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Quarterly Report

HIGH ALTITUDE RADIATION MEASUREMENTS

1 October 1971 - 31 January 1972

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## Abstract

This report summarizes project activity during the period 1 October 1971 to 31 January 1971. Problems in the measurement of high resolution CO<sub>2</sub> spectra at 4.3 μm and 15.0 μm and medium resolution O<sub>3</sub> spectra at 9.6 μm are noted. Data analysis for the 15 μm CO<sub>2</sub> are essentially completed. Only an initial inspection of the 4.3 μm CO<sub>2</sub> has been made, however the data looks precise enough to allow absolute transmissivities to be obtained. The disagreement of the present 9.6 μm O<sub>3</sub> data with Walshaw's results is discussed. Analysis of the 15 μm CO<sub>2</sub> isotope data is well underway.

## I. Introduction

This is the 9th Quarterly Progress Report on Contract No. NSR 23-005-376, covering the period 1 October 1971 to 31 January 1972. The additional month has been added to this quarterly report period to cover the one month "no cost" extension of the contract from 1 October 1971 to 31 October 1971.

The project effort during this time was divided among the following tasks.

- A. High resolution measurements (L. W. Chaney).
- B. Analysis of High Resolution CO<sub>2</sub> Spectra (S. R. Drayson)
- C. Medium Resolution Measurements of the 9.6 μm Absorption Band of O<sub>3</sub> (L. T. Loh and P. A. Titus)
- D. Analysis of the Medium Resolution 9.6 μm O<sub>3</sub> Spectra (W. R. Kuhn).
- E. Study of the Spectra of CO<sub>2</sub> Isotopes (J. B. Russell).

## II. High Resolution Measurements (L. W. Chaney)

### A. 4.3 μm CO<sub>2</sub> Band

At the end of the last reporting period the spectrometer was completely set up to make detailed line measurements.

The spectral measurements required for the study have been completed. A total of 100 spectral scans were made at various pressures and broadened with various amounts of nitrogen.

During the course of the measurements two significant problems occurred. First the last available carbon element for the water cooled infrared source burned out. The elements had been made in a university

instrument shop which no longer exists. Since the drawings available did not precisely describe the part, some experimentation was required to obtain a satisfactory replacement.

An attempt was made to make a permanent element of molybdenum. This did not work because the "O" rings intended to separate the cooling water from the heated element were not completely effective. As a consequence, molybdenum pentoxide was formed and condensed on the focusing lens. It could be identified by its blue color. The effect could be modified but not eliminated by changing the argon purge.

As a result of this experience, we learned that the water leakage on the carbon elements produced  $\text{CO}_2$  and CO. The normal argon purge eliminated the  $\text{CO}_2$ , but a higher purge was required to eliminate the CO from the spectra being studied.

The second problem concerned detector noise. The detector used for this study was a photo-voltaic indium antimonide detector obtained from Texas Instruments. The nominal bias under test conditions was zero millivolts. However, by placing a band pass interference filter on the cold shield the impedance of the detector increased considerably. The optimum bias for best signal to noise ratio was then increased to 6 millivolts. The exact voltage was very critical for a change of  $\pm 1.0\text{mv}$  would produce a factor of 2 increase in total noise. Furthermore, the detector bias voltage was a critical function of the temperature of the spectrometer. Probably the slit jaws were viewed by the detector. A temperature change of  $1^\circ\text{C}$  produced a bias voltage change of about  $1.2\text{mv}$ . Another complication was the fact that the detectivity of the detector changed with the spectrometer temperature.

After the problem was understood, the detector bias was set immediately before each scan, and no scans were taken before the instrument was stabilized to within 2 degrees of room temperature. The room temperature was held to within one degree during all scans, and usually after about two hours of operation the spectrometer would fall within this range.

