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Quarterly Report

HIGH ALTITUDE RADIATION MEASUREMENTS

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*(Fred not
Lester)*
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Abstract

This report summarizes project activity during the period 1 February 1972 to 30 April 1972. Results of the analysis of high resolution spectra of CO₂ in the 15 μm region are given in 2 tables. Modifications of the White Cell used for medium resolution 9.6 μm O₃ data are described and results with the modified White Cell are given. Technical Reports on the work already carried out are being prepared.

I. Introduction

This is the 10th Quarterly Progress Report on Contract No. NSR 23-005-376, covering the period 1 February to 30 April 1972.

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

- A. High resolution measurements (L. W. Chaney)
- B. Analysis of High Resolution CO₂ Spectra (S. R. Drayson)
- C. Medium Resolution Measurements of the 9.6 μ m Absorption Band of O₃ (L. T. Loh and P. A. Titus)
- D. Analysis of the Medium Resolution 9.6 μ m O₃ Spectra (W. R. Kuhn).
- E. Study of the Spectra of CO₂ Isotopes (J. B. Russell).

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

The high resolution measurements of the 15 μ m and 4.3 μ m bands of CO₂ have now been completed. During this time interval the instrument was used for measurements of 2.3 μ m and 4.6 μ m bands of CO on another contract. After this work was completed the instrument was turned back over to the Willow Run Laboratory personnel who are responsible for the instrument for use on one of their contracts. Arrangements are being made to use the equipment for high resolution measurements of O₃ starting in approximately February 1973.

A technical report summarizing the high resolution measurements has been started. The report will describe experimental details and contain analog records of the data taken.

III. Analysis of High Resolution CO₂ Spectra (S. R. Drayson)

Preparation of a technical report on the analysis of the high resolution spectra of CO₂ in the 15 μ m region is continuing. Tables 1 and 2 summarize the most important results obtained. The spectra have also been used to estimate the intensities of some of the weaker bands, while others remain to be completed (See Table 2).

Line positions are have
been calculated in preparation for the analysis of the high resolution spectra taken in this region. Comparison of experimental and theoretical spectra should yield good estimates of band intensities of some of the weaker bands whose intensities have not previously been estimated.

IV. Medium Resolution Measurements of the 9.6 μ m Absorption Band of O₃ (L. T. Loh and P. A. Titus).

The Perkin-Elmer #221 spectrophotometer developed operational problems in February, a gradual loss of detector sensitivity and erratic action of the slit system. The bad detector was replaced with a good thermocouple made by Charles M. Reeder & Company, Ann Arbor, Michigan. The cause of slit trouble was traced to 2 loose set screws on the shaft of slit servo-motor. It was fixed. The electron circuits and the optical components were also checked and aligned.

The White cell which contains the O₃ sample was coated with teflon. Mixing of the O₃ mixture was improved by the installation of a stirring device.

The teflon coating was applied after covering all the mirrors with thin polyethylene and the KBr windows with several layers of lens tissue

Table 1: Vibrational and rotational constants for CO₂. All units are cm⁻¹.

