AD/A-001 097

ABSORPTION COEFFICIENT MEASUREMENTS OF CO2 HDO-N2, AND CH4-AIR USING A DF LASER

F. S. Mills, et al

Ohio State University

Prepared for:

Defense Advanced Research Projects Agency
Rome Air Development Center

August 1974

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER
RADC-TR-74-295

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER
AD/A-001 097

4. TITLE (and Subtitle)
ABSORPTION COEFFICIENT MEASUREMENTS OF CO_2, $HDO-N_2$, AND CH_4-AIR USING A DF LASER

5. TYPE OF REPORT & PERIOD COVERED
Final Report

6. PERFORMING ORG. REPORT NUMBER
ESL 3271-10

7. AUTHOR(s)
F. S. Mills
R. K. Long

8. CONTRACT OR GRANT NUMBER(s)
F30602-72-C-0016

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Ohio State University ElectroScience Laboratory
Department of Electrical Engineering
Columbus OH 43212

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
12790502

11. CONTROLLING OFFICE NAME AND ADDRESS
Defense Advanced Research Projects Agency
1400 Wilson Blvd
Arlington VA 22209

12. REPORT DATE
August 1974

13. NUMBER OF PAGES
20

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
Rome Air Development Center (OCSE)
Griffiss AFB NY 13441

15. SECURITY CLASS. (of this report)
UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
N/A

16. DISTRIBUTION STATEMENT (of this Report)
Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)
Same

18. SUPPLEMENTARY NOTES
Project Engineer:
James W. Cusack (OCSE)
Griffiss AFB NY 13441
AC 315 330-3145

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Molecular absorption
Laser Propagation
DF laser
DF
CH_4 methane
CO_2 carbon dioxide
HDO heavy water
Water vapor
Molecular Spectroscopy
Atmosphere
Atmospheric absorption

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
This report presents measurements of the absorption of $HDO-N_2$ mixtures when illuminated with a DF laser operating on the 3-2 P(6) to P(8) lines. Similar data is presented for pure CO_2 and the 2-1 P(8) DF line. Measurements of CH_4-Air mixtures are presented for the 2-1 P(6) - P(8) DF lines.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

ABSORPTION COEFFICIENT MEASUREMENTS OF CO_2 $HDO-N_2$, AND CH_4-AIR USING A DF LASER

F. S. Mills
R. K. Long

Contractor: The Ohio State University
Contract Number: F30602-72-C-0016
Effective Date of Contract: 23 June 1971
Contract Expiration Date: 31 August 1974
Amount of Contract: $3330,718.00
Program Code Number: 0E20

Principal Investigator: Dr. Ronald K. Long
Phone: 614 422-6077

Project Engineer: James W. Cusack
Phone: 315 330-3145

This research was supported by the Defense Advanced Research Projects Agency of the Department of Defense and was monitored by James Cusack, RADC (OCSE) GAFB NY 13441 under Contract F30602-72-C-0016, Job Order No. 12790502.

FOREWORD

This report, Ohio State University Research Foundation Report Number 3271-10 (Tenth Quarterly Report), was prepared by The Ohio State University ElectroScience Laboratory, Department of Electrical Engineering, Columbus, Ohio. Research was conducted under Contract F30602-72-C-0016, Job Order 12790502. Mr. James W. Cusack, RADC (OCSE), of Rome Air Development Center, Griffiss Air Force Base, New York is the Project Engineer.

This report has been reviewed by the RADC Information Office (OI), and is releasable to the National Technical Information Service (NTIS).

This technical report has been reviewed and is approved.

James W Cusack
RADC Project Engineer

TABLE OF CONTENTS

I. INTRODUCTION

Contributions to the molecular absorption coefficient for DF lasers arise from absorption by N_2O, CH_4, CO_2, HDO, and a water continuum.

Report RADC-TR-73-389[1] gave calculated values for the absorption coefficient for each of the above components. Since issuance of that report the following additional information has come to our attention.

According to Professor Benedict[2] the CH_4 calculations from the AFCRL data tape may be less accurate than the other coefficients in the 3.8μ wavelength region.

Dr. Orlo Myers[3] has looked at CO_2 absorption experimentally and has found that the absorption coefficient in some cases is four orders of magnitude higher than shown in TR-73-389. We have also measured the CO_2 coefficient for the 2-1 P(8) line and have confirmed this result. Our data is included with this report. The reason for the discrepancy, apparently, is that an isotopic CO_2 band exists in this region which was not included in the AFCRL data tape. The CO_2 coefficient is of the order of 10^{-4} km^{-1} and therefore is still small compared to the water vapor coefficient at sea level.

Experimental results were given in a recent report[4] for five DF lines where N_2O absorption was considered important.

Since the water coefficients are quite small their accurate measurement is difficult. In the case of the HDO component we have enhanced the absorption by using an enriched gas mixture (6.2 parts HDO to 100 parts total water) in the multi-path cell. The first data from these experiments is given in this report. It will be seen that the data scatter in these experiments is already very small.

Future work will include a more complete study of the limitations involved in extrapolation of the results of these experiments to normal atmospheric conditions; extension to more DF lines; and more careful analysis of the gas composition of the mixture.

Burch[5] studied the 3.8μ water continuum by measuring the absorption of high pressure samples of pure water in an elevated temperature long path cell. It was then necessary to assume a broadening coefficient and to extrapolate temperature in order to estimate the coefficient for normal atmospheres. This was the method used in the calculations of TR-73-389.

We present here the derivation of formulas which will make easier the comparison of Burch's results with our experimental coefficients in km^{-1}. Burch[6] has pointed out that whether the continuum arises from line wings, pressure induced bands, or dimers the pressure dependence is the same, i.e., the absorption coefficient is proportional to pressure.

