

AD-A016 435

SPECTROPHONE MEASUREMENT OF THE WATER VAPOR CONTINUUM
AT DF LASER FREQUENCIES

E. K. Damon, et al

Ohio State University

Prepared for:

Defense Advanced Research Projects Agency
Rome Air Development Center

August 1975

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

308103

ADA016435

RADC-TR-75-203
Interim Technical Report
August 1975

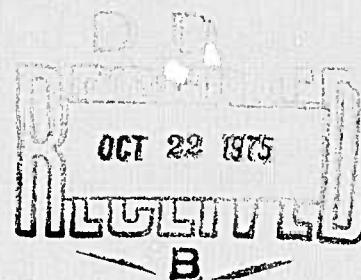


SPECTROPHONE MEASUREMENT OF THE WATER VAPOR
CONTINUUM AT DF LASER FREQUENCIES

Ohio State University

Sponsored by
Defense Advanced Research Projects Agency
ARPA Order No. 1279

Approved for public release;
distribution unlimited.



The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the U. S. Government.

Rome Air Development Center
Air Force Systems Command
Griffiss Air Force Base, New York 13441

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
US Department of Commerce
Springfield, VA. 22151

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER RADC-TR-75-203	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SPECTROPHONE MEASUREMENT OF THE WATER VAPOR CONTINUUM AT DF LASER FREQUENCIES		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
7. AUTHOR(s) E. K. Damon F. S. Mills J. C. Peterson R. K. Long		6. PERFORMING ORG. REPORT NUMBER ESL 4045-1
9. PERFORMING ORGANIZATION NAME AND ADDRESS Ohio State University/ElectroScience Laboratory 1320 Kinnear Road Columbus OH 43212		8. CONTRACT OR GRANT NUMBER(s) F30602-75-C-0029
11. CONTROLLING OFFICE NAME AND ADDRESS Defense Advanced Research Projects Agency 1400 Wilson Blvd Arlington VA 22209		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62301E 12790506
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Rome Air Development Center (OCSE) Griffiss AFB NY 13441		12. REPORT DATE August 1975
		13. NUMBER OF PAGES 38
		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 RADC Project Engineer: James W. Cusack (OCSE)		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) DF laser Methane Molecular absorption Nitrous oxide Spectrophone Water vapor Laser propagation		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The results of a field measurement program conducted by the Ohio State University in cooperation with the United Aircraft Research Laboratories is described. A laser-illuminated spectrophone is used to measure the absorption of water vapor at six DF laser lines of interest. These measurements are related to the absorption coefficients of CH ₄ , N ₂ O, HDO, and the known line structure of H ₂ O to infer the extinction coefficient arising from the water vapor continuum in the region 2550-2750 cm ⁻¹ .		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

SPECTROPHONE MEASUREMENT OF THE WATER VAPOR
CONTINUUM AT DF LASER FREQUENCIES

E. K. Damon
J. C. Peterson
F. S. Mills
R. K. Long

Contractor: Ohio State University
Contract Number: F30602-75-C-0029
Effective Date of Contract: 1 October 1974
Contract Expiration Date: 30 June 1975
Amount of Contract: \$124,969.00
Program Code Number: 5E20
Period of work covered: 1 October 1974 -
30 December 1974

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

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

Approved for public release;
distribution unlimited.

This research was supported by the Defense
Advanced Research Projects Agency of the
Department of Defense and was monitored by
James W. Cusack, RADC (OCSE), Griffiss AFB
NY 13441.

TABLE OF CONTENTS

		Page
I.	INTRODUCTION	1
II.	EXPERIMENTAL MEASUREMENTS	2
III.	CALIBRATION OF SPECTROPHONE	8
IV.	MODEL ATMOSPHERE ABSORPTION MEASUREMENTS WITH THE SPECTROPHONE	16
V.	CONCLUSIONS	27
Appendix		
I.	DESCRIPTION OF HDO WHITE CELL CALIBRATION AND CLARIFICATION OF BURCH WATER CONTINUUM EXPERIMENTS [12]	28
	REFERENCES	31

I. INTRODUCTION

This report describes the results of a field measurement program conducted by the Ohio State University in cooperation with the United Aircraft Research Laboratories (UARL), Hartford, Connecticut. UARL supplied and operated, at their Hartford facility, the cw DF laser (POSM). This laser with an output of approximately one watt per line was used to illuminate the differential spectrophone designed and operated by the Ohio State University ElectroScience Laboratory.