#### B. 15 $\mu\text{m}$ $\text{CO}_2$ Band

The modified Ge:Cu detector mounting described in the last report was tested in the spectrometer. The nitrogen cooled shield around the detector element reduced the drifting of the detectivity as was expected. However, the thermal noise increased to almost twice its best value. Texas Instruments claimed that this might be due to contamination which is always a danger when the flake is exposed to the atmosphere. However, the detector is superior to the new Ge:Cu detector obtained from them.

Although the detector was marginal for line width studies, a series of 25 scans were taken on two individual lines. The lines were broadened with various amounts of nitrogen. The data is being saved for possible analysis at a later date. The spectrometer is now being modified for other spectral studies.

### III. Analysis of High Resolution $\text{CO}_2$ Spectra (S. R. Drayson)

#### A. Bands of $\text{CO}_2$ between 12 and 18 $\mu\text{m}$

The analysis of the high resolution spectra of the samples of  $\text{CO}_2$  of normal isotopic abundance has been virtually completed. Most of the remaining analysis is for the bands of the less common isotopic molecules



which are probably better left for the analysis of the enriched samples. A technical report is being prepared describing the experimental procedure and the method of analysis of the spectra. It will also contain the results of the analysis of each band, including the band center and rotational constants, with estimates of the errors associated with the determination of the constants. Selected spectra will be included.

#### B. The 4.3 $\mu\text{m}$ bands of $\text{CO}_2$

Only preliminary work has been done towards the analysis of the high resolution spectra. Calcomp plots have been made of each of the scans and an examination of these has determined that the stability of the background is sufficiently high to allow absolute transmittances to be obtained.

#### IV Medium Resolution Measurements of the 9.6 $\mu\text{m}$ Absorption Band of $\text{O}_3$ . (L. T. Loh and P. A. Titus)

During the initial part of this work period, the operation of the PDP-8 computer used for data handling became intermittantly bad.

From time to time, the % of transmission vs wavelength curves obtained from the IBM cards differed from the analog plot recorded on the Perkin Elmer spectrophotometer. Since the trouble appeared very infrequently, its detection was not an easy task. Finally it was located within the computer itself. The better part of two weeks was required before the repair was completed.

During the time that the computer was not working, alternative schemes to keep the ozone work going without the use of this computer were studied. These schemes included manual data reduction using chart

record from Perkin - Elmer recorder, data acquisition using a Hewlett-Packard system we purchased a long time ago, or using a new system to be acquired. These deliberations were discontinued when the system became operable again.

The ozone work was started again on November 10, and continued to January 27. Emphasis was put on measuring ozone spectra of very low ozone concentrations (of the order of 0.01 atmosphere-cm) in the White cell 3200 cm absorption path. A study was made to find the relation between the accuracy of ozone measurement and percent transmission. This study showed that at low concentrations of a few hundredths atm - cm. of ozone in this White cell, the accuracy of the quantitative measurement of ozone would be poor. The situation can be improved by reducing the path length for the infrared spectra while maintaining that same path for the ultraviolet. It may also be necessary to determine ozone by the chemiluminescent method, which is adaptable to concentration of ozone similar to those in the upper atmosphere.

#### V. Analysis of the Medium Resolution O Spectra (W. R. Kuhn)

Absorptivities for the  $9\mu\text{m}$  region are given in table 1. The total absorptivity as well as the individual contributions of the  $9\mu\text{m}$  and  $9.6\mu\text{m}$  bands are given. Absorptivities were calculated for pressures from 7.5 to 437 mm Hg, and for ozone mass paths from 0.029 to 10.04 atm-cm. Column 6 gives the  $9.6\mu\text{m}$  absorptivity as predicted from the empirical formula of Walshaw (1957), while the last column is the relative difference between the predicted Walshaw value and the present results.