Thus we can write

(1) $$T = e^{-[C_s\ e/760\ +\ C_b\ P'/760]u} = e^{-k\cdot 1}$$

where C_s = self-broadening coefficient ($mol^{-1} cm^2 atm^{-1}$)
C_b = foreign broadening coefficient
e = water vapor pressure in torr
P = total pressure in torr
P' = broadener pressure in torr = (P-e)
u = water content of sample ($mol\ cm^{-2}$)
T = transmittance
k = absorption coefficient (km^{-1}).

The water content of a one km path is given by

(2) $$u = .734 \times 10^{22}\ (e/760/T) \times 10^5\ mol\ cm^{-2}$$

where T is now temperature in deg K.

Now assume $C_b/C_s = .12$[5] and combine equations (1) and (2) leading to,

(3) $$k = 1.53 \times 10^{20}\ \frac{C_s\ e}{T}\ [7.3\ e + P] \quad km^{-1}.$$

This formula used with the extrapolated Burch data[5] for 296 K will yield the values in report RADC-TR-73-389. We intend to state the results of our planned spectrophone experiments in terms of C_s so that an easy comparison with previous work will be possible.

The experiments referred to will be performed using a spectrophone illuminated with a DF laser and using water vapor-nitrogen mixtures at ambient temperature. The laser is located at UARL in Hartford, Connecticut.

Calculated results are given in report RADC-TR-73-389 for 30 DF laser lines. Although most of these lines may eventually be studied experimentally, the present phase of the work is concentrated on a smaller number of lines.

For HDO we are studying,

3-2 P(6), P(7), P(8)
2-1 P(6), P(7), P(8)
1-0 P(11)

and for N_2O,

3-2 P(6), P(7), P(8)
2-1 P(10), P(11).

II. HDO MEASUREMENTS

The equipment and data recording procedures for these experiments were identical to those described for the N_2O measurements[4] and hence the description will not be repeated.

We are labeling the HDO data preliminary at this time since these measurements were performed using the same detector linearity corrections as were used with the N_2O measurements.

Further detector calibration work is required for two reasons. First there is the possibility of detector and or electronic circuitry changes with time of the order of months since the last calibration. Second the laser power output is in general much higher for 2-1 lines than for 3-2 lines thus requiring a calibration over different detector voltage ranges.

In these experiments it was necessary to devise a careful sample preparation procedure.

In the steady state, HDO does not exist alone but rather in equilibrium with H_2O and D_2O according to the following equation:

$$(4) \qquad H_2O + D_2O \rightleftharpoons 2HDO.$$

The relative concentrations of the three types of water can be calculated from the equilibrium constants, $K_{293°} = 3.543$ and $K_{293°} = 3.506$[7] for the liquid and gas phases respectively.

The procedure used in preparing the samples for the work presented here was to mix a known amount of D_2O with a known amount of H_2O and calculate the resulting amount of HDO using the equilibrium constant. A formula relating the final amount of HDO to the initial amounts of D_2O and H_2O can be derived as follows:

Let C_{H_2O} be the initial volume of H_2O, C_{D_2O} be the initial volume of D_2O, and C_{HDO} be the final volume of HDO. Using these definitions Eq. (4) becomes

$$(5) \qquad (C_{H_2O} - C_{HDO}/2)\ H_2O + (C_{D_2O} - C_{HDO}/2)\ D_2O \rightleftharpoons C_{HDO}\ HDO.$$

The terms in parentheses in Eq. (5), $(C_{H_2O} - C_{HDO}/2)$ and $(C_{D_2O} - C_{HDO}/2)$ are the final amounts of H_2O and D_2O respectively. The final amounts of H_2O, D_2O and HDO are related to the appropriate equilibrium constant K by

$$\frac{(C_{HDO})^2}{(C_{H_2O} - C_{HDO}/2)(C_{D_2O} - C_{HDO}/2)} = K \tag{6}$$

or

$$\frac{(C_{HDO})^2}{C_{H_2O}\, C_{D_2O} - \frac{C_{HDO}}{2}(C_{H_2O} + C_{D_2O}) + \frac{(C_{HDO})^2}{4}} = K. \tag{7}$$

Equation (7) may be written as follows.

$$(C_{HDO})^2\,(4-K) + 2K\, C_{HDO}\,(C_{H_2O} + C_{D_2O}) - 4K\, C_{H_2O}\, C_{D_2O} = 0. \tag{8}$$

Equation (8) may now be solved for C_{HDO} using the quadratic formula.

$$C_{HDO} = \frac{-K(C_{H_2O}+C_{D_2O}) + \sqrt{K^2(C_{H_2O}+C_{D_2O})^2 + 4K(4-K)C_{H_2O}C_{D_2O}}}{(4-K)}\,. \tag{9}$$

For the measurements reported here the enhanced HDO mixture was prepared by mixing 10 ml. D_2O with 300 ml. H_2O. This results in a mixture of liquid water containing 0.116% D_2O and 6.219% HDO with the remainder being H_2O, or a gaseous mixture containing 0.118% D_2O and 6.216% HDO with the remainder being H_2O. The concentration of HDO was taken to be 6.22% since the original amounts of D_2O and H_2O could not be measured accurately enough to justify carrying the third decimal place. The absorption due to D_2O was not measured separately so there may be a small contribution to the absorption coefficients reported here which is caused by D_2O as well as HDO.

In spite of the fact that the sample is approximately 94% H_2O one can assume that the water continuum absorption in a one km path is so small that it will not cause an appreciable error in the measured HDO coefficients[1].

There is another potential problem which could be encountered when the enhanced sample is introduced into the White cell. This is caused by the fact that HDO is less volatile than H_2O and therefore remains preferentially in the condensed phase. It has been reported[8] that in thermodynamic equilibrium water vapor over liquid water will contain 8% fewer HDO molecules than the liquid water. When the water vapor is being introduced into the White cell, the liquid and gas are certainly not in thermodynamic equilibrium so the HDO concentration could be quite uncertain. This problem was overcome by filling a small bottle with just enough of the enhanced water to fill the White cell with the desired amount of water vapor and evaporating the sample completely.

