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Final Report

ATMOSPHERIC ABSORPTION BY CARBON DIOXIDE,  
WATER VAPOR AND OXYGEN

by

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## ABSTRACT

The carbon dioxide absorption bands between 12 and 18 microns are of great importance for atmospheric long wave radiative transfer. Theoretical calculations require an accurate knowledge of the frequencies, intensities and half-widths of the individual absorption lines. The method of calculating the frequencies and relative intensities is described, including tables of the necessary parameters. Band intensities and half-width are deduced from high and low resolution experimental spectra. Comparisons between the experimental and theoretical data are presented, showing generally satisfactory agreement.

Also presented are the results of partially completed studies of the rotational water vapor band and the oxygen 'A' band.

## 1. Introduction

The work performed under this contract has been primarily concerned with the theoretical calculation of atmospheric transmittances in the  $15\mu$  spectral region, and is a continuation of research begun under Contract No. Cwb - 1116. A full report on the results of the investigation of the  $15\mu$   $\text{CO}_2$  bands is contained in Chapter 2.

Other molecular absorption bands which have been studied are the pure rotational water vapor band (Chapter 3) and the oxygen 'A' -band (Chapter 4).

In addition to the material covered in this final report, several papers have been published, or presented at meetings. Published papers are:

1. Chaney, L. W., S. R. Drayson and C. Young, (1967): Fourier transform spectrometer - radiative measurements and temperature inversion. *Applied Optics* 6, 347-349. (Paper sponsored jointly by NASA).
2. Drayson, S. R. and C. Young, (1967): Band strength and line half-width of the 10.4 micron  $\text{CO}_2$  band. *J. Quant. Spectros. Radiat. Transfer* 7, 993-995.

Those presented at meetings:

3. Drayson, S. R. and C. Young, (1966): Intensities of the carbon dioxide bands in the 12 to 18 micron spectral region. Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, Ohio, September 6-10, 1966.
4. Drayson, S. R. and C. Young, (1967): Determination of meteorological variables from atmospheric thermal radiation measurements. American Meteorological Society Conference on Physical Processes in the



Lower Atmosphere, Ann Arbor, Michigan, March 20-22, 1967.

(Paper sponsored jointly by NASA).

One other technical report has been produced under the contract:

5. Drayson, S. R. and C. Young, (1967): The frequencies and intensities of the carbon dioxide absorption lines between 12 to 18 microns.

University of Michigan, College of Engineering, Technical Report  
08183-1-T.

## 2. The 15 Micron Carbon Dioxide Bands

### 2.1 Introduction

The perpendicular vibration-rotation carbon dioxide bands which occupy the 12 to 18 micron spectral region are of great importance in atmospheric studies since they are responsible for atmospheric heating and cooling. In addition, radiance measurements made in this spectral region from satellites can be used to infer the atmospheric temperature profile, provided that accurate atmospheric transmittances are available. Before performing atmospheric transmittance calculations, it is necessary to have a sound knowledge of the intensities of the individual bands and the collisional broadened half-widths of the lines.

In this study we have collected and critically examined the basic parameters needed to perform such calculations. Our basic approach was to calculate the rotational line positions and strengths for the bands, using them to compute the transmittances by direct integration with respect to frequency for various homogeneous paths. These calculations were then compared with experimental measurements, and conclusions drawn regarding band intensities and half-widths.

## 2.2 Calculation of Rotational Line Positions

The rotational line positions were calculated using the standard formulae (Herzberg, 1945; Courtoy, 1959). Table 2.1 lists the vibrational energy levels used, while Table 2.2 displays the rotational constants. In the calculations Fermi resonances,  $l$ -type doubling and centrifugal stretching have been taken into account. The rotational constants have the superscripts c and d using Courtoy's (1959) notation, corresponding to levels with even J positive or odd J positive (J is rotational quantum number).

We considered the following isotopes:  $^{12}\text{C } ^{16}\text{O}_2$ ,  $^{13}\text{C } ^{16}\text{O}_2$ ,  $^{12}\text{C } ^{16}\text{O } ^{18}\text{O}$ ,  $^{12}\text{C } ^{16}\text{O } ^{17}\text{O}$ ,  $^{13}\text{C } ^{16}\text{O } ^{18}\text{O}$ . We included only 15 bands for the  $^{12}\text{C } ^{16}\text{O}_2$  molecule, although there are more bands associated with this molecule that are capable of absorbing radiation in this spectral region. However they are probably very weak and their intensities are unknown. For the remaining isotopes only the stronger bands were considered. It should be noted that the vibrational energy level 010:1 for the  $^{12}\text{C } ^{16}\text{O } ^{18}\text{O}$  molecule has been assigned the value  $662.39 \text{ cm}^{-1}$  (Madden, 1961), since it gave better agreement with experimental results than Courtoy's value.

Amat and Pimbert (1965) discussed the possibility that the traditional assignments  $\nu_1$  and  $2 \nu_2$  for  $^{12}\text{C } ^{16}\text{O}_2$  should be reversed. Gordon and McCubbin (1966) confirmed that the assignments should indeed be changed. We have labeled our levels according to the old notation, since no new labeling has yet gained general acceptance.

TABLE 1 Vibrational Energy Levels for Carbon Dioxide in the  
12-18 Micron Region (Units  $\text{cm}^{-1}$ )

Isotope  $^{12}\text{C} \ ^{16}\text{O}_2$

LEVEL		G		$\nu_o$
Lower	Upper	Lower	Upper	
000:0	010:1		667.379 <sup>(1)</sup>	667.379
010:1	020:0	667.379 <sup>(1)</sup>	1285.412 <sup>(1)</sup>	618.033
010:1	100:0	667.379 <sup>(1)</sup>	1388.187 <sup>(1)</sup>	720.808
010:1	020:2	667.379 <sup>(1)</sup>	1335.129 <sup>(1)</sup>	667.750
020:0	030:1	1285.412 <sup>(1)</sup>	1932.466 <sup>(1)</sup>	647.054
020:0	110:1	1285.412 <sup>(1)</sup>	2076.859 <sup>(1)</sup>	791.447
020:2	030:1	1335.129 <sup>(1)</sup>	1932.466 <sup>(1)</sup>	597.337
020:2	110:1	1335.129 <sup>(1)</sup>	2076.859 <sup>(1)</sup>	741.730
020:2	030:3	1335.129 <sup>(1)</sup>	2003.28 <sup>(2)</sup>	668.151
100:0	030:1	1388.187 <sup>(1)</sup>	1932.466 <sup>(1)</sup>	544.279
100:0	110:1	1388.187 <sup>(1)</sup>	2076.859 <sup>(1)</sup>	688.672
030:3	040:2	2003.28 <sup>(2)</sup>	2584.9 <sup>(2)</sup>	581.62
030:3	120:2	2003.28 <sup>(2)</sup>	2760.75 <sup>(2)</sup>	757.47
030:1	120:2	1932.466 <sup>(1)</sup>	2760.75 <sup>(2)</sup>	828.284
030:1	120:0	1932.466 <sup>(1)</sup>	2670.83 <sup>(3)</sup>	738.364

2.1b Isotope  $^{13}\text{C} \ ^{16}\text{O}_2$

LEVEL		G		$\nu_0$
Lower	Upper	Lower	Upper	
000:0	010:1		648.52 <sup>(2)</sup>	648.52
010:1	020:0	648.52 <sup>(2)</sup>	1265.81 <sup>(2)</sup>	617.29
010:1	100:0	648.52 <sup>(2)</sup>	1370.05 <sup>(2)</sup>	721.53
010:1	020:2	648.52 <sup>(2)</sup>	1297.40 <sup>(2)</sup>	648.88
020:0	030:1	1265.81 <sup>(2)</sup>	1896.54 <sup>(2)</sup>	630.73
020:2	030:3	1297.40 <sup>(2)</sup>	1946.69 <sup>(3)</sup>	649.29
100:0	110:1	1370.05 <sup>(2)</sup>	2037.11 <sup>(2)</sup>	667.06