The 9.6 $\mu$ m and 9 $\mu$ m absorptivities were determined by two different methods. The upper line in table 1 is the absorptivity for a division of the two bands at 9.35 $\mu$ m which corresponds to the separation used by McCaa and Shaw (1967). In the second method the  $\nu_1$  band was considered to be symmetric about 9.07 $\mu$ m, which implies that there is no contribution to the absorptivity from the  $\nu_3$  band beyond this wavelength. This method was discussed in the previous report and the results are given by the lower line for each pressure and mass path in table 1. The two methods give differences which are well within the experimental error for the  $\nu_3$  band; however, because of the smaller absorptivity of the  $\nu_1$  band, the two methods show appreciable differences being as large as 50% for the smaller mass paths. Clearly, both methods are somewhat arbitrary, and the  $\nu_1$  absorptivities can only be viewed as being very approximate.

The present results for the 9.6 $\mu$ m band are consistently smaller than those predicted from Walshaw's formula, the relative difference being approximately 20%. It is interesting to note that this is a systematic difference as can be seen from Figure 1. Only those results have been plotted which fall within the mass path range used by Walshaw. It would appear that the present results indicate a larger ozone mass path than would have been found by Walshaw. This difference cannot be accounted for by different ultraviolet absorption coefficients since the present mass paths were adjusted for use in Walshaw's formulae, i. e. Walshaw's adopted ultraviolet absorption coefficients for the 2536 and 2893 Å lines were corrected to Hearn's (1961) values of 133.9 and 17.2 (cm NTP<sup>-1</sup>) respectively. A study is presently underway to ascertain the possible errors and quantitatively, their relative significance,

such as the temperature difference within and outside the White cell, ozone decay rates, and possible non uniform mixing of ozone within the cell. When these uncertainties have been resolved, additional measurements will be made for pressures and mass paths corresponding to typical atmospheric conditions. If these later results are compatible with those of McCaa and Shaw both their results and those of the present study will be used to develop an empirical expression for the absorptivity for the entire  $9\mu\text{m}$  region for use in stratospheric energy budget studies (Walshaw's empirical formula cannot be used for this purpose since it does not include the contribution from the  $\nu_1$  band). If the discrepancy between the two sets of data persists, then a detailed comparison of the present experimental technique with that of McCaa and Shaw must be undertaken. A computer program is presently being developed which will estimate the variation in stratospheric flux divergence studies due to uncertainties in the experimental absorptivities.

#### VI. Study of the Spectra of $\text{CO}_2$ Isotopes (J. B. Russell)

This work on the isotopic spectra of  $\text{CO}_2$ , the PhD dissertation of J. B. Russell, is being done in absentia.

Four of the six programs necessary to perform a line position analysis of the  $\text{CO}_2$  isotopes have been written to be compatible with both the University of Michigan Computer System and the U. S. Naval Avionics Facility, Indianapolis (NAFI) Computer System. The four are as follows. One program calculates line positions in the terms of  $\text{cm}^{-1}$  from spectrometer drum turn positions and lines whose position in  $\text{cm}^{-1}$  is known well enough already to be used as calibration lines. Another program analyzes the line positions of the Q-branches to determine the wavenumber of the band center and the two rotational constants B and D. The other two programs

analyze the P and R branches, one by analyzing them separately and the other by analyzing the sum of the P and R line positions. The result of these analyses is also the wavenumber of the band center and two rotational constants. Yet to be written are the programs which analyze the P and R lines in  $\pi - \pi$  and higher order bands where a total of 5 unknowns are possible, the band center and four rotational constants (2 B's and 2 D's).

Analysis of the  $^{13}\text{C}^{16}\text{O}_2$  isotope has been started. The major part of the work on this isotope should be completed by June 1. The remaining two programs will therefore also be completed by this date.

Turn around time for computer runs at NAFI has improved greatly in the last few months.

#### VII. References:

1. Hearn, A. G. 1961: Proc. Phys. Soc. 78, 932
2. Walshaw, C. D. 1957: Quart. J. Roy. Meteor. Soc. 83, 315.
3. McCaa, D. J., and J. H. Shaw, 1967: The Infrared Absorption Bands of Ozone, Sci. Rep. No. 2 Project No. 7670, Ohio State University, 94 pp.