Isotope	Level	Vibrational Energy	B _c	B _d	D _c	D _d
626	000:0	0.0	.3902196	.3902196	13.31x10 ⁻⁸	13.31x10 ⁻⁸
626	010:1	667.381	.3906393	.3912539	13.49x10 ⁻⁸	13.51x10 ⁻⁸
626	(100:0)I	1388.185	.3901878	.3901878	11.42x10 ⁻⁸	11.42x10 ⁻⁸
626	(100:0)II	1285.410	.3904812	.3904812	15.63x10 ⁻⁸	15.63x10 ⁻⁸
626	020:2	1335.131	.3916723	.3916646	13.97x10 ⁻⁸	13.64x10 ⁻⁸
626	(110:1)I	2076.855	.3904025	.3913282	12.28x10 ⁻⁸	11.81x10 ⁻⁸
626	(110:1)II	1932.473	.3907321	.3916753	14.37x10 ⁻⁸	15.26x10 ⁻⁸
626	030:3	2003.238	.3923879	.3923811	13.88x10 ⁻⁸	13.90x10 ⁻⁸
626	001:0	2349.144	.3871396	.3871396	13.24x10 ⁻⁸	13.24x10 ⁻⁸
636	000:0*	0.0	.3902350	.3902350	13.10x10 ⁻⁸	13.10x10 ⁻⁸
636	010:1	648.4816	.3905975	.3912357	12.90x10 ⁻⁸	12.93x10 ⁻⁸
636	020:2	1297.269	.3916147	.3916032	13.74x10 ⁻⁸	13.14x10 ⁻⁸
628	000:0*	0.0	.3681640	.3681640	11.10x10 ⁻⁸	11.10x10 ⁻⁸
628	010:1	662.368	.3685961	.3690900	12.08x10 ⁻⁸	12.08x10 ⁻⁸

* constants for ground states of isotopic molecules from W. S. Benedict (private communication)

Table 2: Band centers and intensities of CO₂ bands between 12 and 18 μm. Band centers in cm⁻¹, intensities are at 300K in units cm⁻¹ (atm cm)⁻¹_{300K}. Values in parentheses are less certain.

Band	Upper	Lower	Isotope	Center	Intensity
1	010:1	000:0	626	667.381	194.0
2	(100:0)II	010:1	626	618.029	4.27
3	(100:0)I	010:1	626	620.805	5.0
4	020:2	010:1	626	667.751	15.0
5	(110:1)II	(100:0)II	626	647.063	0.7
6	(110:1)I	(100:0)II	626	791.446	0.022
7	(110:1)II	020:2	626	597.342	0.14
8	(110:1)I	020:2	626	741.724	0.144
9	030:3	020:2	626	668.107	0.85
10	(110:1)II	(100:0)I	626	544.288	0.01
11	(120:2)II	030:3	626	(581.67)	0.0084
12	(120:2)I	030:3	626	(757.52)	0.009
13	(120:2)I	(110:1)II	626	(828.28)	(0.0002)
14	(200:0)II	(110:1)II	626	(738.64)	(0.014)
15	(110:1)I	(100:0)I	626	688.670	0.3
1	010:1	000:0	636	648.482	*
4	020:2	010:1	636	648.787	*
1	010:1	000:0	628	662.368	*
1	010:1	000:0	627	664.72	*

* intensities for isotopes are obtained by multiplying the 626 intensities by the relative abundancies of the isotopic species.

and two layers of masking tape. The teflon spray was type GS-3 made by RAM Chemicals of Gardena, California. Altogether 8 lbs. of the spray were used, 4 lbs. on the wall of the cover, and 4 lbs. on the remaining surfaces. With the coating, the rate of loss of ozone was decreased particularly after the first and the second runs.

The stirring device was used twice during the runs of spectra #87 to 92. It appeared to be leak-tight and free from outgassing. The vacuum side of this device was made of ozone resisting materials. The vacuum seal to the stirrer shaft was provided by a compressed viton O-ring with Ascolube silicone grease made by Asco Manufacturing Company, Pompano Beach, Florida.

With the teflon coating and the stirring device, the sample White cell could be charged with a quantity of ozone and additional oxygen added to adjust the total pressure. The cell could be valved off and its contents mixed by the stirrer. The ozone will stay almost constant for the time of a run. Twelve ozone scans were taken, #81-92, after the modification, for low ozone mass-path, with the White cell path length set to 400 cm. Runs #89-92 were made with the use of stirring device.