2.1c Isotope  $^{12}\text{C} \ ^{16}\text{O} \ ^{18}\text{O}$

000:0	010:1		662.39 <sup>(4)</sup>	662.39
010:1	020:0	662.39 <sup>(4)</sup>	1365.84 <sup>(2)</sup>	703.55
010:1	100:0	662.39 <sup>(4)</sup>	1259.43 <sup>(2)</sup>	597.14
010:1	020:2	662.39 <sup>(4)</sup>	1325.01 <sup>(3)</sup>	662.72
020:0	030:1	1365.84 <sup>(2)</sup>	2049.25 <sup>(3)</sup>	683.41

2.1d Isotope  $^{12}\text{C} \ ^{16}\text{O} \ ^{17}\text{O}$

000:0	010:1		664.72 <sup>(3)</sup>	664.72
010:1	020:2	664.72 <sup>(3)</sup>	1329.79 <sup>(3)</sup>	665.07

2.1e Isotope  $^{13}\text{C}$   $^{16}\text{O}$   $^{18}\text{O}$

LEVEL		G		$\nu_0$
Lower	Upper	Lower	Upper	
000:0	010:1		643.49 <sup>(3)</sup>	643.49

- (1) Gordon and McCubbin (1965)
- (2) Courtoy (1959)
- (3) Stull, Wyatt and Plass (1962)
- (4) Madden (1961)

TABLE 2. Rotational Constants for Carbon Dioxide in the  
12 to 18-Micron Region (Units  $\text{cm}^{-1}$ )

2a					
Isotope $^{12}\text{C}^{16}\text{O}_2$					
Level	$B^c$	$B^d$	$D^c$	$D^d$	
000:0	0.39021	0.39021	$13.5 \times 10^{-8}$	$13.5 \times 10^{-8}$	(3)
010:1	0.390635	0.391245	$13.8 \times 10^{-8}$	$13.7 \times 10^{-8}$	(1)
020:0	0.390476	0.390476	$16.1 \times 10^{-8}$	$16.1 \times 10^{-8}$	(1)
100:0	0.390201	0.390201	$12.8 \times 10^{-8}$	$12.8 \times 10^{-8}$	(1)
020:2	0.391657	0.391657	$13.9 \times 10^{-8}$	$13.7 \times 10^{-8}$	(1)
030:1	0.390756	0.391675	$14 \times 10^{-8}$	$14.6 \times 10^{-8}$	(1)
110:1	0.390372	0.391326	$12 \times 10^{-8}$	$10.6 \times 10^{-8}$	(1)
030:3	0.39236	0.39236	$13 \times 10^{-8}$	$13 \times 10^{-8}$	(2)
120:0	0.388525	0.388525	$13 \times 10^{-8}$	$13 \times 10^{-8}$	(3)
040:2	0.39187	0.39187	$13 \times 10^{-8}$	$13 \times 10^{-8}$	(3)
120:2	0.39152	0.39152	$12.2 \times 10^{-8}$	$12.2 \times 10^{-8}$	(2)
2b					
Isotope $^{13}\text{C}^{16}\text{O}_2$					
000:0	0.39025	0.39025	$13.7 \times 10^{-8}$	$13.7 \times 10^{-8}$	(3)
010:1	0.39064	0.39126	$13.7 \times 10^{-8}$	$13.7 \times 10^{-8}$	(3)
020:0	0.390935	0.390935	$15.9 \times 10^{-8}$	$15.9 \times 10^{-8}$	(3)
100:0	0.389745	0.389745	$12.2 \times 10^{-8}$	$12.2 \times 10^{-8}$	(3)
020:2	0.39165	0.39165	$13.3 \times 10^{-8}$	$13.3 \times 10^{-8}$	(3)
030:1	0.39090	0.39216	$13 \times 10^{-8}$	$13 \times 10^{-8}$	(3), (4)
110:1	0.39023	0.39084	$13 \times 10^{-8}$	$13 \times 10^{-8}$	(3), (4)
030:3	0.39096	0.39096	$13 \times 10^{-8}$	$13 \times 10^{-8}$	(3), (4)

2c Isotope  $^{12}\text{C } ^{16}\text{O } ^{18}\text{O}$

000:0	0.36820	0.36820	$11.5 \times 10^{-8}$	$11.5 \times 10^{-8}$	(3)
010:1	0.36857	0.36912	$11.5 \times 10^{-8}$	$11.5 \times 10^{-8}$	(5)
020:0	0.36851	0.36851	$11 \times 10^{-8}$	$11 \times 10^{-8}$	(5)
100:0	0.36811	0.36811	$11 \times 10^{-8}$	$11 \times 10^{-8}$	(5)
020:2	0.36948	0.36948	$11 \times 10^{-8}$	$11 \times 10^{-8}$	(5)
030:1	0.36924	0.37008	$11 \times 10^{-8}$	$11 \times 10^{-8}$	(5)

2d Isotope  $^{12}\text{C } ^{16}\text{O } ^{17}\text{O}$

000:0	0.37922	0.37922	$12.5 \times 10^{-8}$	$12.5 \times 10^{-8}$	(6)
010:1	0.37826	0.37884	$12.5 \times 10^{-8}$	$12.5 \times 10^{-8}$	(7)
020:2	0.37923	0.37923	$12.5 \times 10^{-8}$	$12.5 \times 10^{-8}$	(7)

2e Isotope  $^{13}\text{C } ^{16}\text{O } ^{18}\text{O}$

000:0	0.36820	0.36820	$11.5 \times 10^{-8}$	$11.5 \times 10^{-8}$	(3)
010:1	0.36727	0.36785	$11.5 \times 10^{-8}$	$11.5 \times 10^{-8}$	(5)



- (1) These values were obtained from the values given by Gordon and McCubbin (1965) using Courtoy's (1959) values for the 000:0 level as a base value.
- (2) Benedict (1957).
- (3) Courtoy (1959).
- (4) The D's were calculated using  $D = 4 B_e^3 / \nu_1^2$
- (5) Calculated using Courtoy's (1959) constants, Fermi resonances were taken into account in the calculations.
- (6) The rotational constants were obtained by linear interpolation using the other isotopes as base values.
- (7) Calculated using interpolated parameters.

### 2.3 Calculation of Rotational Line Intensities

The calculation of rotational line intensities is relatively straight forward once the band intensities are known, (see Penner, 1959). The partition functions for  $^{12}\text{C } ^{16}\text{O}_2$  were calculated by interpolation on the values given by Gray and Selvidge (1965). For the remaining isotopes the partition functions were calculated using the harmonic oscillator partition functions, (Herzberg, 1945). The band intensities for the various isotopes were weighted by their abundance relative to  $^{12}\text{C } ^{16}\text{O}_2$  in the earth's atmosphere.

The accuracy of the calculation of the rotational line intensities was checked by calculating the line intensities for each band separately and adding them together. The results agreed closely with the original band intensities.

We neglected the influence of the Coriolis vibration-rotation interaction on the intensity distribution within a particular band. This correction is relatively easy to apply, but unfortunately the necessary parameters are not well known.