One other problem which might possibly affect the HDO concentration would be preferential adsorption of HDO by the walls of the White cell. The cell has been tested several times for H_2O adsorption and none has been detected. However this test has not been made with HDO. It is our intention to sample some enhanced water vapor-nitrogen mixtures and send them to a commercial laboratory for mass spectrographic analysis. Pending that analysis it is our belief that preferential HDO adsorption is not a problem.

We are also adding a mass spectrometer analyzer to our White cell so that the HDO/H_2O ratio can be monitored as a function of time in order to evaluate some of the above potential problems. We do not expect that our instrument will be accurate enough for absolute concentration determinations. For that we intend to rely on the equilibrium constant method and the commercial laboratory analysis.

Figures 1, 2 and 3 show the results for the 3-2 P(6), P(7) and P(8) lines respectively. The absorption cell path length was 731.7 meters and originally contained 15 torr of the 6.22 parts HDO to 100 parts total water mixture plus nitrogen to a total pressure of 760 torr. The lower points on the curve were then obtained by partial pumpout of the sample followed by a refill to 760 torr with nitrogen.

For each line a least squares fit of the data to an expression of the form $K = Ap + Bp^2$ was made, where K is the absorption coefficient and p is the partial pressure of enriched water vapor in torr. The derived expression is presumed to be a more accurate characterization of the absorption coefficient than any individual data point. The expressions for the measured absorption coefficients for the three lines are presented in column 3 of Table I. The expressions are valid for 760 torr total pressure with p being the partial pressure of the enriched water. The absorption coefficients extrapolated to .03% HDO and 14.26 torr water vapor are presented in column 4 of Table II. These coefficients were obtained by evaluating the expressions in column 3 for p = 14.26 torr and multiplying by .03/6.22. This procedure assumes that line broadening caused by HDO - HDO collisions is about the same as line broadening due to HDO - H_2O

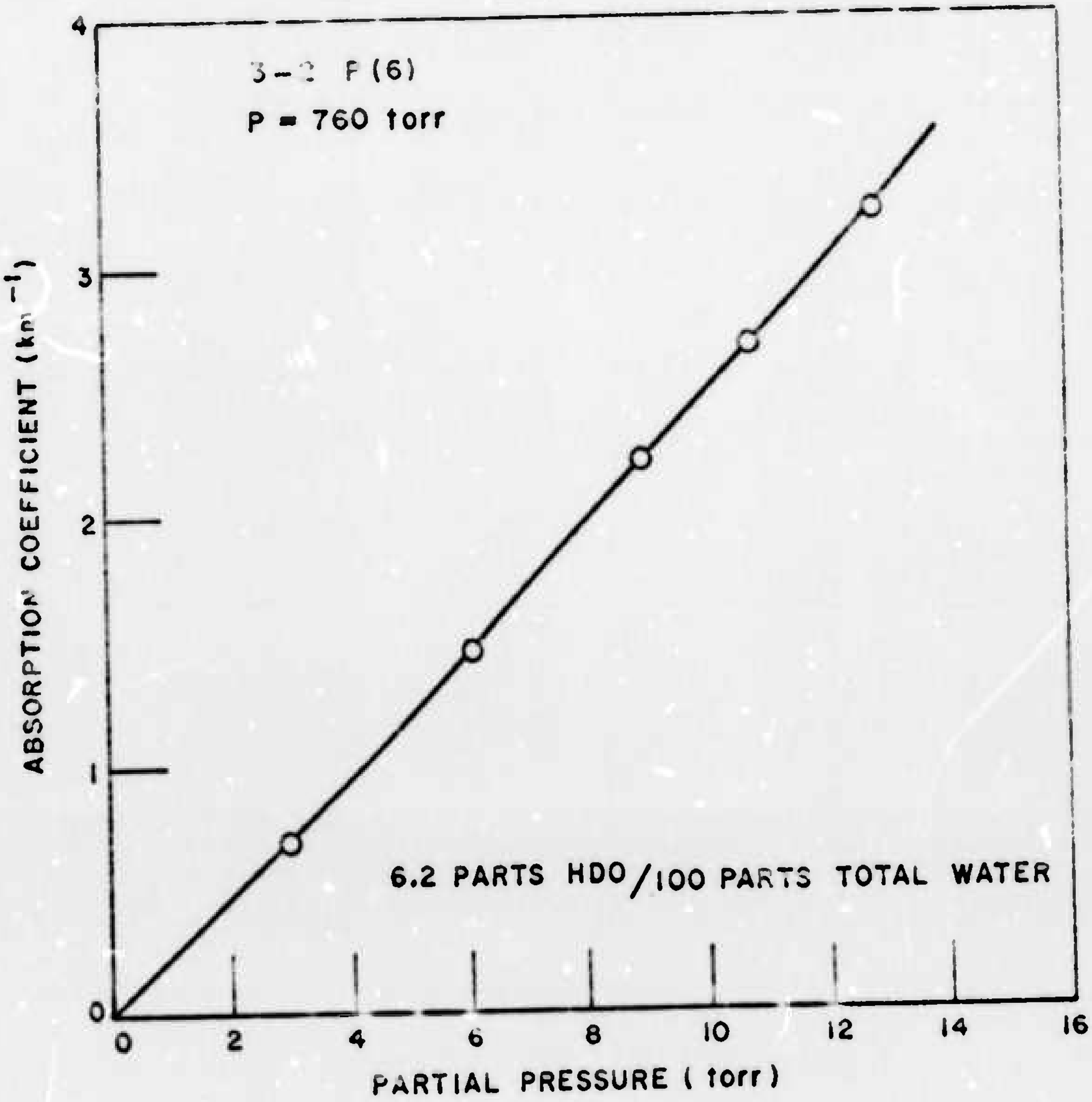

Fig. 1. Measured HDO-N_2 absorption coefficient for 3-2 P(6) line.