The DF laser operates at wavelengths that fall within a relatively good atmospheric transmission window. There are, however, several absorbers present which will influence the propagation of high power lasers. It is the intent of this report to examine these contributions and to discuss new measurements of interest. Considerable progress has been made in both the calculation [1,2] and measurement [3] of this transmission, but results are not yet completely satisfactory. These points will be discussed more fully.

Techniques for the calculation of atmospheric absorption have been discussed in previous reports [2,4] and will not be repeated here.

The H_2O absorption at 5 DF lines of interest has been measured [5], as well as CH_4 , CO_2 , and HDO at several frequencies [3]. These results are summarized in Table I. In addition to the differences shown, CO_2 absorption in the range of 10^{-4} km^{-1} can be expected due to isotopic CO_2 constituents which are not listed in the data tape. Recent calculations will be described in Section IV of this report.

TABLE I

Comparison of measured and calculated sea level absorption coefficients. Assumed are: 0.28 ppm N_2O , 1.6 ppm CH_4 , 14.26 torr H_2O of which 0.03% is HDO .

Absorber	Iden.	(cm^{-1})*	K_{meas}	$K_{\text{calc}} (\text{km}^{-1})$	% diff.
H_2O	3-2 P(7)	2570.522	.0373	.0371	.54
	3-2 P(8)	2546.375	.0214	.0214	0.
	2-1 P(10)	2580.095	.0453	.0463	2.2
	2-1 P(11)	2553.951	.00969	.0105	7.7
	3-2 P(6)	2594.198	.00227	.00230	1.3
CH_4	2-1 P(6)	2680.178	.00152	.0003059	80
	2-1 P(7)	2655.863	.00113	.000719	36.4
	2-1 P(8)	2631.067	.000859	.000826	3.8
HDO	3-2 P(6)	2594.198	.0174	.00723	58.6
	3-2 P(7)	2570.522	.00861	.00463	46.2
	3-2 P(8)	2546.375	.00246	.00115	53.2

*Measured Roh, Heath, Rao, Ohio State University
Department of Physics, 1975 (to be published).
Accuracy $\pm .005 \text{ cm}^{-1}$.

II. EXPERIMENTAL MEASUREMENTS

The laser-illuminated spectrophone used for the measurements is shown in Fig. 1. The spectrophone, whose ideal response is directly proportional to absorption, offers significant advantages over apparatus where the absorption must be determined from the difference of two nearly identical values of transmission.

The basic concept of the spectrophone is simply that a gas cell experiences a temperature increase when the gas absorbs radiation. In a constant-volume cell, a corresponding pressure rise will also ensue. The pressure rise is the more easily measured of the two effects.

The technique has been used for many years. Among the early workers were Bell [6,7], Tyndall [8], and Roentgen [9]. Delany [10] gives an excellent account of the early history. Since the advent of the laser, there has been increased interest in the application of this opto-acoustic effect, since there is now significant amounts of optical power available within narrow linewidths.

For a cw laser as a source, it can be shown [11] that the pressure rise from ambient, A , is given by the relationship

$$(1) \quad A = \frac{\alpha BWP}{4\pi\kappa T} F$$

where α is the absorption coefficient, B is a dimensionless geometric term relating illuminated gas volume to total gas volume, W is the illuminating laser power, P is the ambient pressure, κ is the thermal conductivity of the gas, T is the ambient temperature of the gas, and F is a proportionality factor which is frequency-sensitive if a chopped laser beam is used. In practice, the small pressure rise due to the thermal deposition in weakly absorbing gases is difficult to separate from the pressure rise due to thermal and leakage drifts. A chopped laser signal is therefore used to reduce drift effects.