Table I. Comparison of Absorptivities

Pressure (mm Hg)	Mass path (cm STP)	9.6 $\mu$ m	9.0 $\mu$ m	Total	Walshaw 9.6 $\mu$ m	Walshaw-Present Walshaw
7.5	.141	10.1 10.3	.93 .70	11.0	13.02	.22
11.3	.588	26.8 26.6	2.1 2.3	28.9	31.07	.14
11.5	.069	6.6 6.6	.31 .26	6.89	10.42	.37
11.9	.500	28.0 27.8	2.5 2.8	30.5	30.48	.08
12.4	.029	2.9 2.8	.20 .24	3.1	5.78	.50
12.5	9.4	91.7 93.0	31.8 38.2	123.5		
13.8	1.097	39.8 39.6	3.6 4.1	43.4	46.32	.14
16.4	1.002	43.6 43.3	5.1 5.7	48.6		
21.6	.440	29.5 29.3	1.7 1.9	31.2	35.82	.18
23.3	.213	19.6 20.0	.58 .24	20.2	24.6	.20
24.0	.103	11.9 12.2	.55 .26	12.4	16.35	.27
27.0	.296	24.3 24.3	1.1 1.1	25.4	30.61	.21
32.	.900	43.3 43.3	3.7 4.0	47.0	52.18	.17
34.9	1.450	55.2 54.9	6.3 7.3	61.5		
35.7	.630	38.4 38.3	2.4 2.6	40.9	46.66	.18
40.1	.096	13.1 13.4	1.6 1.3	14.7	17.94	.27
40.8	.351	30.9 31.0	.13	31.1	38.22	.19
44.5	2.5	67.2 67.2	10.1 11.6	77.3		
47.2	2.37	67.5 67.6	11.0 12.8	78.6		
47.5	1.878	63.6 63.4	8.3 9.6	71.8		

Table I (Continued)

51.7	2.6	69.7 69.8	11.5 13.4	81.2		
52.3	1.310	54.8 54.8	3.7 3.9	58.6	63.73	.14
53.5	.599	41.8 41.9	.92 .75	42.7	49.4	.15
60.4	1.330	55.2 55.1	5.2 5.7	60.4	65.13	.15
67.3	3.0	74.8 75.0	13.5 15.8	88.3		
73.7	2.63	72.9 72.9	11.7 13.7	84.6		
74.2	1.016	53.2 53.3	3.3 3.2	56.5	62.90	.15
76.5	3.4	72.5 72.6	12.2 14.0	84.6		
76.6	2.68	72.9 73.0	12.3 14.2	85.2		
83.9	1.97	64.8 64.8	7.9 9.0	72.7		
84.7	2.4	70.3 70.1	8.1 9.0	78.3		
91.4	3.8	77.9 78.2	16.2 19.2	94.1		
113.	3.2	75.3 75.5	14.0 16.3	89.2		
119.	4.57	81.9 82.1	18.9 22.8	100.8		
121.	5.23	84.0 84.7	19.2 22.4	103.2		
132.	4.8	82.3 82.7	17.6 20.8	99.9		
134.	5.4	81.4 81.8	18.6 22.0	100.0		
146.	2.65	71.4 71.3	9.2 10.6	80.6		
163.	5.1	81.5 81.6	19.1 22.9	100.7		
193.	6.7	87.4 88.1	24.7 29.4	112.1		
197.	8.4	90.1 91.2	27.2 32.4	117.3		
198.	6.8	88.5 89.1	24.7 29.6	113.2		

Table I (Continued)

202.	8.5	89.0 90.1	27.0 32.2	116.1
226.5	.440	44.6 44.5	2.7 3.0	47.3
258.	9.43	91.7 93.	31.8 38.2	123.5
282.	7.52	90.9 91.9	27.1 32.4	118.
303.	7.9	90.7 91.6	28.7 34.3	119.4
328.	4.68	85.4 85.5	16.6 19.9	102.
332.	10.9	93.6 94.8	35.2 42.4	128.8
432.	10.04	92.7 93.7	34.6 41.9	127.3