V. Analysis of the Medium Resolution 9.6 μ m O₃ Spectra (W. R. Kuhn)

As discussed in the last quarterly report our 9.6 μ m ozone absorptivities were about 15 % larger than those of Walshaw (1957). Possible sources for the discrepancy were a non uniform mixing of the ozone in the cell, and interaction of ozone with the cell walls. In order to minimize these effects the cell was teflon coated, and a stirring device was installed. Additional measurements were then made and some typical

results are presented in Table 3. For this work, the $9.6\mu\text{m}$ band was considered to extend from 9.35 to $11.35\mu\text{m}$. The first five runs were made after the cell had been coated; runs 6 and 7 included the fan, but inoperative, while in the last four runs the fan operated for 10 sec periods with 15 sec intermissions.

Table 3: Comparison of 9.6μ absorptivities with Walshaw's empirical formula for selected pressures and mass paths.

Pressure (mmHg)	Mass Path (cm STP)	Absorptivity (cm^{-1})		$\frac{\text{Present-Walshaw}}{\text{Present}}$
		Present ($9.6\mu\text{m}$)	Walshaw ($9.6\mu\text{m}$)	
5.5	0.072	9.05	9.3	0.12
6.1	0.058	8.30	7.6	0.092
15.1	0.184	20.6	20.3	0.015
15.2	0.177	20.3	20.1	0.01
15.4	0.168	20.0	18.8	0.064
30.5	0.680	47.1	46.6	0.011
31.0	0.630	44.5	45.4	-0.022
31.3	0.592	43.3	44.3	-0.023
47.6	0.966	56.3	57.0	-0.012
47.7	0.937	55.8	58.5	-0.046
47.8	0.906	55.2	57.8	-0.045

Walshaw, C. D., 1957: Quart. J. Roy. Meteor. Soc. 83, 315.

These latest results show considerably better agreement with those from Walshaw's empirical expression, the differences being only on the order of a few percent except at very low pressures and mass paths. Note also that most of the discrepancy with Walshaw was apparently due to interaction of ozone with the cell, i. e., there was no apparent better agreement with his data for the last four runs when the stirring device was operating than in the first five runs when it was not. It is felt that our measurements substantiate Walshaw's empirical expression. His r. m. s. value for the difference between the observed and measured absorptivities, expressed as a percentage of the observed band area is 2.4, which compares favorably with those results in Table 3.

Although we feel Walshaw's empirical formula adequately represents the absorptivity over the range for which it was intended, there is a need for additional measurements for conditions which are found in the stratosphere, i. e., for low pressures and mass paths. For example, the $9.6\mu\text{m}$ band makes its maximum contribution to the flux divergence near the stratopause where a five km thick layer would contain about 0.005 atm. cm ozone at a pressure of about 0.8 mm Hg. These values are well below those used by Walshaw (e. g. minimum pressures and mass paths are 11.2 mm Hg with 0.026 atm cm, and 0.00278 atm cm at 728 mm Hg), and while it is doubtful if our measurements could be made for these low pressures and mass paths nevertheless we should be able to extend Walshaw's results. Also Walshaw does not include the $9\mu\text{m}$ band in his empirical formula. For atmospheric work, however, one requires the total absorption in the $9\mu\text{m}$ region. Although small in comparison to the absorptivity of the $9.6\mu\text{m}$

band (e. g. at 27 mm Hg and 0.15 atm cm, the absorptivity from the 9 m band is about 4% that of the 9.6 band), present levels of sophistication for radiative transfer calculations in the stratosphere dictate its inclusion.

VI. Study of the Spectra of CO₂ Isotopes (J. B. Russell).

The work on the isotopic spectra of CO₂, the PhD dissertation of J. B. Russell, is being done in absentia.

Several computing errors were discovered and corrected after running the programs written at U. S. Naval Avionics Facility, Indianapolis (NAFI) on the University of Michigan Computer.

Analysis of the ¹³C¹⁶O₂ isotope is continuing.

VII. Plans for Future Work.

The work for the remainder of this contract year will consist of medium resolution measurements of O₃ at temperatures lower than room temperature, of the analysis of existing O₃ and CO₂ data and of the writing of reports on the work already completed.

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