The particular spectrophone used is based on a novel design developed at this laboratory. It is a differential type whose objective is canceling the false pressure signal from the cell windows. The system is shown in Fig. 2.

Cell A of the differential spectrophone is long and of small diameter, consistent with the laser beam diameter. An acoustical signal equal to the sum of the absorption signal and the window signal will be generated and transmitted to one side of the differential pressure sensor. In cell B a similar signal will be generated, but the absorption coefficient will be much smaller because of the shorter length. The window signal, if the windows are identical to those of

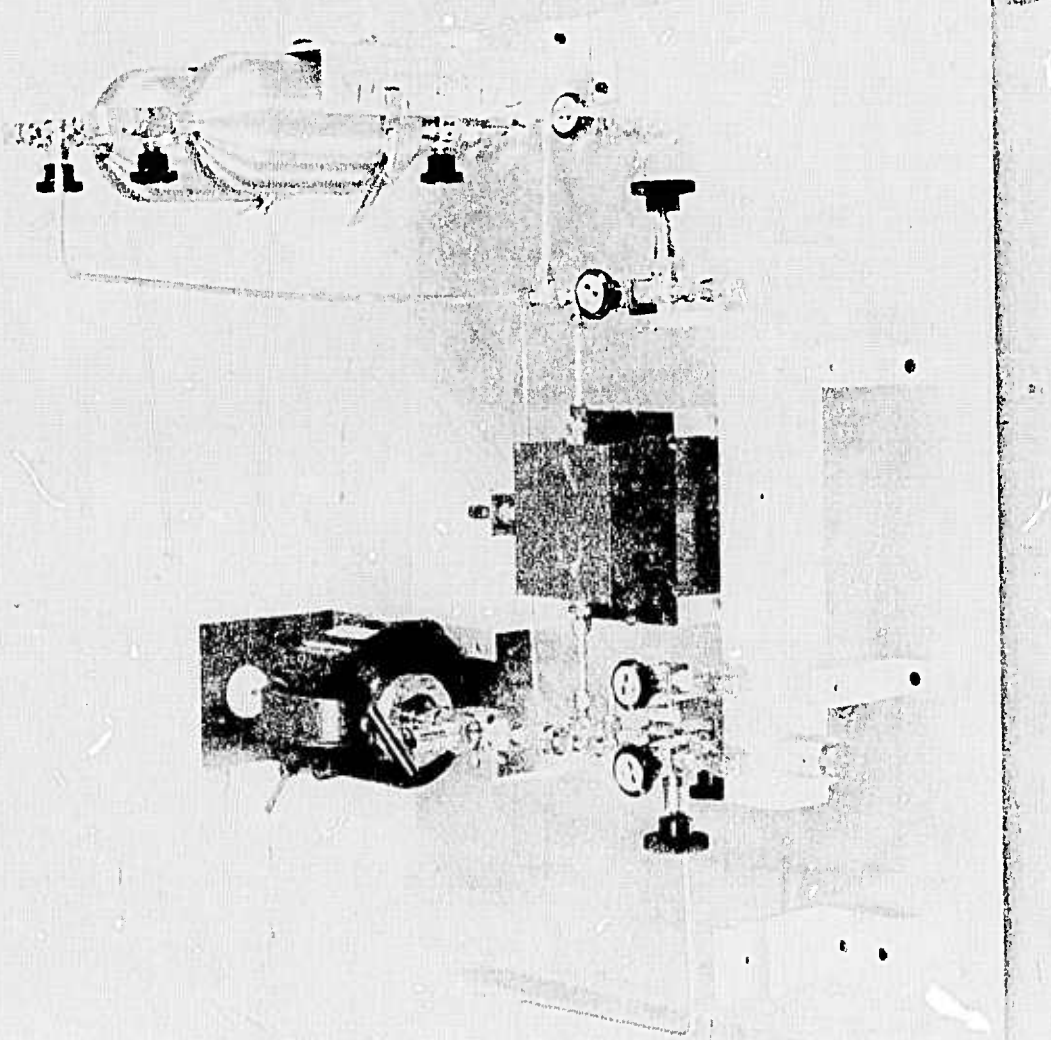


Fig. 1. Photograph of the differential spectrophotone.

