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## Abstract

This report summarizes project activity during the period 1 July 1971 to 30 September 1971. Problems in the measurement of the  $4.3\mu\text{m CO}_2$  and  $9.6\mu\text{m O}_3$  Band and efforts to obtain a detector suitable for precision measurements of intensity in the  $15\mu\text{m CO}_2$  band are noted. Progress in the analysis of the  $15\mu\text{m CO}_2$  data for accurate vibrational and rotational constants for several isotopes is noted. Analysis of the  $4.3\mu\text{m CO}_2$  data for line intensities and half widths has been started. Analysis of the  $9.6\mu\text{m O}_3$  data is underway, preliminary comparisons with Walshaw's data are described.

## I. Introduction

This is the 8th Quarterly Progress Report on Contract No. NSR 23-005-376, covering the period 1 July 1971 to 30 September 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 $\mu$ m Absorption Band of O<sub>3</sub> (L. T. Loh and P. A. Titus).
- D. Analysis of the Medium Resolution 9.6 $\mu$ m 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. Detector Investigation

During the last period it was observed that the two Cu:Ge detectors being used did not give the same results. One had a high signal to noise ratio, and poor stability and the other a low signal to noise ratio and good stability. The best features of both detectors are needed for precise intensity measurements in the 15 $\mu$ m band of CO<sub>2</sub>.

Parts were interchanged between the detectors, but no improvement was obtained. It was decided to build a new nitrogen shield for the detector with the best signal to noise ratio. The new nitrogen shield almost completely surrounds the helium port and will



hopefully stabilize the temperature and improve the stability of this detector. The parts have been made, but not tested.

#### B. 4.3 $\mu$ m CO<sub>2</sub> Band Study

The spectrometer had been previously set up to study the 4.6 $\mu$ m CO band, thus no optical changes were required to study the 4.3 $\mu$ m CO<sub>2</sub> band.

A relatively low resolution (0.3 cm<sup>-1</sup>) survey was made of the entire band and the areas to be studied in detail were selected.

A detailed study was begun to cover the R<sub>2</sub> - R<sub>0</sub> - P<sub>2</sub> - P<sub>4</sub> lines. A typical spectrum is shown in fig. 1. A major problem developed. The background scans were not free of CO<sub>2</sub>. It was decided that there were several leaks in the main frame of the spectrometer which had to be repaired. After the repair the vacuum was still not satisfactory. More investigation showed that the mechanical pump was at fault. A search of all our laboratory equipment turned up a satisfactory pump. The new pump has been installed and the tank can now be pumped to better than 10 $\mu$  Hg.

After removing all traces of CO<sub>2</sub> from the main tank by pumping a small amount of CO<sub>2</sub> was still noticed in the background. This was due to the short path between the source and the cell, and the cell and the spectrometer window. A purge was set up to flow nitrogen gas across both ends of the cell. The background is now completely free of CO<sub>2</sub> lines. The equipment is ready for data collection.

#### C. Future Work

Detailed measurements at many different pressures in several

regions of the  $4.3\mu\text{m}$   $\text{CO}_2$  band will be made.

The Cu:Ge detector will be tested with the new liquid nitrogen shield.

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

The analysis of the high resolution  $\text{CO}_2$  spectra is continuing for two spectral regions.

a) The  $15\mu\text{m}$  region. Here the aim of the work is to provide accurate vibrational and rotational constants for the main isotopic molecule and also the less abundant isotopes (see section VI). The very accurate laser measurements have now been incorporated into the analysis of the data by means of an iterative technique, providing what should prove to be a very reliable set of constants. A critical test is being undertaken by examining the constants for the  $(110:1)$  energy level ( $(110:1)_I$  in the new notation) which is the upper energy level of transitions from the  $(020:2)$ ,  $(020:0)$  and  $(100:0)$  levels. The agreement for the constants of the upper energy level obtained by analysis of the spectra from these three bands will provide a measure of the accuracy of the results.

b) The  $4.3\mu\text{m}$  region. Spectra in this region are being obtained to estimate the line intensities and half-widths of the  $\text{CO}_2$  near  $4.3\mu\text{m}$ . In support of this work, line positions and intensities of the various bands are being generated, similar to those obtained earlier in the  $15\mu\text{m}$  region. They will be used to compare with the

high resolution measurements described in this report and with existing low resolution spectra.

#### IV. Medium Resolution Measurements of the 9.6 $\mu$ m Absorption Band of O<sub>3</sub> (L. T. Loh and P. A. Titus).

When the Perkin-Elmer service engineer realigned the detector optics, the detector response was peaked without the White cell in place. The performance with the White cell was not optimum. Since then numerous adjustments have been made in order to improve its resolution. On July 7, the transfer mirror M-9 of the White cell for the sample beam was adjusted. This adjustment not only increased the output but also the resolution, so that, at the 3.508 $\mu$ m line of polystyrene, the resolution with the White cell was 90% of that without the White cell. This was considered satisfactory.

The sliding contact on the slit servo potentiometer again deteriorated. The slit mechanism, as a result, operated rather unsteady. Instead of superficial cleaning, the sliding contact was taken off of the spectrometer, and its worn contact milled flat on the Unimat machine. This operation made the slit mechanism function the way it was designed.