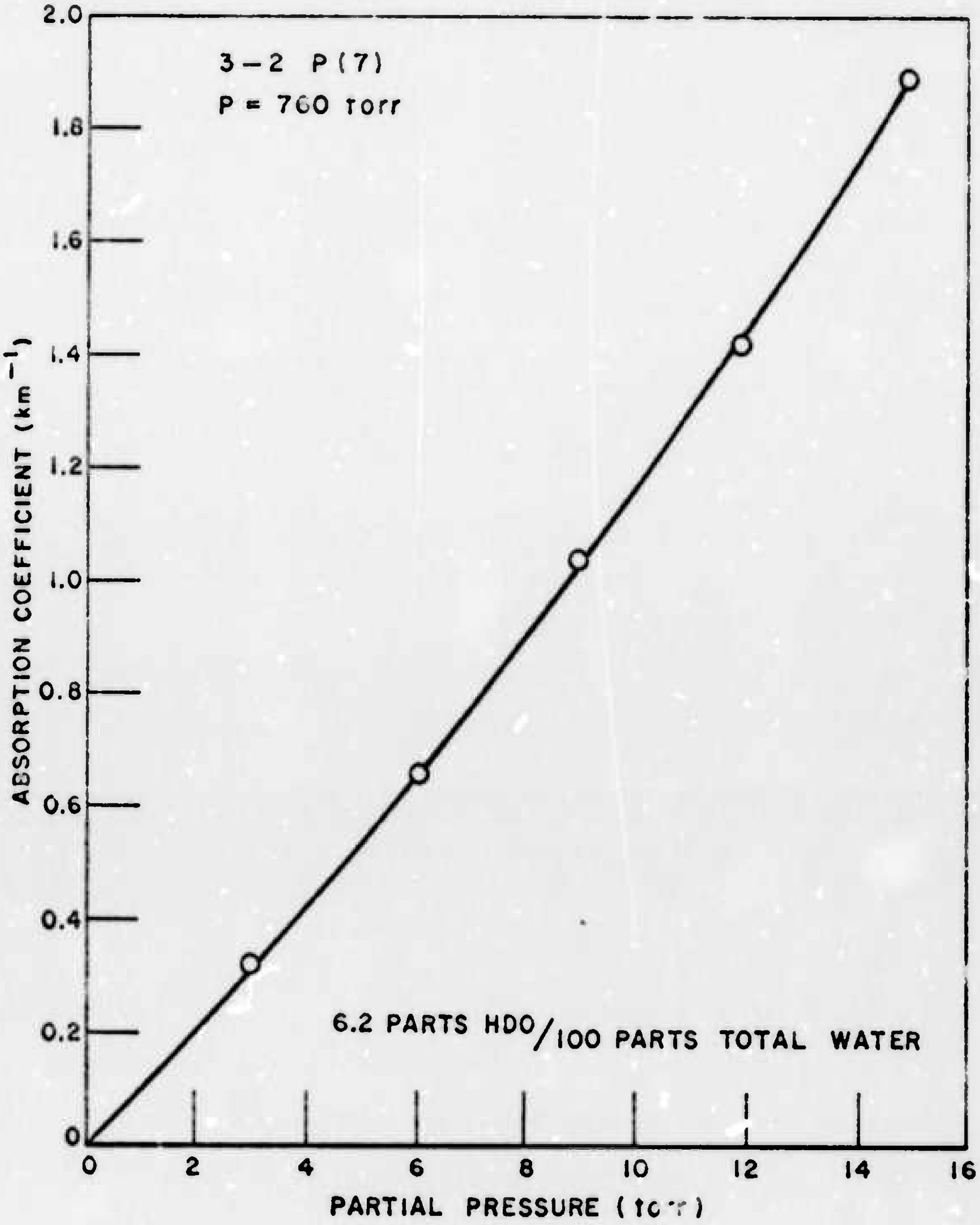

Fig. 2. Measured HDO-N_2 absorption coefficient for 3-2 P(7) line.