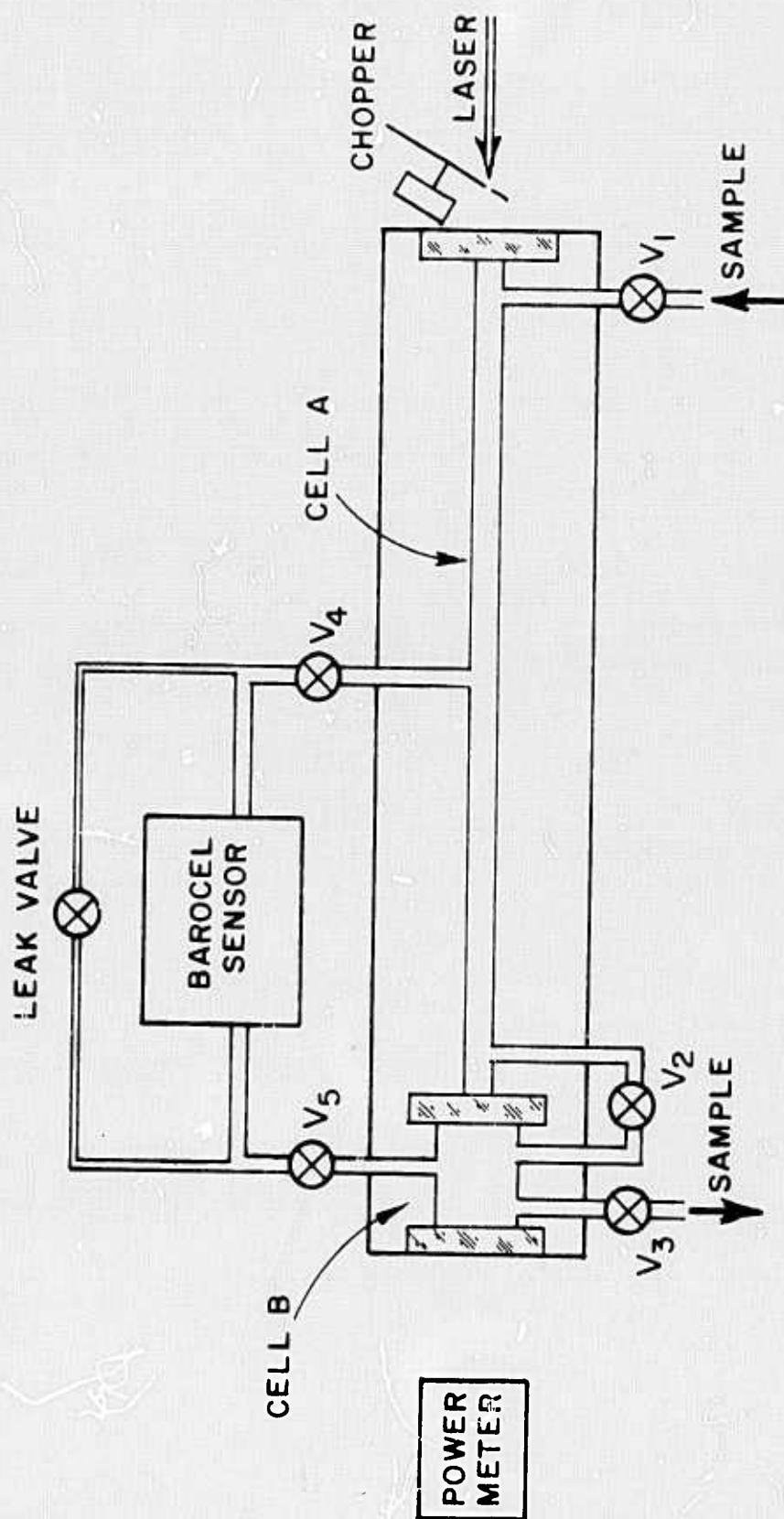


Fig. 2. Differential spectrophone.

cell A and if the cell volumes are identical, will be identical to the window signal from cell A and will therefore cancel it at the differential pressure sensor. The volume of cell B could be adjusted to allow complete cancellation, but this feature was not used in this series of measurements. The absorption signal will not be completely canceled, and should be proportional to the difference in path length between the two cells. Elimination of the window background signal is therefore achieved at a rather nominal cost in system sensitivity.