During this quarter, many ozone spectra were recorded. The spectra were done in 2 bands in the NaCl prism range, 3.00 - 6.58 $\mu$ m and 7.76 - 11.34 $\mu$ m. All the spectra were recorded on Perkin-Elmer charts. Most of the spectra were also recorded on the PDP-8 computer, recording a 16 - reading average for each data - point, 100 data - points for each  $\mu$ m of wavelength, and the precise time of each point.

The data processing system was inoperative for five weeks during this quarter. The computer-to-peripheral devices interface became defective and had to be repaired. Then the computer memory stack was found to be defective. It was replaced with a rebuilt stack which also turned out to be defective. A second rebuilt stack was ordered and installed, and has operated properly for the balance of the twenty ozone spectra runs made during the quarter.

During the ozone run of September 15, the ozone generator blew a fuse. Investigation showed that the high voltage lead arced over to the case of the transformer. It was cured by interposing a sheet of Lucite under the case of this transformer.

The Jarrell-Ash power supply/amplifier in the UV ozone monitor system went bad. Circuit trouble shooting revealed an open circuit in the 1800V photomultiplier supply transformer. A new transformer was ordered from the factory. To expedite the ozone work, a Fluke regulated power supply and a Keithley electrometer were hooked together to work in place of the bad Jarrell-Ash unit. They worked very well.

The flowmeter in the ozone generator system was used in a manner quite different from the factory calibration. Therefore it was calibrated right on our system together with its metering valve.

A table showing various data on methane, nitrous oxide, and carbon monoxide was prepared. It will be useful in planning future studies of their infrared spectra.

#### V. Analysis of the Medium Resolution $9.6\mu\text{m}$ $\text{O}_3$ Spectra (W. R. Kuhn).

An analysis of the low resolution transmission profiles of

the  $9.6\mu$  region is presently underway. Ten profiles have been completed with ozone mass paths varying from 0.12 to 7.6 atm cm., and total pressure from about 7 to 285 mm Hg. It is anticipated that future work will be carried out at the lower mass paths and pressures so that a comprehensive comparison can be made with the work of Walshaw (1957).

A few of our experimental absorptivities are given in table 1, along with the predicted values from Walshaw's (1957) empirical formula. The absorptivity was determined from the profiles (fig. 2) with a planimeter. Since Walshaw did not include the  $9.0\mu$  band, this region was excluded by assuming the band is symmetric (shown dashed), and that the overlap region between the  $9.6$  and  $9\mu$  bands can be represented by the product of the absorptivities. Clearly, this latter assumption is only completely valid when absorptivities are independent, which is not true for absorption bands for the same molecule; however, this approximation should be at least as accurate, and hopefully more so than simply constructing a smooth curve through the  $9.0\mu$  region. The contribution to the absorptivity from the  $9\mu$  region is also shown in table 1. Note that this region contributes about 5 to 10% of the  $9.6\mu$  absorptivity.

Mass Path (atm cm)	.35	1.1	3.2
Pressure (mm Hg)	227	14.4	112
Absorptivity (cm <sup>-1</sup> ) <sub>(9.6<math>\mu</math>)</sub>	2.1	2.1	8.0
Absorptivity (cm <sup>-1</sup> ) <sub>(9.0<math>\mu</math>)</sub>	46.5	41.2	8.3
Walshaw (empirical)	55	45.4	---

Table 1. Experimental absorptivities and comparison with Walshaw's (1957) empirical formula

Although a direct comparison with the results of Walshaw will not be possible until additional measurements are made, nevertheless our absorptivities appear to be somewhat lower, even if one includes the contribution from the  $9\mu$  region. The percent differences between the measured and empirically derived values (relative to the measured) are 18 and 10% respectively, which are larger than the uncertainties quoted by Walshaw. Estimates as to the uncertainty in absorptivity due to the varying mass path and pressure will be made, and if the uncertainties are such that the empirical formula gives results differing by more than a few percent of the measured value, an improvement to this formula will be attempted.

VI. Study of the Spectra of CO<sub>2</sub> Isotopes (J. B. Russell).

This work on the isotopic spectra of CO<sub>2</sub>, the Ph. D. dissertation of J. B. Russell, is being done in absentia.

The last couple of months have been spent in adapting computer programs written for the University of Michigan computer system so that they are compatible with the system at U. S. Naval Avionics Facility, Indianapolis (NAFI). One of the programs important in the analysis of the CO<sub>2</sub> isotope infrared absorption spectra has compiled on the system at NAFI.

Several problems contribute to the difficulty in adapting the programs. One is the difference in the Fortran compilers used at the two locations. For example, the IBM system at the University of Michigan allows mixed-mode arithmetic statements to be used,

whereas the Honeywell system at NAFI does not. Another problem is the large amount of "downtime" that the NAFI system has experienced recently. The computer at NAFI is relatively new and attempts to update the software in the system has led to numerous difficulties. Turn around time experienced so far on a batch job has been one day.

## VII. References

1. Walshaw, C.D., Quart. J. Roy. Met. Soc., 83, 315 (1957).

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