Table 2.3 lists the band intensities finally chosen, a point that will be discussed later. The isotopic bands considered can be obtained from Table 2.1. The integrated band intensity, including the isotopes, is  $224.3 \text{ cm}^{-1} (\text{atm cm})_{300\text{K}}^{-1}$  at 300K. Table 2.4 presents a comparison between integrated intensities of the 15 micron carbon dioxide bands which have been obtained by various experimenters. The optimistic error estimates of some experimenters is clearly evident.

In the calculation of rotational line intensities we neglected lines with intensities less than  $10^{-6} \text{ cm}^{-1} (\text{atm cm})_{300\text{K}}^{-1}$  at 300K, but nevertheless obtained about 7000 lines. Since the calculation of transmittances using this number of lines would be an exceedingly lengthy task, the number of lines was reduced. Examination of the line intensities showed that most were in the range  $10^{-4}$  to  $10^{-6} \text{ cm}^{-1} (\text{atm cm})_{300\text{K}}^{-1}$  at 300K. Near strong lines very weak lines have little influence, except for long absorption paths at very low pressures. Consequently the spectral range  $500$  to  $800 \text{ cm}^{-1}$  was divided into  $5 \text{ cm}^{-1}$  intervals, retaining only those lines in the interval with intensities lying in the range formed by the strongest line and  $10^{-3}$  times its intensity. This criterion reduced the number of lines to around 2200, a more manageable number. In spectral regions where there are only weak lines, all lines are retained, while in those regions containing strong and weak lines the strong lines and some of the weak lines are retained, the very weak lines being discarded.

TABLE 2.3 Band Intensities Used in Calculating  
Rotational Line Intensities

LEVEL		BAND	INTENSITY
Lower	Upper	Center ( $^{12}\text{C}^{16}\text{O}_2$ )	$(\text{cm}^{-1}(\text{atm cm})^{-1})_{300^\circ\text{K}}$ at $300^\circ\text{K}$
000:0	010:1	667.379	194 <sup>(1)</sup>
010:1	020:0	618.033	4.27 <sup>(1)</sup>
010:1	100:0	720.808	5.0 <sup>(4)</sup>
010:1	020:2	667.750	15 <sup>(4)</sup>
020:0	030:1	647.054	1.0 <sup>(1)</sup>
020:0	110:1	791.447	0.022 <sup>(2)</sup>
020:2	030:1	597.337	0.14 <sup>(1)</sup>
020:2	110:1	741.730	0.12 <sup>(4)</sup>
020:2	030:3	668.151	0.85 <sup>(2)</sup>
100:0	110:1	688.672	0.3 <sup>(3)</sup>
100:0	030:1	544.279	0.004 <sup>(1)</sup>
030:3	040:2	581.62	0.0042 <sup>(2)</sup>
030:3	120:2	757.47	0.0059 <sup>(2)</sup>
030:1	120:2	828.284	0.00049 <sup>(2)</sup>
030:1	120:0	738.364	0.014 <sup>(2)</sup>

(1) Madden (1961)

(2) Yamamoto and Sasamori (1958)

(3) Yamamoto and Sasamori (1964)

(4) Our estimation

Integrated intensity including the isotopes  $^{12}\text{C}^{16}\text{O}_2$ ,  $^{13}\text{C}^{16}\text{O}_2$ ,  $^{12}\text{C}^{16}\text{O}^{18}\text{O}$ ,  $^{12}\text{C}^{16}\text{O}^{17}\text{O}$ ,  $^{13}\text{C}^{16}\text{O}^{18}\text{O}$  is  $224.3 \text{ cm}^{-1} (\text{atm cm})^{-1}$  at  $300^\circ\text{K}$ .

TABLE 2.4 Integrated Intensity of the 15 Micron  
CO<sub>2</sub> Bands

	Integrated Intensity (cm <sup>-1</sup> (atm cm) <sup>-1</sup> <sub>300K</sub> at 300K)
Eggers and Crawford (1951)	146 ± 18
Weber et al. (1952)	170 ± 34
Thorndike (1947)	170 ± 18
Varanasi and Lauer (1966)	200 ± 10
Kaplan and Eggers (1956)	217 ± 5
Schurin (1960)	217 ± 5
Overend et al. (1959)	218 ± 5
Wolk (1967)	225 ± 7
Burch et al. (1962)	300 ± 80

The line intensity calculations were performed for six temperatures (300, 275, 250, 225, 200 and 175K); intensities for other temperatures may be readily obtained by interpolation. A listing of these lines has been published as a separate report (Drayson and Young, 1967a).

#### 2.4 Half-Widths and Line Shapes

One of the most important parameters needed is the Lorentz or collisional half-width, i. e. half the line width at half the maximum value of the absorption coefficient. The most generally used value for the nitrogen-broadened Lorentz half-width  $\alpha_L$  is  $0.064 \text{ cm}^{-1}$  at 1 atm and 298K, given by Kaplan and Eggers (1956). Madden (1961) has shown that for self-broadened carbon dioxide the half-width varies with rotational quantum number J. He obtained a half-width of  $0.126 \text{ cm}^{-1}$  (1 atm, 300K) for the J = 4 line of the P-branch of the  $\nu_2$  fundamental and  $0.06 \text{ cm}^{-1}$  for the J = 56 line of the same branch of the same band.

Experimental measurements by Burch et al. (1965) in the near infrared show variations of self-broadened half-width with J-number similar to those obtained by Madden for the 15 micron bands, but with the values of  $\alpha_L$  some 5 to 20% lower.

Recently the  $\text{CO}_2$  laser has been used to make measurements of  $\alpha_L$  for several lines in the  $10.4\mu$   $\text{CO}_2$  band (McCubbin et al., 1966; McCubbin and Mooney, 1967; Drayson and Young, 1967b), with results close to the values of Madden. Those of Rosetti et al. (1967) are considerably smaller, but may be modified if the experimental data is re-analysed (see Drayson and Young, 1967b).