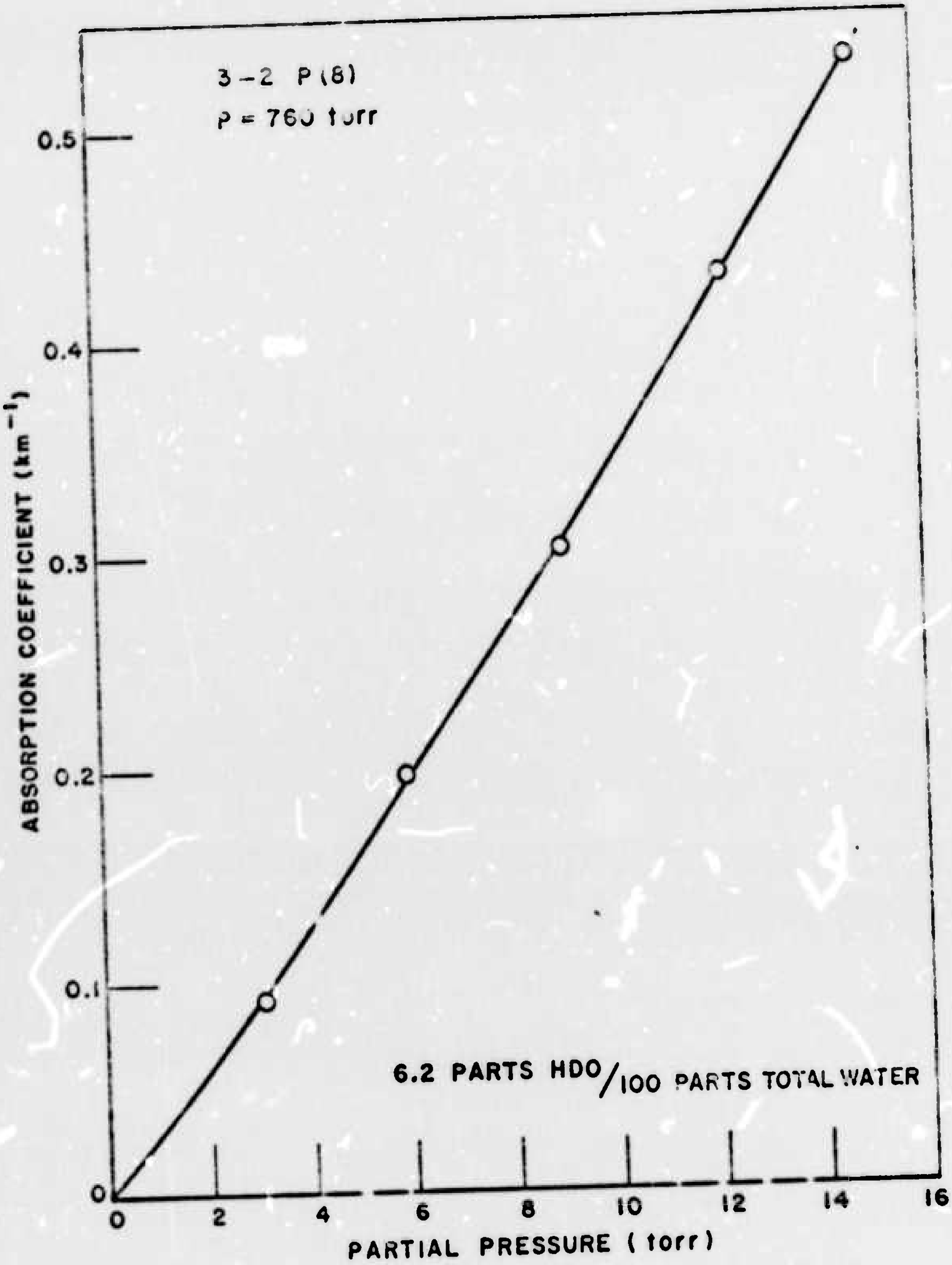

Fig. 3. Measured HDO-N_2 absorption coefficient for 3-2 P(8) line.

collisions. The absorption coefficients calculated from the AFCRL tape for 14.26 torr water and 760 torr total pressure[1] are presented in column 5 for comparison.

TABLE I

Col. 1	Col. 2	Col. 3	Col. 4	Col. 5
Iden	V cm^{-1}	K_{exp} at 0.22% HDO (km^{-1})	$K^{OSU}_{.03\% HDO}$, 14.26 torr H_2O (km^{-1})	K_{calc} (km^{-1})
3-2 P(6)	2594.25	$.231p+1.58x10^{-3}p^2$	.0174	.00667
3-2 P(7)	2570.51	$9.77x10^{-2}p+1.93x10^{-3}p^2$	.00861	.00478
3-2 P(8)	2546.42	$3.00x10^{-2}p+4.01x10^{-4}p^2$	.00246	.00135

III. PURE CO_2 ABSORPTION

Absorption of the 2-1 P(3) DF laser line at 2631.06 cm^{-1} by pure CO_2 was measured for CO_2 pressure of 248, 503, and 761 torr in a path of 731.7 meters. The result of that measurement is shown in Fig. 4. The results of this experiment are less reliable than the HDO measurements because the detector calibration was not sufficiently well known. The point at 761 torr is probably within 10% with the other two points being somewhat worse. The measured absorption coefficient was 1.6 km^{-1} at 761 torr. Assuming a broadening coefficient of 1 this corresponds to 5.3×10^{-4} km^{-1} at 330 ppm CO_2 and 1 atmosphere total pressure. As discussed in the introduction this is higher than one computes from the AFCRL data tape[1] because the necessary CO_2 line data is not included in the tabulation.

IV. CH_4 - AIR ABSORPTION

Absorption of the 2-1 P(6), 2-1 P(7), and 2-1 P(8) DF Laser lines by methane-air mixtures was also measured. The absorption cell was set for a path length of 731.7 meters and originally contained 2263 parts per million methane plus dry air to a total pressure of 760 torr. Lower concentrations were then obtained by partially evacuating the cell and refilling to 760 torr with dry air.