The advantage over the use of two identical cells, with the reference cell filled with a reference gas, is that the leak valve, see Fig. 2, can equalize the static pressure in the two cells. This avoids the necessity for static balance devices or the possibility of a static imbalance which may drive the sensor beyond its design range. There is furthermore a distinct problem in selecting a nonabsorbing reference gas with thermal properties similar to the absorbing sample. For one example, the pressure-induced absorption in pure nitrogen is itself of interest at some DF wavelengths and could not be used as the reference gas.

In Fig. 2 there are valves V₄ and V₅ between the sensor and the cells. If one of these is closed, the result is that the sensor is connected to the other cell as a normal non-differential spectrophone. This is useful as a trouble-shooting aid. It did not prove to be foolproof however. During system checkout and evaluation at 10.6 microns, the differential signal was not, in general, numerically equal to the difference between the cell signals measured individually. The reason for this behavior has not yet been discovered. The instrument gave zero output, as expected, when valves V₂, V₄, and V₅ were all open so that identical pressure signals were on both sides of the sensor. Signal waveshapes and phases were as expected. The net result is that the window signal is not properly compensated and a residual output is obtained with the nonabsorbing reference atmosphere. Since the prime goal was the measurement of the water vapor continuum, this difficulty was not a limiting factor and the continuum can be determined by the increase in signal as water vapor is added.

The spectrophone can be calibrated, in principle, from a knowledge of sensor sensitivity, cell geometry, and thermal constants. It was considered preferable, however, to calibrate with absorber samples that had been carefully measured in the Ohio State University White cell. This procedure is explained more fully in a following section.

The spectrophone is an extremely sensitive device for measuring absorption. It therefore follows that great care must be taken in handling the gas samples to assure their continued purity. The gas mixing and handling system is shown schematically in Fig. 3. The