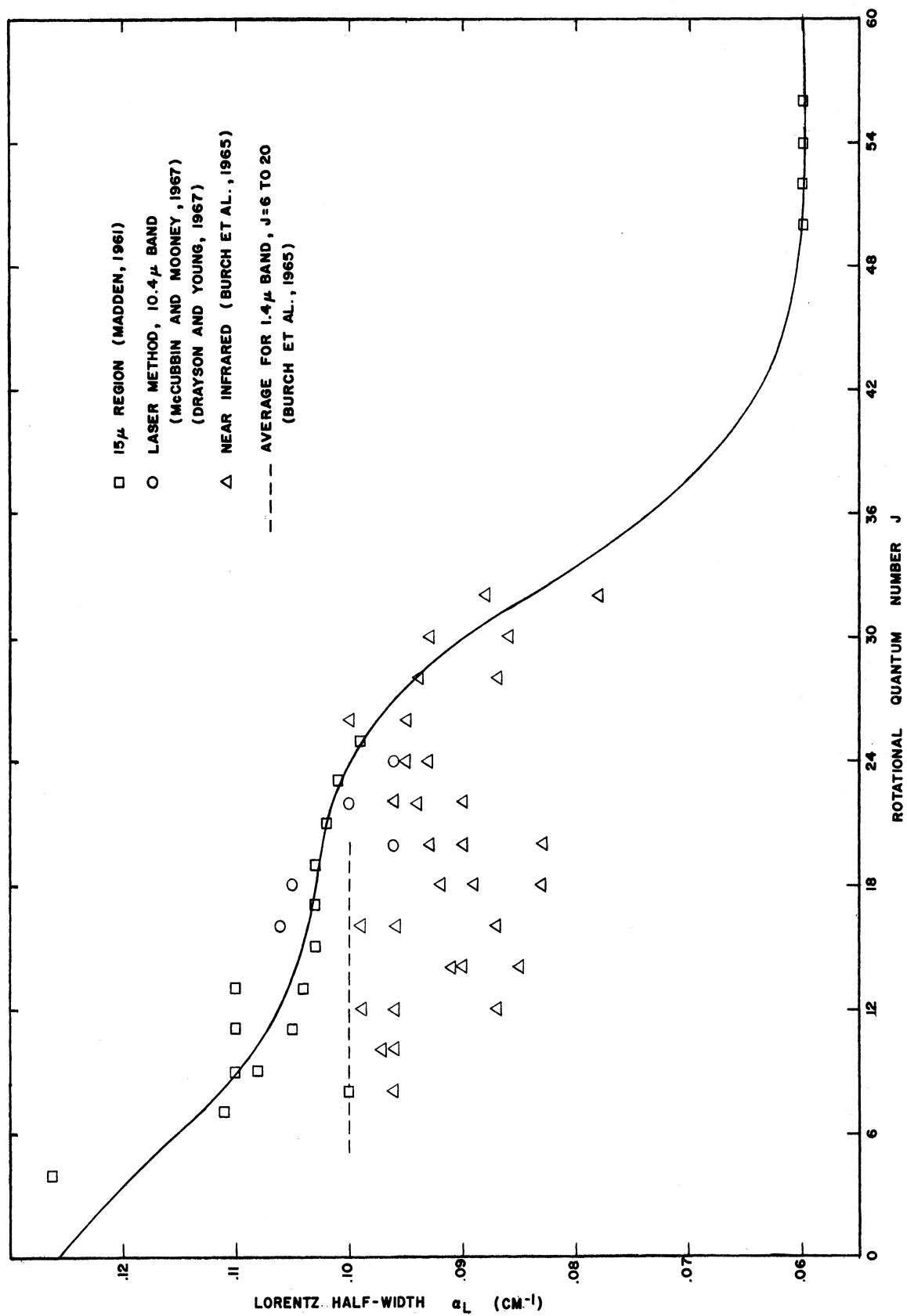


FIGURE 2.1 Lorentz half-widths of carbon dioxide absorption lines. Solid line is variation adopted in the present calculations.

Experimental values are summarized in Figure 2.1. The tendency for smaller values at higher frequencies is immediately noticeable. Also apparent is the lack of measurements beyond about  $J = 30$ , except for four measurements by Madden between  $J = 50$  and  $J = 56$ . A smooth curve has been drawn through the scattered experimental data, with the 15 micron and 10.4 micron measurements most heavily weighted. Beyond  $J = 30$  the shape of the curve is uncertain, but can be re-estimated if further data become available.

We used the average self-broadening coefficient of 1.3 given by Burch et al. (1962), which agrees well with laser determinations by McCubbin and Mooney (1967) and of Patty et al. (1967). A laser determination by Boutin et al. (1967) is somewhat lower (1.12).

Previous transmittance calculations have generally used a constant half-width. The value  $\alpha_L = 0.064 \text{ cm}^{-1}$  given by Kaplan and Eggers (1956) was commonly used. However recent calculations have used somewhat higher values, for example Gray and McClachey (1965) used  $0.07 \text{ cm}^{-1}$  for the 4.3-micron bands. The results discussed above on variation of half-width with J-number indicate that if we accept a self broadening coefficient of 1.3,  $\alpha_L = 0.08 \text{ cm}^{-1}$  is a reasonable value for J up to about 25. This point will be discussed later when the results of the calculations are presented.

In view of the above discussions, we calculated transmittances using constant half-widths, and the variable half-widths shown in Figure 2.1.

## 2.5 Calculation of Transmittances

We are generally interested in the transmittance  $\bar{\gamma}_\nu$ , averaged over some finite wavenumber interval  $\Delta \nu$ , weighted by some function  $\phi(\nu)$  which

may, for example, be a spectrometer slit function, i. e.

$$\bar{\gamma}_\nu = \frac{\int_{\Delta_\nu} \phi(\nu) \gamma_\nu d\nu}{\int_{\Delta_\nu} \phi(\nu) d\nu}$$

where  $\gamma_\nu$  is the monochromatic transmittance at wavenumber  $\nu$ . It is possible to use standard quadrature techniques to calculate  $\bar{\gamma}_\nu$  to any desired accuracy provided that  $\gamma_\nu$  can be obtained at any wavenumber in the integration interval. However,  $\gamma_\nu$  typically includes contributions from many spectral lines and is a rapidly varying function of wavenumber, requiring repeated evaluation for even a small wavenumber interval. Band models were introduced to overcome this difficulty. However, in recent years advances in digital computers have made the direct numerical evaluation of the weighted transmittance  $\bar{\gamma}_\nu$  possible. Several successful calculations have been made, for example Hirschfeld and Houghton (1961), Shaw and Houghton (1964), Gates et al. (1963), Gates and Calfee (1966) and Drayson (1966).

The technique we adopted is essentially that discussed by Drayson (1966), with some improvements to speed computation. The Lorentz line profile was used at pressures higher than 0.1 atmospheres and the mixed Doppler-Lorentz (Voigt) profile at lower pressures, using the method described by Young (1965), with slight modifications to increase speed and accuracy.

## 2.6 Comparison Between Calculated and Experimental Transmittances

As already emphasized the two most important sets of parameters needed for calculation transmittances are the intensities of the individual bands and the Lorentz half-widths of the lines. Our initial band intensities were



taken from Yamamoto and Sasamori (1958) and Madden (1961). These values provided a reasonable starting point. We compared our calculations with the low resolution measurements of Burch et al. (1962) and the high resolution measurements of Madden (1961).

The most important change was in the intensity of the (010:1 - 020:2) band, the second strongest band in the spectral region. Madden (1961) gave the value  $30 \text{ cm}^{-1} (\text{atm cm})_{300\text{K}}^{-1}$  at 300K. Calculations using this value gave rather poor agreement with the low resolution experimental spectra of Burch et al. (1962), with considerable over-estimation of the absorption. In addition, Madden's value led to a total band intensity which is considerably greater than the best current estimates from high pressure low resolution measurements (Wolk, 1967).

Comparison with Madden's original data showed that a band intensity of  $15 \text{ cm}^{-1} (\text{atm cm})_{300\text{K}}^{-1}$  at 300K, i. e. half Madden's estimate and close to the value suggested by Kaplan and Eggers (1956), gave results that were in as good or better agreement with the experimental than the larger value. However it is impossible to deduce an accurate value from the high resolution data because of the strong interference from the fundamental and the experimental noise. The lower value gives excellent agreement with Wolk's (1967) experimental value of total intensity, which we believe to be the most accurate determination.

An independent confirmation of the lower value was obtained from radiance measurements in the 15-micron region using a Michaelson interferometer flown in a high altitude balloon. Atmospheric transmittances were calculated using both values, and theoretical radiances computed from

radiosonde temperature soundings (Chaney et al., 1967). The smaller value gave agreement to within the expected experimental error, while the larger produced values which lay well outside the error limits.

Small adjustments were made in some of the other band intensities to give better agreement with experimental results.

Table 2.5 displays calculated and experimental equivalent widths for a range of pressures and optical masses. The agreement between the experimental and calculated values for both the variable half-width and  $\alpha_L = 0.08 \text{ cm}^{-1}$  is quite good, except for the large optical masses at higher pressures. The calculations using  $\alpha_L = 0.06 \text{ cm}^{-1}$  gave poorer overall agreement. The use of the variable half-width gave somewhat better agreement than  $\alpha_L = 0.08 \text{ cm}^{-1}$ , particularly for the larger optical masses. The agreement to within experimental error shown in Figure 2.2a and b is typical of all the runs at the two lower pressures, while the differences shown in Figure 2.2c are characteristic of the large optical masses at the high pressure. There are several possible reasons for the differences. Small errors in wavenumber calibration in the experimental data can produce marked differences in total absorption, particularly critical at wavenumbers where the slope of the transmittance curve is steep. Comparison with experimental results of Yamamoto and Sasamori (1963), indicate somewhat lower transmittance than given by Burch et al. (1962), but not as low as our calculation indicate.