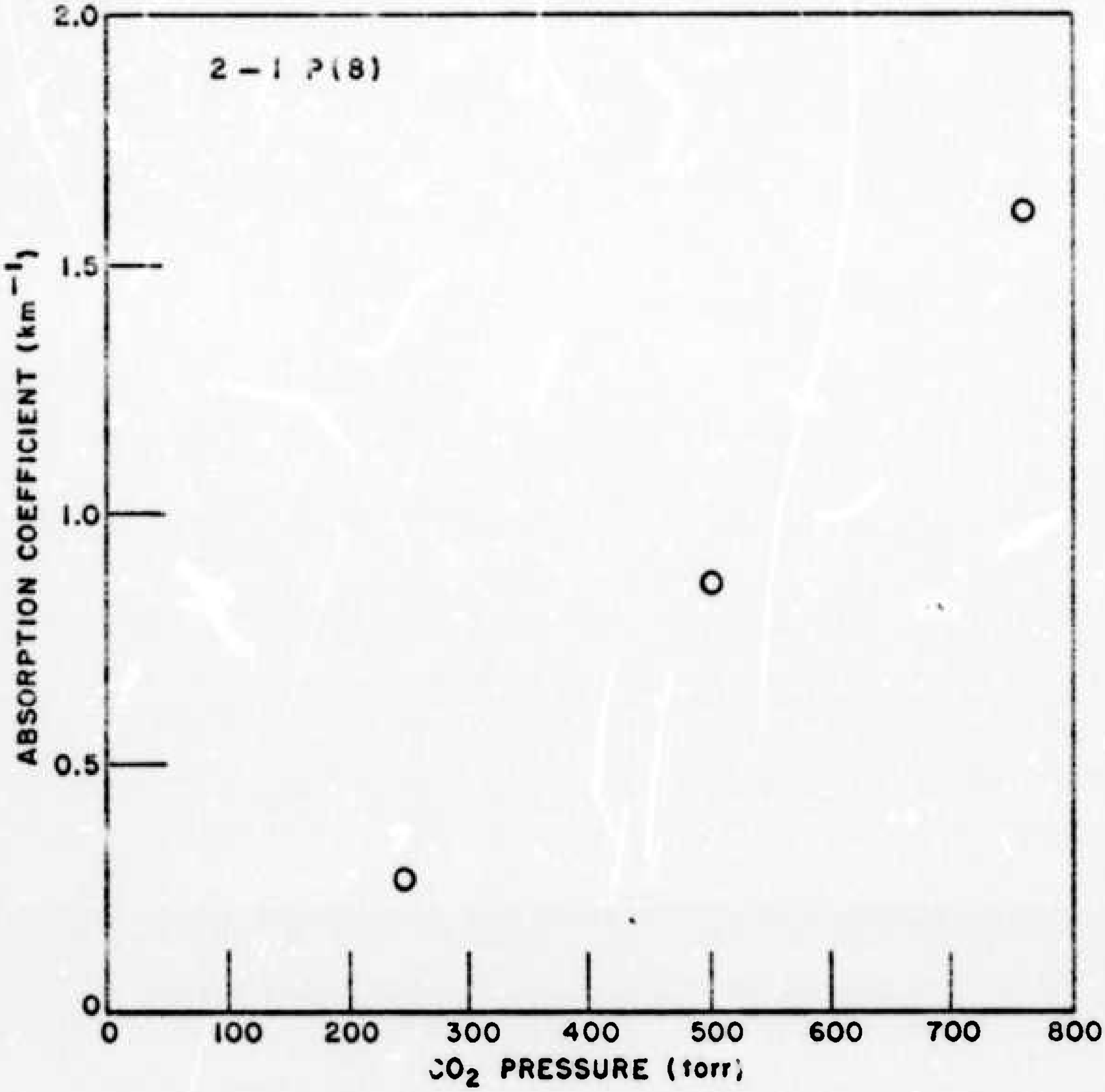

Fig. 4. Measured CO_2 absorption coefficient for 2-1 P(8) line.

Before these measurements were made the detectors were calibrated for the 2-1 band using the 2-1 P(10) DF laser line. The equipment and calibration procedure used were identical to those for the 3-2 band calibration reported earlier[4] and will therefore not be repeated.

Figures 5, 6, and 7 show the measured absorption coefficients versus CH_4 concentration for the 2-1 P(6), P(7), and P(8) lines respectively. For each line, a least squares fit of the data to a straight line through the origin was made.

