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Broadening of the Rotational Lines of Carbon Monoxide by HCl and by Argon[1]

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The present work deals with the broadening of rotational lines of the carbon monoxide 2–0 band by both argon and hydrogen chloride. A high resolution grating spectrometer with a spectral slit width of 0.07 cm^{-1} was used, necessitating only a small correction in observed half-width values. Sufficiently small contributions of CO self-broadening were obtained by using long pathlength cells of 12 meters for CO-argon mixture and 1 meter for CO-HCl mixture. Half-width results, which are considered accurate to within ± 5 percent, are presented in the form of a table and by a graph.

It is to be hoped that the study of widths, shapes, and shifts of lines in molecular absorption spectra will eventually lead to a wealth of information about intermolecular forces. While the results obtained thus far have not been incorporated into a more complete kinetic theory, a considerable amount of information regarding molecular interactions has been obtained at high pressures by Vodar [1].[3] He has shown that diatomic molecules at pressures greater than 40 atm lose their individual rotational lines and develop a Q branch. At lower pressures the rotational lines are broadened by an increase in pressure.

Several interesting phenomena have been observed. Most interesting is the J-dependence of line width and shift. That is to say, in a given absorption band, each individual line is broadened and shifted differently. The majority of the published work has been on HCl gas pressurized by itself and by a variety of foreign gases. HCl was an obvious first choice because it has a simple spectrum with well reported and fairly wide lines. But in order to extend the range of observations it is now desirable to make measurements on other molecules.

Self-broadening of carbon monoxide lines has been measured [2, 3, 4] and foreign gas broadening of CO due to CO_2 has been also reported [5]. In this study the broadening of lines in the 2–0 band of CO due to argon and HCl was determined. These lines are narrow and a spectrometer of very high resolving power is required. Line width is proportional to the pressure of the broadening gas and better accuracy is obtained by using high pressures. In practice a compromise must be drawn between the advantages of broad lines and the difficulties of making reliable corrections for the overlapping of adjacent lines.

The spectrometer used was the grating instrument described by Plyler and Blaine [6], used double passed. In the region of the band under study the spectral slit width was 0.07 cm^{-1}.

The half width γ of a line is defined as half its width at half its maximum height on the plot of extinction coefficient (in cm^{-1}) versus frequency (in cm^{-1}). The half width of a line in the spectrum of a mixture of gases may be expressed as the sum of contributions from each component of the mixture

$$\gamma = \gamma_A^0 P_A + \Sigma \gamma_i^0 P_i$$

where γ_A^0 is the broadening constant (in cm^{-1} atm^{-1}) of the absorbing gas and γ_i^0 the broadening constant of the ith foreign gas. The half widths of the lines actually observed were between 0.1 and 0.2 cm^{-1}. The ratio of slit width to line width was between 0.3 and 0.1, and accordingly small enough to make possible the accurate application of direct-instrumental corrections after the manner of Kostkowski and Bass [7]. The correction tables of Izatt [8] were used for the purpose, since these embrace a larger range of values than those presented by Kostkowski and Bass. The instrumental correction to the line half width amounted in most cases to between 1 and 5 percent and the largest correction was 8 percent.

It was decided not to depend upon the published values for the self-broadening constant of CO and for this reason long absorbing paths were used so that the quantity of CO was negligible by comparison with the quantity of foreign gas broadener.

The broadening constants listed in the table were calculated from the spectra of samples under the following conditions:

3 mm CO+4 atm argon; pathlength 12 M
20 mm CO+3 atm argon; pathlength 12 M
50 mm CO+2.22 atm HCl; pathlength 1 M

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[3] Figures in brackets indicate the literature references at the end of this paper.

The unsmoothed results are shown in table 1. Each point in figure 1 represents the mean of the values for corresponding lines in the P and R branches.

Babrov, Ameer, and Benesch [9] have reported the widths of HCl lines broadened by CO. This is the first available set of data on line widths with complementary pairs of gases. It is hoped that by using the combined data and by making plausible assumptions about the relationship between the partial collision diameters in the two cases, direct information about interaction energies will be forthcoming. Calculations along these lines are in progress.

TABLE I. γ° (cm^{-1} atm^{-1}) *of* CO *lines due to broadening by* HCl *and by* Ar

$\|m\|$	γ°_{HCl}		γ°_{Ar}	
	P-branch	R-branch	P-branch	R-branch
1	0.096	0.095	0.069	0.070
2	.081	.090	.064	.063
3	.082	.081	.058	.057
4	.079	.078	.056	.051
5	.073	.073	.052	.048
6	.075	.078	.049	.048
7	.072	.075	.045	.046
8	.077	.073	.042	.043
9	.075	.070	.042	.043
10	.079	.076	.044	.041
11	.076	.075	.043	.042
12		.075	.042	.041
13		.071		.041
14	.074	.073	.042	.042
15		.073		.038
16		.072		.042
17	.073	.072		.042
18		.072		.042
19		.072	.040	.035
20			.039	.038
21			.037	.036
22				.033
23				.036

NOTE: While the present work was in process of publication, values for the half-width parameters of CO broadened by argon were reported by Rank and co-workers. See D. H. Rank, D. P. Eastman, B. S. Rao, and T. A. Wiggins, J. Mol. Spec. **10,** 34 (1963).

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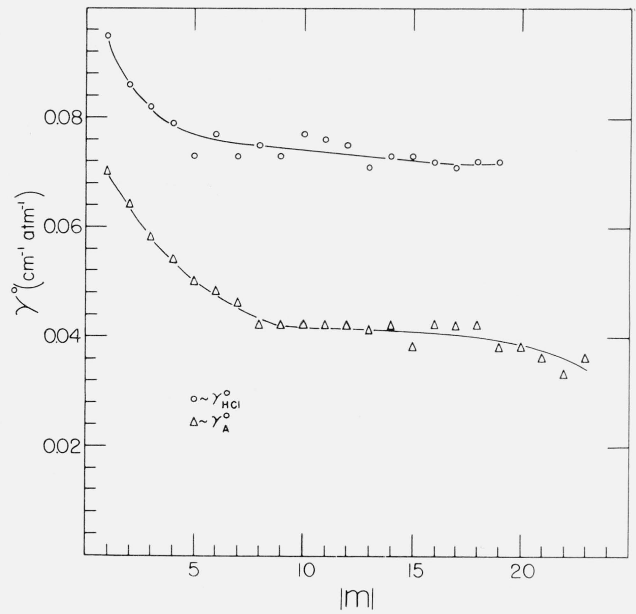

FIGURE 1.—*A plot showing the broadening constants,* γ° (cm^{-1} atm^{-1}), *for* CO *lines of the 2–0 band as a function of* $|m|$.

The circles represent the broadening produced by HCl and the triangles represent the broadening produced by argon.

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