We have been unable to provide a satisfactory explanation for the differences between the experimental and theoretical results at the high pressure. Any explanation must leave the spectra unchanged at the lower pressures.

TABLE 2.5 Comparison of Experimental and Calculated  
Equivalent Widths. Experimental Values  
From Burch et al. (1962)

Equivalent Pressure*	Optical Mass	Equivalent Width ( $\text{cm}^{-1}$ )			
		Experimental	$\alpha_L$ Variable	$\alpha_L =$ $0.08 \text{ cm}^{-1}$	$\alpha_L =$ $0.06 \text{ cm}^{-1}$
(atm)	(atm cm) <sub>300K</sub>				
0.02053	51.0	71.5	74.2	77.2	70.6
	6.30	34.6	33.3	34.7	31.1
	0.20	7.46	6.51	6.72	6.09
0.0857	212.1	143	143.6	146.4	140.3
	26.37	91.6	89.4	92.5	86.3
	12.64	70.7	70.8	73.4	67.6
	6.30	54.7	54.8	56.9	51.9
	0.82	22.6	21.9	22.6	20.5
	0.42	16.4	15.4	15.9	14.5
	0.10	7.11	6.72	6.90	6.36
1.00	212.1	183	194.7	197.0	190.8
	106.2	164	174.2	176.2	170.5
	51.0	141	153.5	155.2	149.9
	25.6	125	134.7	135.3	131.7
	12.6	113	115.7	117.6	113.5
	6.30	95.3	97.0	99.0	95.1

\*Equivalent pressures of experimental vary by a few percent from listed values.

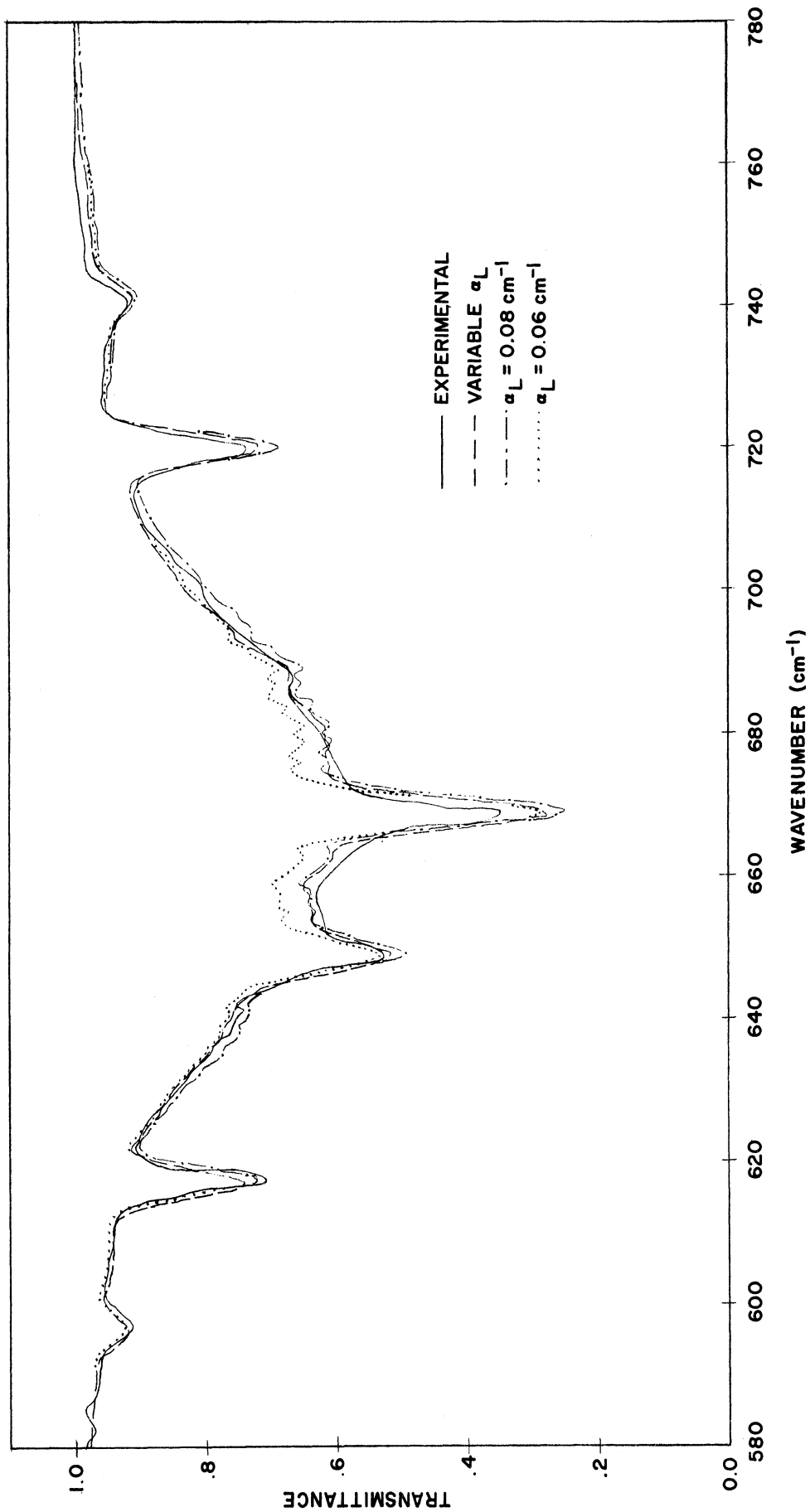


FIGURE 2.2 Comparison of low resolution spectra (Burch et al., 1962) with theoretical calculations

a Equivalent pressure 0.02053 atm., optical mass 6.30 (atm cm) 300K.