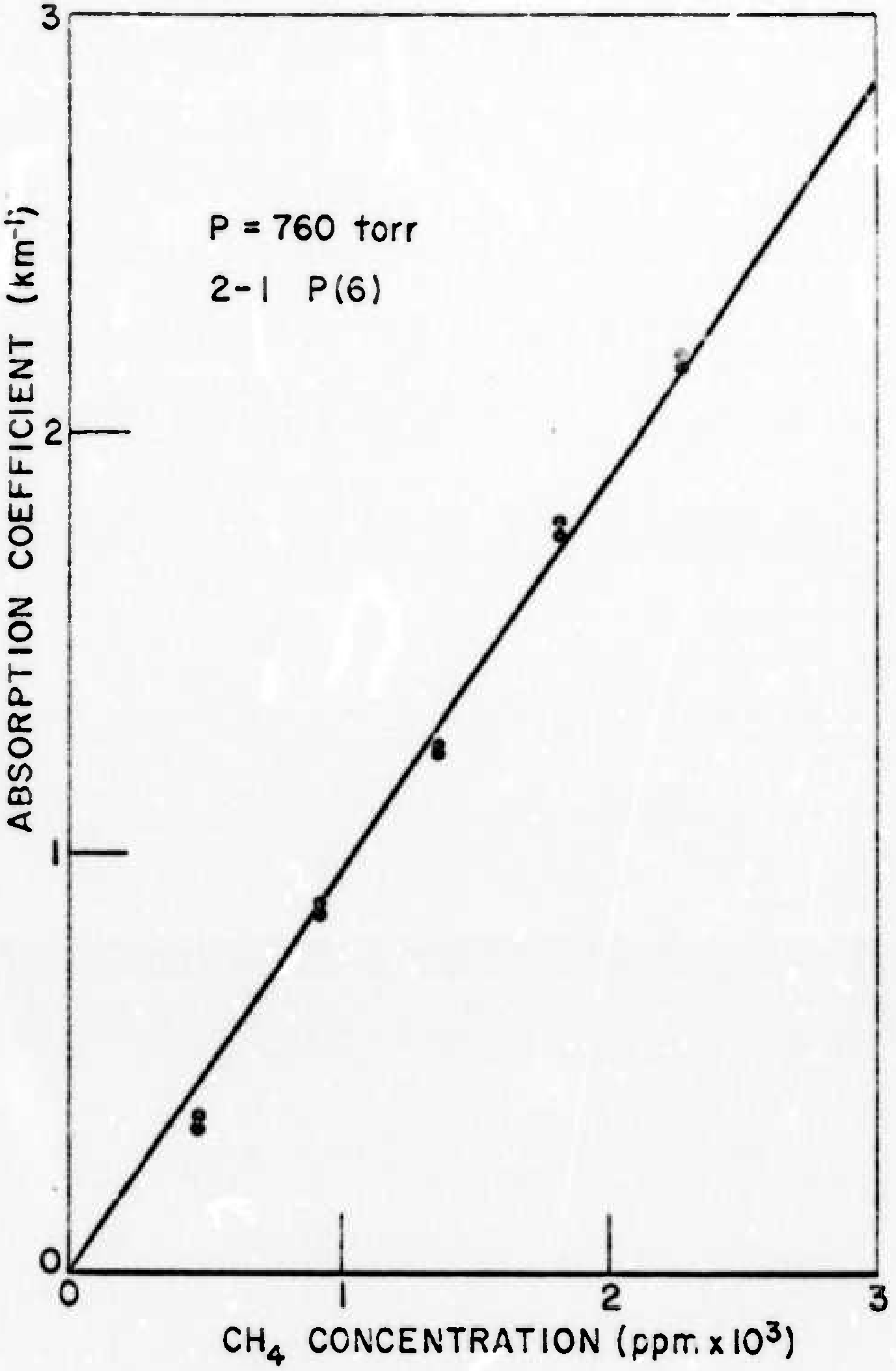

Fig. 5. Measured CH$_4$ - Air absorption coefficient for 2-1 P(6) line.

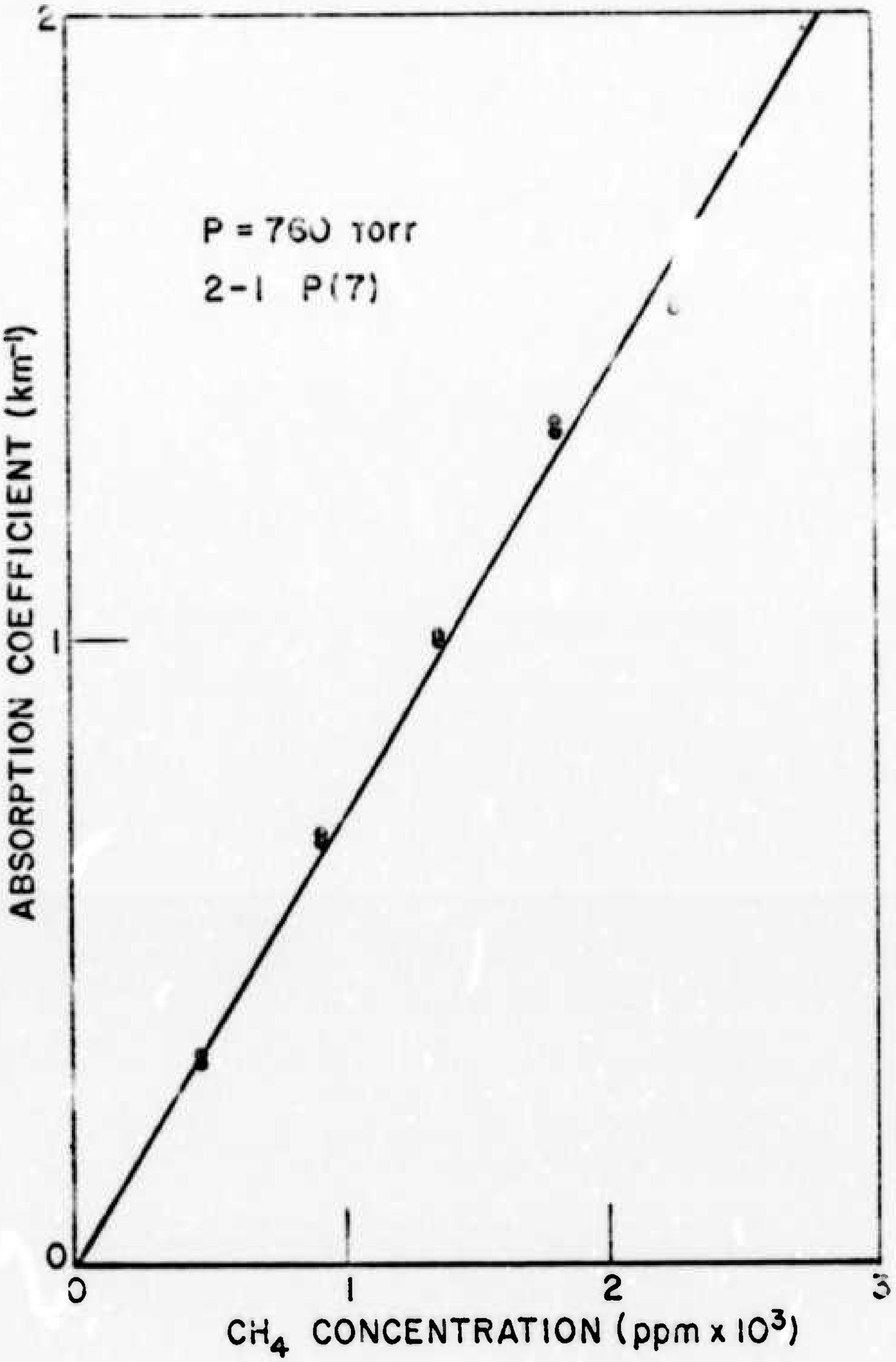

Fig. 6. Measured CH4 - Air absorption coefficient for 2-1 P(7) line.