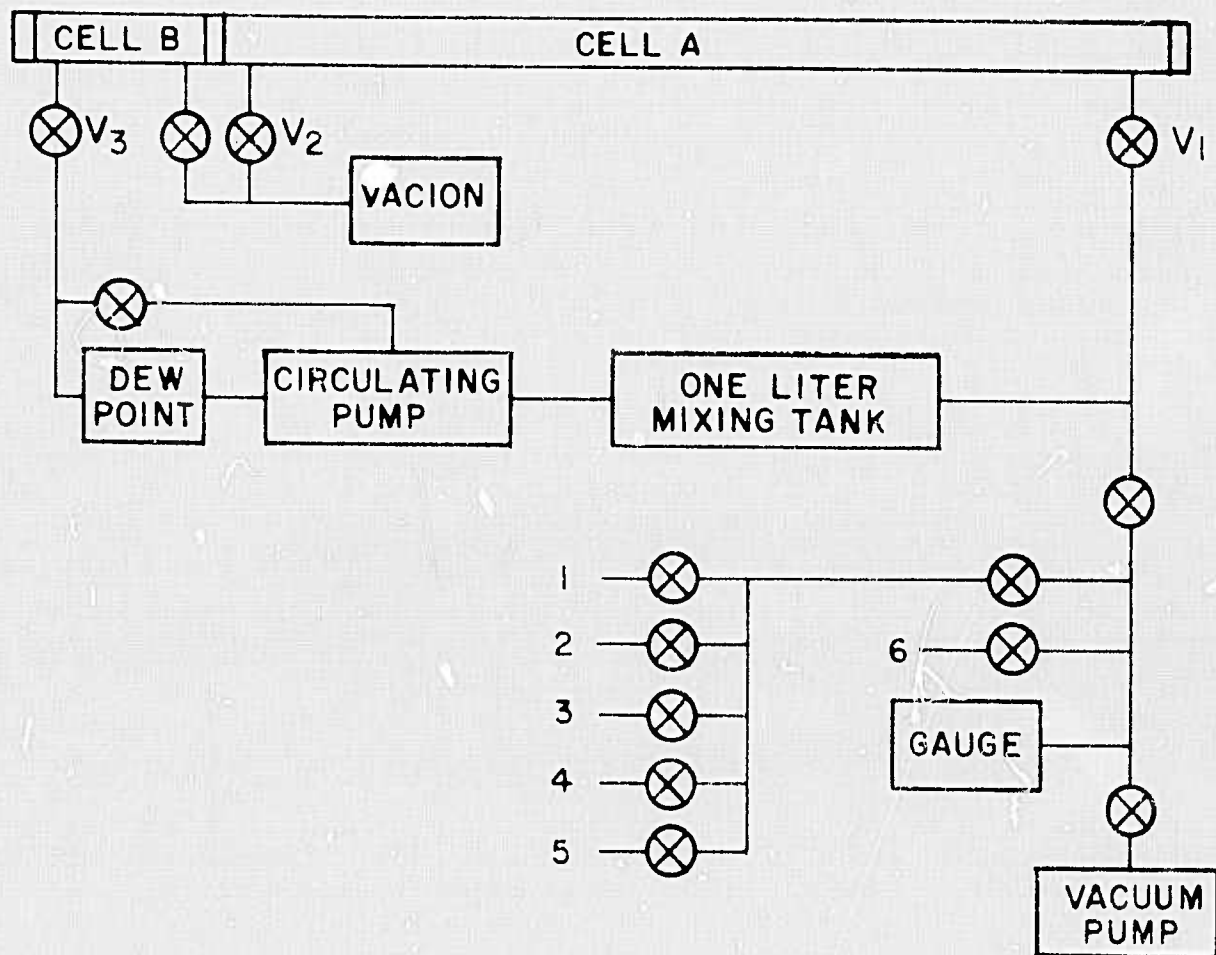


Fig. 3. Gas handling system.

spectrophone cells were aluminum with BaF₂ windows; most of the associated plumbing and valves were stainless steel. The total system was checked with a helium leak detector, and then pumped with moderate heating for several weeks with the Vacion pump to remove contaminants. Substantial contaminant outgassing did occur during this stage, as evidenced by 10 micron measurements during this period.

The experimental procedure finally developed for handling gas samples was generally as follows. After roughing the system by a mechanical pump (isolated by a molecular sieve trap), the mechanical pump would be valved off and the system pumped by the Vacion pump, preferably overnight. Thorough pumping was particularly essential before measuring low absorption or dry samples. Sample gases of

interest were connected to ports 1-5 and a water container to port 6. Interconnecting lines were evacuated, using the mechanical pump, and flushed several times. The water sample was outgassed similarly.

Pressure measurements were made with Wallace and Tiernan mechanical gauges. A 62B-4D-0800 was used for pressures to 800 torr, and an FA141 for increased accuracy below 35 torr. The desired dew point was approximated in filling the system, but values used were measured by an EG and G Model 880 thermoelectric dew point hygrometer which had been previously calibrated against known water samples. All readings were recorded on a digital printing data logger (Digitec 1267). Laser power, spectrophone output, cell temperature, and dew point reading were each printed out every five seconds during the recording phase. The ratio of spectrophone output to laser power was calculated for each of these and then averaged for the number S/W. The lock-in amplifier used for the spectrophone signal was a PAR 128A with a synchronizing signal derived from the optical chopper.

The sample gases used were of high purity, but because of the sensitivity of the spectrophone and the complex infrared spectra of hydrocarbons, there is concern about the actual purity. In future experiments it will be recommended that the diluent gases be passed through a heated catalyst bed to obtain a hydrocarbon content below 0.01 ppm, which is some one hundred times purer than present assurances. Some concern must also be expressed about the significance of absorption calculations which must presently ignore atmospheric hydrocarbons because of insufficient data.