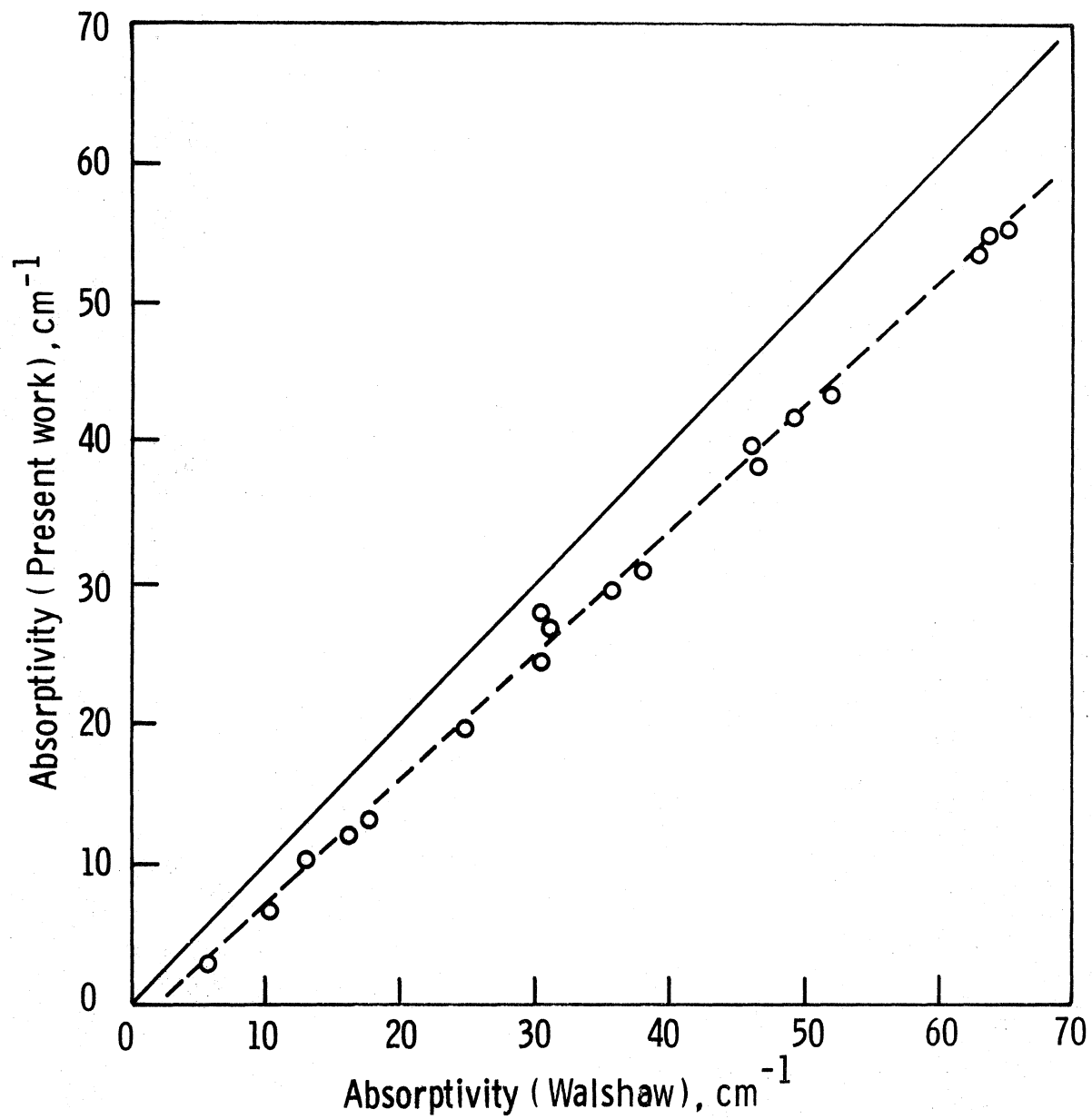


Figure 1. Comparison of absorptivities

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