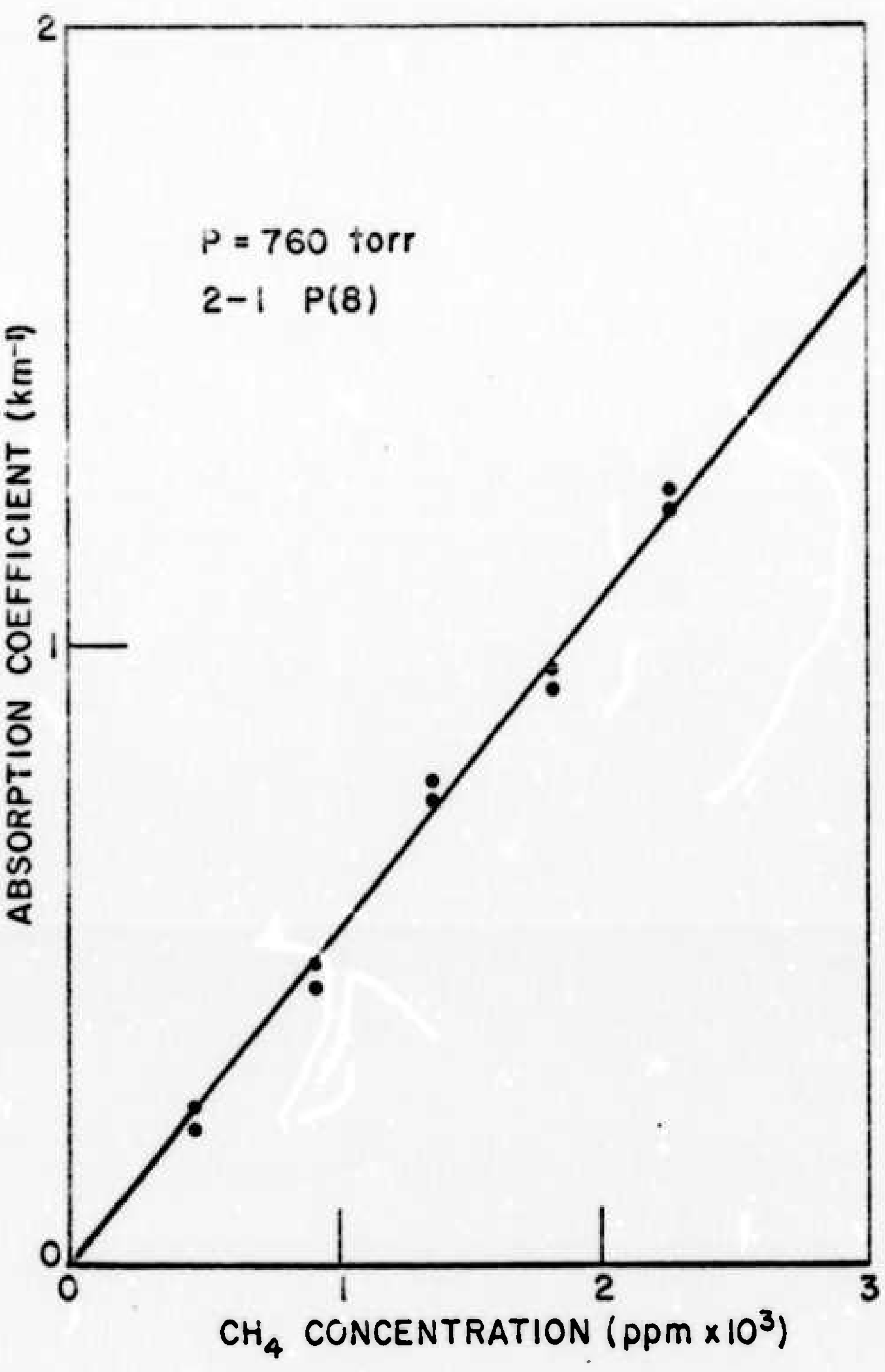

Fig. 7. Measured CH_4 - Air absorption coefficient for 2-1 P(8) line.

Assuming a natural CH_4 abundance of 1.6 ppm[9], Table II gives the CH_4 absorption coefficients for the three laser lines as extrapolated from the experimental data For comparison the calculated values[4] are also given.

TABLE II

	V (cm^{-1})	K^{OSU}_{exp} (km^{-1})	K_{calc} (km^{-1})
2-1 P(6)	2680.17	15.2 E-4	3.103 E-4
2-1 P(7)	2655.85	11.3 E-4	6.015 E-4
2-1 P(8)	2631.06	8.59 E-4	7.884 E-4

These measurements will be used to calibrate the spectrophone for the United Aircraft experiments.

V. SUMMARY

Recent DF laser absorption measurements made with the multi-traversal cell have been presented.

An experiment using a one watt DF laser and an acoustic spectrophone is being planned. With this device we will examine normal sea level air as well as some of the special mixtures which have been studied in the multi-traversal cell.

REFERENCES

[1] R. K. Long, F. S. Mills and G. L. Trusty, "Calculated Absorption Coefficients for DF Laser Frequencies," Report 3271-7, November 1973, The Ohio State University ElectroScience Laboratory, Department of Electrical Engineering; prepared under Contract F30602-72-C-0016 for Rome Air Development Center. (RADC-TR-73-389)

[2] Professor W. S. Benedict, Private Communication, University of Maryland.

[3] Orlo Myers, Private Communication, General Dynamics, Convair Aerospace Division, San Diego, California.

[4] F. S. Mills and R. K. Long, "Measured N_2O-N_2 Absorption at Five DF Laser Frequencies," Report 3271-9, March 1974, The Ohio State University ElectroScience Laboratory, Department of Electrical Engineering; prepared under Contract F30602-72-C-0016 for Rome Air Development Center. (RADC-TR-74-89)

[5] Burch, Gryvnak and Pembrook, "Investigation of the Absorption of Infrared Radiation by Atmospheric Gases: Water, Nitrogen, Nitrous Oxide," AFCRL-71-0124, Philco-Ford Corp, January 1971.

[6] Burch, Gryvnak and Piper, "Infrared Absorption by H_2O and N_2O," AFCRL-TR-73-0530, Philco-Ford Corp., July 1973.

[7] Spencer, Denault and Takimoto, "Atmospheric Gas Absorption at DF Laser Wavelengths," The Aerospace Corporation.

[8] Ehhalt and Östlund, Journal of Geophysical Research, Vol. 75, No. 12, April 20, 1970.

[9] R. A. McClatchey, et al., AFCRL-72-0497, 24 August 1972.