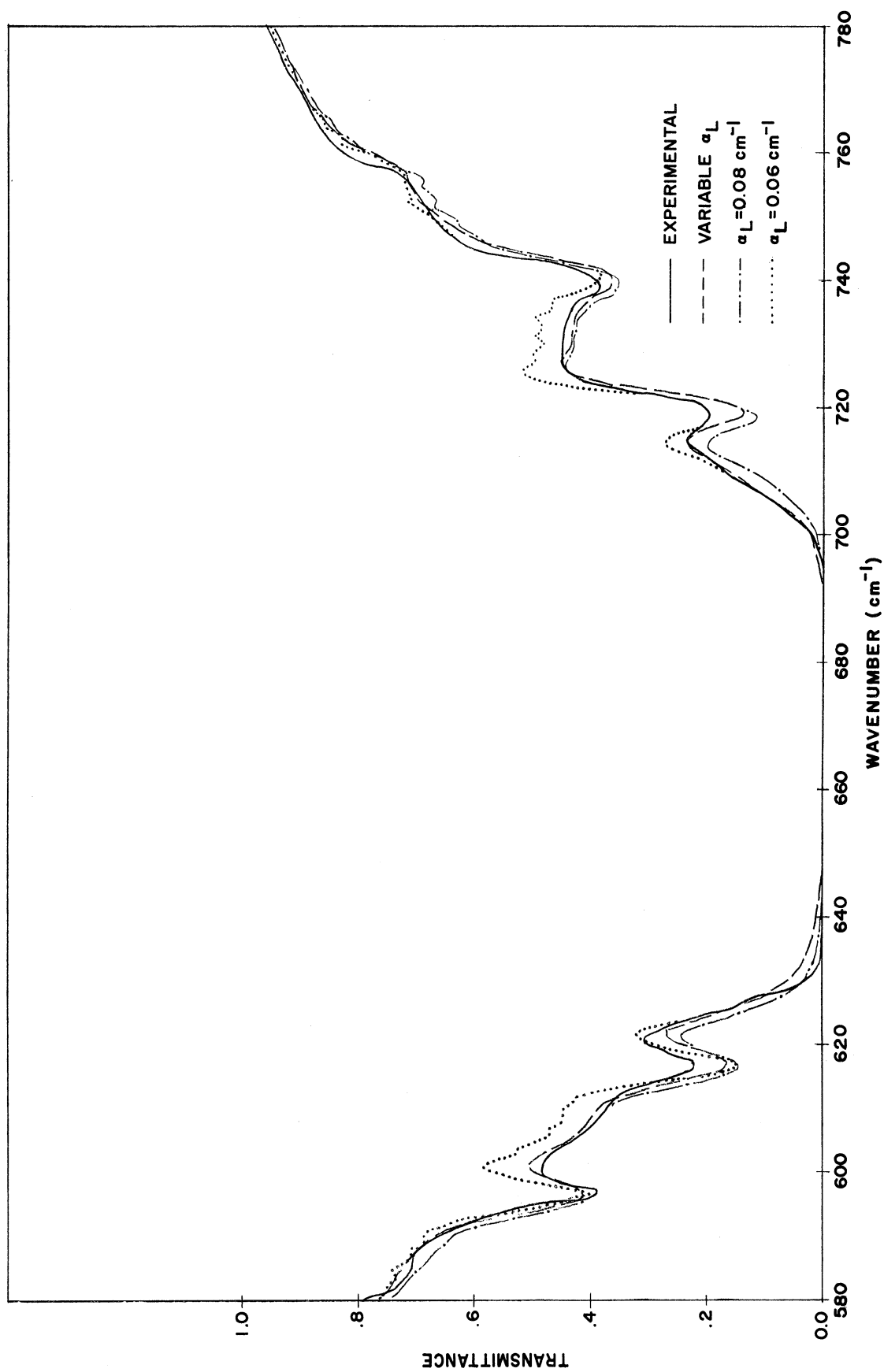


FIGURE 2.2b Equivalent pressure 0.0857 atm., optical mass 212.1 (atm cm) 300K.

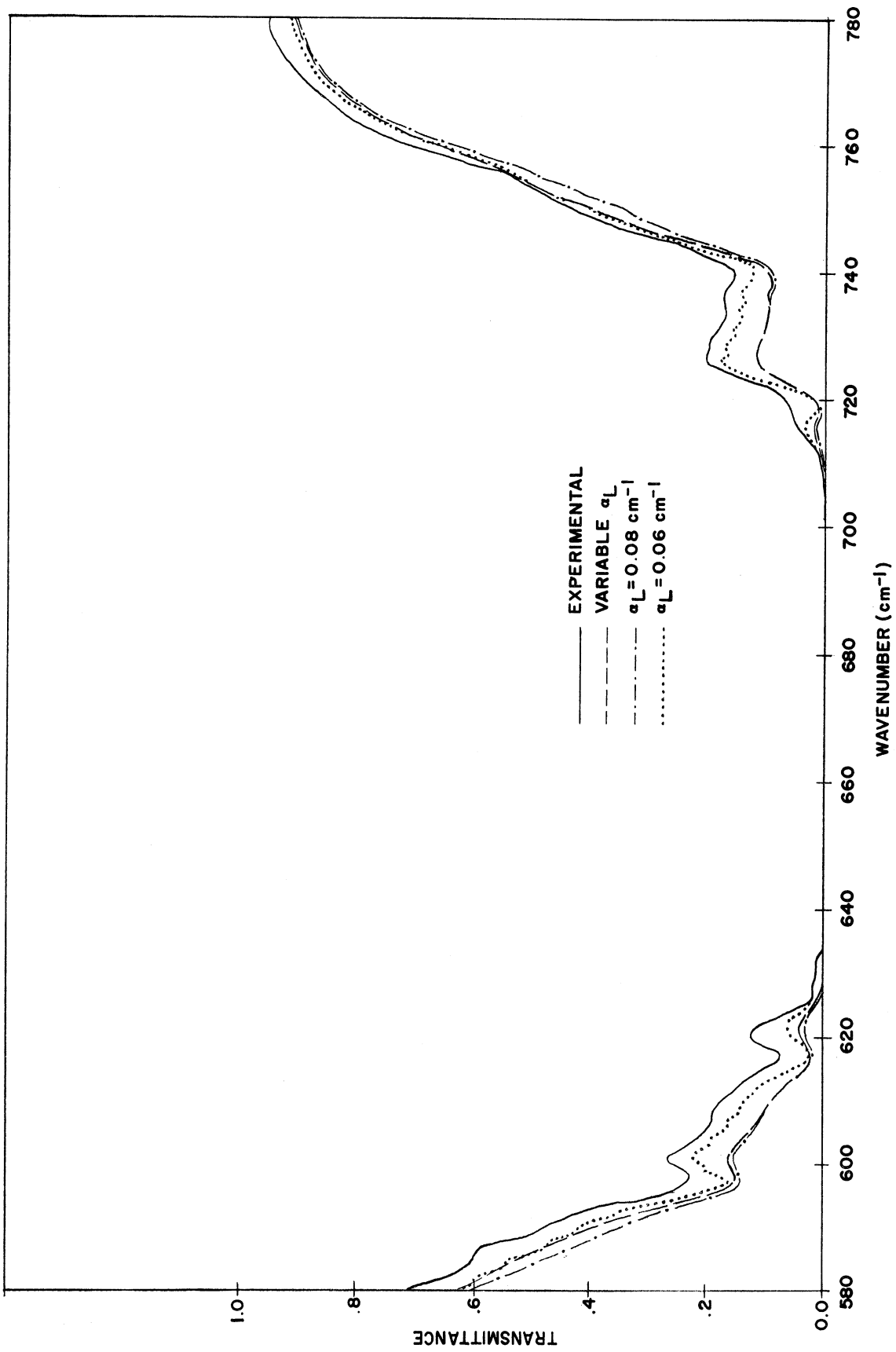


FIGURE 2.2c Equivalent pressure 1.00 atm., optical mass 106.2 (atm cm)300K.

## 2.7 Conclusions

On the whole the agreement between the experimental and calculated transmittances is quite good and within experimental error if the band intensities given in Table 2.3 are used. The variable Lorentz half-width from Figure 2.1 gave the most satisfactory agreement, although the constant value  $\alpha_L = 0.08 \text{ cm}^{-1}$  also produced close agreement. We feel that transmittance calculations for the  $15\mu \text{ CO}_2$  bands can be adequately performed for many applications, including atmospheric slant path transmittances for use in remote sensing and in atmospheric radiative transfer computations.

In order to further improve calculations of this nature more experimental measurements are needed. These should include studies of the variation of Lorentz half-width with rotational quantum number, especially the values of  $J$  which have not been previously measured. Our knowledge of the shapes of lines, particularly in the far wings, is incomplete, as is the effect of different broadening gasses on the line shape and Lorentz half-widths. Most of these measurements can be best achieved with high resolution experiments, including the newly developed laser techniques.

