Absorption Line Width in the Infrared Spectrum of Atmospheric Carbon Dioxide*

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(Received January 7, 1953)

Line width in the 15-micron band of atmospheric carbon dioxide has been determined by direct observation of line contour. The influence of finite width of slit has been eliminated by numerical correction. 0.12 cm^{-1} is an upper limit for the CO_2 absorption coefficient half-width at half-height.

I. INTRODUCTION

As is well known, the absorption coefficient half-width, D_0, is an important parameter in the problem of the thermal balance of the atmosphere. It is thus important that D_0 be determined for the radiatively significant constituents of the atmosphere. These are

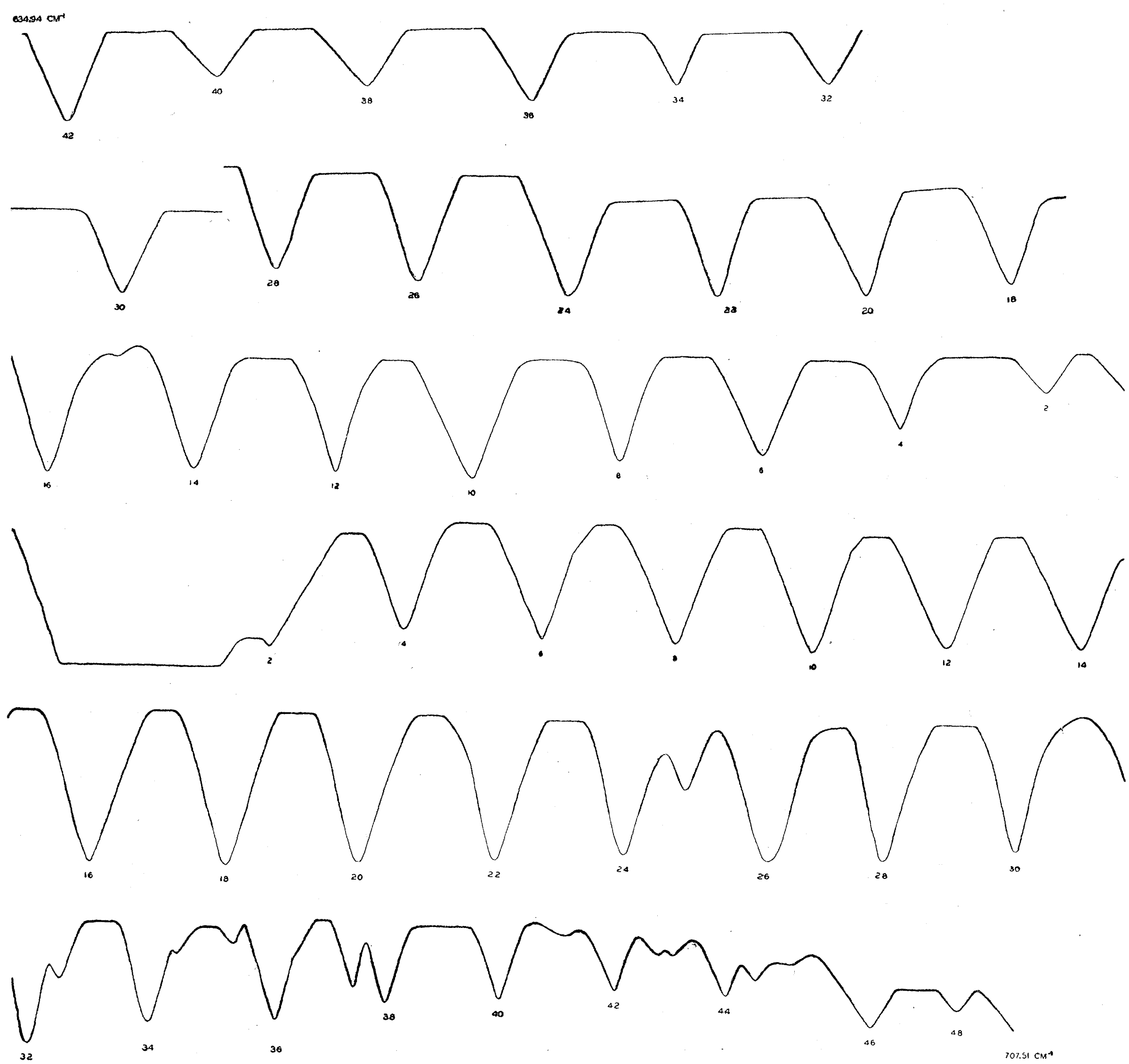

FIG. 1. Line contours in the 15-micron band of CO_2.

