  $\nu = 6988.55$  cm<sup>-1</sup> for all the spectra taken.

Third, in the case of He-broadening, there is a systematic excess of the measured absorption over the calculated by 4–5% in the region of maximum absorption ( $\nu = 6988.55$  cm<sup>-1</sup>). This difference cannot be explained by possible errors in line widths or instrumental function, since a 10% change in these values will change the absorption by only 1–2% under the experimental conditions. We also attempted to assess the effect of non-Lorentzian absorption in the line wings on the absorption near  $\nu = 6988.55$  cm<sup>-1</sup>, where the absorption is determined by the superposition of different parts of line profiles. Since the absorption behavior in the 3v<sub>3</sub>-band wing is similar for He- and N<sub>2</sub>-broadening, the parameters of a Benedict profile found in Ref. 8 were employed to approximate the line wing profile for He-broadening in that band. The use of a Benedict profile (with normalization) reduces the difference at  $\nu > 6988.7$  cm<sup>-1</sup>, but in the vicinity of  $\nu = 6988.55$  cm<sup>-1</sup> the calculated absorption is practically constant and tends to be smaller than the experimental values by 5–7% in the troughs between the lines. Hence, the non-Lorentzian line wings fail to account for the observed absorption behavior, while the line mixing interpretation proposed in Ref. 2 seems to be fairly convincing. However, the effect measured in our experiments turned to be much smaller than that of Ref. 2 for He-broadening, and was not observed for self- and N<sub>2</sub>-broadening. Therefore, the use of a Lorentzian profile superposition to describe the absorption by overlapping lines seems to be quite justified in atmospheric optics problems.

The pressure shift of spectral lines in the band of interest discovered in Ref. 1 is closely related to the above problem. We have measured a number of line shifts in the *P*- and *R*-branches of the 2v<sub>3</sub> band with self-broadening because of their practical importance for studying laser propagation through the atmosphere. The differential scheme used for measurements was as follows. Step-scanning in one

direction (to avoid backlash) the monochromatic radiation was alternately sent to either cell. The first cell contained an absorbing gas whose lines were broadened and shifted due to its own pressure, and the second contained gas at low pressure (1–10 Torr). Recording the signal by turns at different frequencies leads to two spectral line profiles, one being displaced with respect to the other. If the displacement in steps of the scanning element (detector array or encoder) and the step size are known, the line shift due to pressure can be readily found. In our case, the encoder was operated with a scanning step of  $1.17 \times 10^{-3} \text{ cm}^{-1}$ . To increase the signal-to-noise ratio, the detected signal was integrated for each spectral position. The results are plotted in Fig. 4.

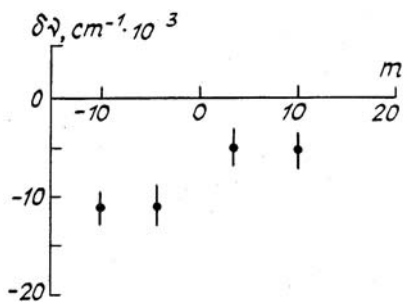


FIG. 4. Line pressure shift vs. rotational quantum number.

The data generally agree with those of Ref. 1. In fact, a negative shift weakly depending on the rotational quantum number was observed for all the lines studied. The average line shift  $-0.014 \pm 0.006 \text{ cm}^{-1} \text{ atm}^{-1}$  in the

$3\nu_3$  band given by Arcas et al.<sup>1</sup> slightly exceeds our values ( $-0.005$  to  $-0.010 \text{ cm}^{-1} \text{ atm}^{-1}$ ). A relative decrease of the line shift in the band center was found to occur.

Since the line shifts are only weakly dependent on the rotational quantum number and the shifts themselves are small, absorption near the band edge is unlikely to be influenced by this effect. Nevertheless, further investigation of the  $\text{CO}_2$  line shifts due to He pressure seems to be warranted.

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