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### 3. Pure Rotational Band of Water Vapor

#### 3.1 Introduction

Radiative transfer by the pure rotational band of water vapor in planetary atmospheres is important not only for energy balance considerations, but also in connection with problems of remote sensing of atmospheric temperature and water vapor distributions. Appreciable atmospheric absorption occurs over a broad spectral interval, from the microwave region to about  $10\mu$ .

In recent years a number of experimental and theoretical studies of the band have been made, but the results are not conclusive. Remote sensing requires accurate values of transmission functions, and this is the primary reason for the present investigation. The validity of different line shapes, the effects of self broadening and the influence of the wings of distant lines are examined in the following sections.

#### 3.2 Calculation Details

The transmissivity  $\gamma_\nu$  at frequency  $\nu$  for a path of optical mass  $u$  is given by

$$\gamma_\nu = \exp \left( - \int_u k_\nu du \right) \quad (3.1)$$

where  $k_\nu$  is the absorption coefficient. For homogeneous paths  $k_\nu$  is not a function of  $u$ , so Eq. 3.1 may be simplified

$$\gamma_\nu = \exp (- k_\nu u)$$

The absorption coefficient is the sum of the absorption coefficients of the individual lines in the absorption band.

$$k_{\nu} = \sum_i k_{\nu}(i)$$

Where the dominant line broadening mechanism is due to collisional processes, the use of the Lorentz line profile to determine  $k_{\nu}(i)$  has proved satisfactory in many spectral regions, for many molecules, particularly in the neighborhood of line centers. In this case  $k_{\nu}(i)$  is given by

$$k_{\nu}(i) = \frac{S_i}{\pi} \frac{\alpha_i}{(\nu - \nu_i)^2 + \alpha_i^2} \quad (3.2)$$

where  $S_i$  is the line intensity,  $\alpha_i$  is the Lorentz half-width and  $\nu_i$  is the frequency of the line center.

Another line shape that has been used for the rotational water vapor band is the Van Vleck Weisskopf (VWV) line shape (Van Vleck and Weisskopf, 1945). The form used in these calculations is due to Farmer (1967)

$$k_{\nu}(i) = \frac{S_i \alpha_i}{\pi} \frac{\nu}{\nu_i} \frac{1 - \exp(-h\nu/kT)}{1 - \exp(-h\nu_i/kT)} \left[ \frac{1}{(\nu - \nu_i)^2 + \alpha_i^2} + \frac{1}{(\nu + \nu_i)^2 + \alpha_i^2} \right] \quad (3.3)$$

If  $h\nu/kT$  and  $h\nu_i/kT$  are small the equation reduces to

$$k_{\nu}(i) = \frac{S_i \alpha_i}{\pi} \left( \frac{\nu}{\nu_i} \right)^2 \left[ \frac{1}{(\nu - \nu_i)^2 + \alpha_i^2} + \frac{1}{(\nu + \nu_i)^2 + \alpha_i^2} \right] \quad (3.4)$$

which is the form originally given by Van Vleck and Weisskopf. In the microwave region the conditions always holds, but diverges in the infrared.

Another form of the VVW line shape has also been used (e. g., Hall et al., 1966).

$$k_{\nu}(i) = \frac{S_i \alpha_i}{\pi} \left( \frac{\nu}{\nu_i} \right) \left[ \frac{1}{(\nu - \nu_i)^2 + \alpha_i^2} + \frac{1}{(\nu + \nu_i)^2 + \alpha_i^2} \right] \quad (3.5)$$

Falcone (1967) has pointed out that the last form is incorrect. However it should be remembered that the assumptions made in deriving the VVW line shape do not hold at frequencies far removed from the line center. When  $\nu - \nu_i$  is small, all forms are very close to Lorentz line shape.

At pressures where Doppler broadening is important the mixed Doppler-Lorentz line shape may be used near the line center and the VVW line shape in the wings.

The VVW line shape presents a difficulty in the interpretation of the line intensity. Normally  $S_i$  is defined by

$$S_i = \int_0^{\infty} k_{\nu}(i) d\nu$$

The integral diverges for the VVW line shape. For large  $\nu$ ,  $k_{\nu}(i)$  behaves like  $1/\nu$  (Eq. 3.3 and 3.5) or tends to a constant value (Eq. 3.4).

To allow for the difference between self-broadened and foreign broadened gasses, the concepts of equivalent pressure  $P$  and self-broadening coefficient  $B$  are often employed, with nitrogen as the standard for foreign broadening.

$$P_e = P + (B-1) p$$

where  $P$  is the total pressure and  $p$  is the partial pressure of the absorbing gas. In the rotational water vapor band, several values of  $B$  are used and are discussed more fully in next section.

The line positions, intensities and half-widths are due to Benedict and Kaplan (1967). The temperature at which the intensities and half-widths are calculated is  $340^{\circ}\text{K}$ , whereas most of the experimental data is at room temperature. The intensities are readily corrected. The half-widths were adjusted assuming that the values were inversely proportional to the square root of the temperature, although it is known that this is only approximately true (Benedict and Kaplan, 1959 and 1964). However, since the difference in temperature is small, little error results from this treatment.

Transmissivities were again calculated by direct integration with respect to frequency, using a computer program similar to that used for the  $\text{CO}_2$  calculations. Only a slight modification was necessary to incorporate the VVW line shape.

### 3.3 Comparison with Experimental Results

Experimental measurements have been made by Palmer (1957a, b), and by Stauffer and Walsh (1966), covering the spectral range  $250$  to  $700\text{ cm}^{-1}$ . Since the spectral resolution of the experimental data varied from about  $2$  to  $5\text{ cm}^{-1}$ , the resolution of the theoretical data was adjusted by trial and error to agree approximately with the experimental spectra. To make comparison

easier the experimental data were replotted on a linear scale, and theoretical spectra were plotted on the same scale directly from the computer output using a Calcomp plotter.

Since our study of the rotational water vapor band has not yet been completed, the results of the investigation will not be given in full detail in this report, but only a summary of the more important conclusions. Firstly, between 250 and 500  $\text{cm}^{-1}$  the agreement between the experimental and theoretical spectra is within experimental error provided the VVW line shape is used. The value of  $B = 5$  gave better agreement for the smaller optical masses, while  $B = 12$  was satisfactory for the larger values. The VVW line shape gave consistently closer agreement with the experimental than Lorentz line shape, although the difference was quite small for the lower pressures and the smaller optical masses. This result is in full agreement with Farmer (1967), who based his arguments on an entirely different set of experimental set of data. In contrast, Hall et al. (1966) came to the opposite conclusion using the same experimental data as the present study. Their theoretical argument is difficult to follow, but it appears that they have applied equations to experimental transmittances that are valid only for monochromatic transmittances. The fact that their results are very sensitive to small changes in the experimental data also suggests that their analysis is unrealistic. Hall et al. also made calculations with the Zhevakin-Naumov line profile, but we did not use it since it gives less absorption than the Lorentz line shape in the high frequency wings of the absorption lines (see also Falcone, 1967).

The agreement between our results and experimental spectra in the 500 to 700  $\text{cm}^{-1}$  spectral region was poor, particularly at the high frequency end. The absorption lines are mostly rather weak within the interval, but wings of lines lying outside the absorption interval contribute strongly. Even with the VVW line shape, the calculated absorptance was much lower than the experimental, particularly under conditions where self-broadening is an important factor. Only for large optical masses at higher pressures, where the water vapor mixing ratio was very small, did the calculated absorptance exceed the experimental values.

From this we can conclude that the shape of the wings of rotational water vapor lines is a critical factor in determining the absorptance in the weaker parts of the band. It is also apparent the variations in the value of self-broadening coefficient are more correctly interpreted as an uncertainty in the line shape. At the moment not enough is known about the line shape, although other measurements have been made near the atmospheric window between 8 and 12 microns (e. g. Bignell et al., 1963) and also in the microwave region (e. g. Frenkel and Woods, 1966), giving much more absorption than predicted by the normal line shapes.