* This work was supported in part by a contract with the United States Air Force, through sponsorship of the Geophysical Research Division, Air Force Cambridge Research Center, Air Research and Development Command.

mainly the polyatomic molecules. D_0 is now known for nitrous oxide and water vapor,[1] and the present report deals with the carbon dioxide molecule.

Line width may be measured quite directly by exploring the absorption line with a sufficiently narrow slit and then making a correction for slit influence.

Infrared lines are generally exceedingly narrow. For example, the directly observed absorption line half-width in N_2O, at a pressure of 30 cm Hg, prior to correction for slit width, was found to be but 0.09 cm^{-1}. The need for narrow slits is evident, for one may hope to explore a line significantly only if the slit is of the order of narrowness of the line itself.

The details of the methods of achieving narrow effective slits and making the correction for finite width of slit are given in reference 1 and so will not be repeated here.

II. EXPERIMENTAL

The second fundamental of atmospheric CO_2 was explored from 634.94 cm^{-1} to 707.51 cm^{-1}, and all lines in between were mapped, from number 42 in the *P* branch through number 48 in the *R* branch. A Pfund-type spectrometer of one meter focal length equipped with a 2400 lines per inch grating, fore-prism, and Nernst glower provided a total atmospheric path of six meters. The effective slit half-width was maintained at 0.14 cm^{-1} over the band.

The lines, arranged in sequence from *P* branch through *Q* and *R* branches, are presented in Fig. 1. Their positions are given by the expression

$$\tilde{\nu}_J = 667.5 \pm 0.780J + 0.00045J^2 \text{ cm}^{-1}.$$

III. REDUCTION

The analysis, reference 1, is valid only for weak lines because of the assumption

$$e^{-k(\nu)t} \cong 1 - k(\nu)t.$$

[1] Arthur Adel, Phys. Rev. **71**, 806 (1947).

TABLE I. Apparent half-widths.

P branch		*R* branch	
Line No.	Apparent half-width *D* (cm^{-1})	Line No.	Apparent half-width *D* (cm^{-1})
42	0.221	2	...
40	0.221	4	0.232
38	0.218	6	0.266
36	0.223	8	0.283
34	0.140	10	0.292
32	0.193	12	0.318
30	0.204	14	0.272
28	0.221	16	0.304
26	0.222	18	0.292
24	0.238	20	0.291
22	0.186	22	0.274
20	0.232	24	0.225
18	0.201	26	0.367
16	0.213	28	0.257
14	0.245	30	0.240
12	0.204	32	0.209
10	0.260	34	0.219
8	0.197	36	0.227
6	0.263	38	0.179
4	0.169	40	0.182
2	0.181	42	0.176
		44	0.151

Application of the analysis to lines of even moderate strength will yield conservative values; that is, values slightly in excess of the true D_0. For this reason the very deep lines, numbers 6 through 30 in the *R* branch, have been excluded from the final reduction (see Table I).

The reduction of the remaining lines was effected by averaging the *apparent* line half-widths (Table I): $D_{Av} = 0.208$ cm^{-1}, and applying the analysis of reference 1. The ratio of average *apparent* line half-width to slit half-width is 1.5, whence the analysis[1] yields $D_0 = D/1.7 = 0.12$ cm^{-1}.

The conservative value 0.12 cm^{-1} is notably smaller than the values heretofore assumed for the absorption coefficient half-width of the rotation-vibration lines of carbon dioxide under atmospheric conditions, and will thus require a re-examination of existing calculations bearing on the thermal structure of the atmosphere.