### 3.4 Conclusions

The agreement experimental spectra and those calculated from the line parameters of Benedict and Kaplan are in good agreement between 250 and 500  $\text{cm}^{-1}$ , especially if the Van Vleck-Weisskopf line shape is used. They appear to be sufficiently good to use for many applications, in particular application to atmospheric radiative transfer problems. Between 500 and 700  $\text{cm}^{-1}$  there is considerable divergence and further investigation, particularly on the problem of line shape, is essential.



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#### 4. The Oxygen 'A' Band

Centered near 7600 Å, the oxygen 'A' band is a weak absorption band which nevertheless gives rise to considerable atmospheric absorption because of the large amount of oxygen in the terrestrial atmosphere. The possibility of determining cloud top heights from satellite measurements of the attenuation of solar radiation reflected from top of clouds has recently renewed interest in this band (Wark and Mercer, 1965). Since small errors in calculating transmittances can produce systematic errors in estimates of cloud top heights, it is important to have an accurate knowledge of the parameters of the band.

Wark and Mercer (1965) deduced values of band intensity and half-width from atmospheric absorption spectra, using the sun as a source. More recently, Burch et al. (1964) and Burch and Gryvnak (1967) have made laboratory absorption measurements, including line to line variations of Lorentz half-width.

The purpose of this study is to calculate atmospheric slant path transmissivities. Before making such calculations it is essential to be able to accurately compute homogeneous path absorption.

The line positions and energy levels were obtained from Wark and Mercer (1965). In addition to the  $^{16}\text{O}_2$  molecules, absorption lines from  $^{16}\text{O}^{17}\text{O}$  and  $^{16}\text{O}^{18}\text{O}$  were included, with relative abundances of  $8 \times 10^{-4}$  and  $4 \times 10^{-3}$  respectively. The weighting functions suggested by Childs and Mecke (1931) were used (see Wark and Mercer, 1965, and Burch et al., 1964). Other parameters were obtained from Burch and Gryvnak (1967) i. e. band strength of  $4.09 \text{ gm}^{-1} \text{ cm}^2 \text{ cm}^{-1}$  and the variation of Lorentz half-width given in their Figure 4. Lines with  $J''$  -number greater than 25 were assumed to have a

half-width of  $0.042 \text{ cm}^{-1}$  at 1 atmosphere. The Doppler half-width at room temperatures is approximately  $0.014 \text{ cm}^{-1}$ , so that the Doppler and Lorentz half-widths of the stronger lines are equal at about 0.25 atm, and at a higher pressure for the weaker lines. Mixed Doppler-Lorentz broadening should therefore be taken into account throughout the atmosphere. For the homogeneous absorption path calculations the Voigt profiles was used for pressures lower than 3 atmospheres.

Calculations were made for conditions corresponding to those of samples 11, 16, 23 and 40-44 of Burch and Gryvnak (1967). Two forms of comparison with their experimental spectra were made. First, the theoretical spectra were plotted directly from the computer by a Calcomp plotter, using the same scales and slit-widths as the experimental data. Typical results are shown in Fig. 4.1. The agreement between the observed and calculated spectra was so good that the two could scarcely be distinguished.

A more discriminating comparison may be obtained by computing the total absorptions for the band. Table 4.1 lists the theoretical and experimental values. Those for samples 40-44 were provided by Dr. Burch (private communication). Again the results show excellent agreement, the greatest difference being 2.4% for sample 4.2. These results show that the analysis applied by Burch et al. and Burch and Gryvnak was accurate, and that their results are self-consistent.

It does not provide an independant check since the band parameters were derived from the same spectra. However, it appears that their estimates of the band strength ( $4.09 \pm 0.25 \text{ gm}^{-1} \text{ cm}^2 \text{ cm}^{-1}$ ) and Lorentz half-widths are correct to within their error estimates.

$u = 156 \text{ gm./cm.}^2$

$P = 1.00 \text{ atm.}$

$\delta = 1.2 \text{ cm.}^{-1}$

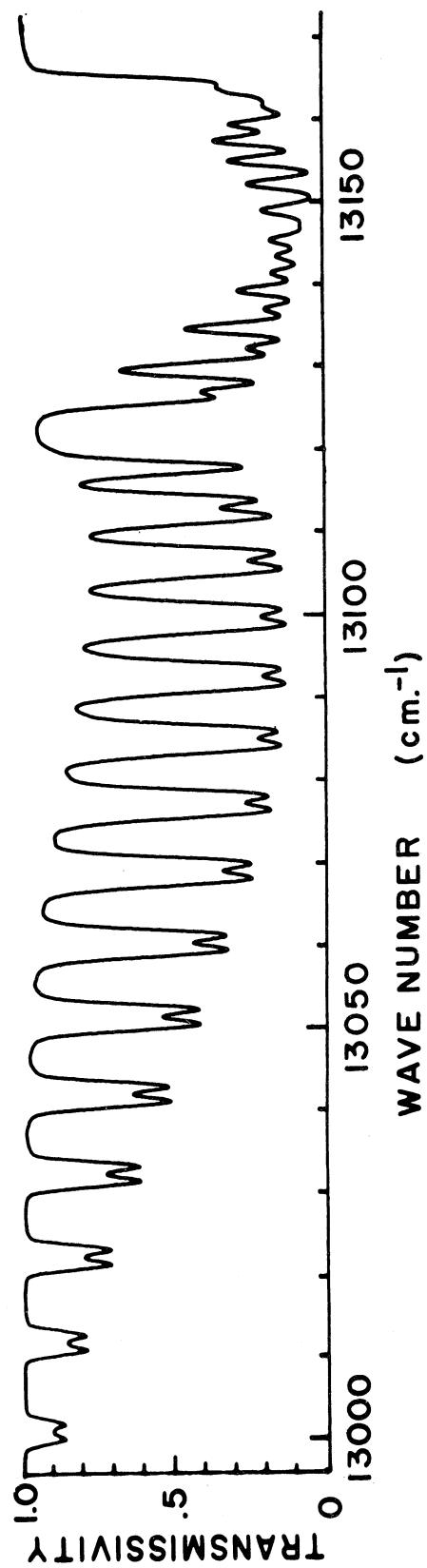


FIGURE 4.1 Theoretically calculated spectrum of oxygen 'A' band for conditions in experimental sample 43.

TABLE 4.1 Summary of Experimental and Theoretical Results  
for the Oxygen 'A' -Band. Experimental Values are  
From Burch and GryvnaK (1967)

Sample No.	P (atm)	u (gm/cm <sup>2</sup> )	Slit Width (cm <sup>-1</sup> )	Experimental	Theoretical	Difference
				$\int A_{\nu} d\nu$ (cm <sup>-1</sup> )	$\int A_{\nu} d\nu$ (cm <sup>-1</sup> )	%
11	13.6	3.91	0.6	14.6	14.6	0.0
23	13.6	36.8	0.6	76.1	76.1	0.0
16	7.1	7.79	0.6	25.7	25.6	0.4
40	0.50	77.8	1.2	39.7	39.7	0.0
41	0.50	31.2	1.2	25.5	25.6	0.4
42	0.50	8.05	1.2	12.4	12.7	2.4
43	1.0	156	1.2	68.5	69.1	0.9
44	2.0	3.1	1.2	100.3	102.2	1.9

Now that the band parameters are accurately known, it is possible to apply them to atmospheric slant paths with a reasonable degree of confidence. This task will form part of the work under the new contract, continuing the present program.

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