Difficulties encountered in laser operation were primarily of three classes. The first several runs were halted by clogging of the burners due to carbon impurities in the helium supplied specifically for the tests. An alternate supply from UARL stocks cured this problem. The second difficulty was the limited run time caused by vacuum blower overheat. This was known in advance, but any delay in spectrophone operation or in gas sample mixing did result in lost data points, for the most part nonrecoverable because of the limited time budgeted to the measurements. The third difficulty was a very small water leak in the blower cooling, inside the vacuum system. The effect of this when combined with the HF exhaust was serious corrosion of bearings and vacuum lines. These problems were particularly evident near the end of the measurement period. It must be remarked that it was only through extreme diligence and cooperation of the UARL laser group that any measurements were achieved in this period, and that the support OSU received during such difficulties was well beyond normal expectations.

III. CALIBRATION OF SPECTROPHONE

The spectrophone was calibrated for each laser line by comparing the spectrophone signal with a laser measurement of absorption using a long path White cell with both devices containing a calibration gas under identical conditions of pressure and temperature.

The calibration gases used were N_2O and CH_4 . Since the absorbing species are present in small concentration, the thermal conductivity of the calibration gas is very nearly the same as for a mixture of 80% nitrogen and 20% oxygen (artificial air). The calibration gases therefore were mixtures of 80% nitrogen and 20% oxygen or 100% N_2 with small amounts of absorbing gas included whose absorption coefficient was determined from White cell measurements. For the lines in the 2-1 band the calibration gas was methane in artificial air. For the lines in the 3-2 band the calibration gas was nitrous oxide in N_2 . The White cell measurements for CH_4 -air mixtures are given in our report RADC-TR-74-295. The White cell measurements for N_2O - N_2 mixtures are given in RADC-TR-74-89. It should be pointed out that the White cell measurements on N_2O were made with N_2 as a broadening gas rather than air. This may introduce some slight error due to the difference in the foreign broadening coefficients of air and nitrogen.

The White cell calibration measurements were performed over a range of absorber concentrations. No deviation from linearity was observed; hence a least-square straight line fit to the measured points which passed through the origin was used. The measured White cell absorption coefficients per ppm of absorber are given in Table II. For comparison the calculated coefficients using the AFCRL data tape are also given. The calculated results for the 3-2 band reflect the newly available DF laser line frequency measurements as noted in the caption. These are preliminary results with an accuracy of $\pm 0.005 \text{ cm}^{-1}$. Additional work now in progress should result in laser line positions accurate to $\pm 0.002 \text{ cm}^{-1}$.

A calibration is not available at this time for the 2-1 P(3) laser line.

The raw data from the spectrophone is given as the ratio of Barocel signal (S) to laser power (W). The ratio S/W is assumed to be directly proportional to the absorption coefficient of the gas being measured. The calibration constant for each laser line which relates S/W to absorption coefficient is found using the data from Table II. Since the spectrophone signal depends on the thermal conductivity of the gas contained in the spectrophone cell, the calibration gas should have the same thermal conductivity as the gas whose absorption coefficient is to be measured.

TABLE II

Comparison of calculated and OSU White cell measured N_2O and CH_4 absorption coefficients for 1 ppm at 760 torr total pressure and 24°C for certain DF laser frequencies.

Iden.	Freq.*	N_2O $\text{km}^{-1}/\text{ppm}$		CH_4 $\text{km}^{-1}/\text{ppm}$	
		(Calc)	(Meas)	(Calc)	(Meas)
3-2 8	2546.375	7.63E-2	7.64E-2	6.82E-4	
2-1 11	2553.951	3.77E-2	3.46E-2	4.70E-5	
3-2 7	2570.522	1.33E-1	1.33E-1	1.94E-5	
2-1 10	2580.195	1.65E-1	1.62E-1	-	
3-2 6	2594.198	8.21E-3	8.11E-3	1.28E-5	
2-1 8	2631.067	-		5.16E-4	5.38E-4
1-0 11	2638.391	-		3.73E-4	
2-1 7	2655.863	-		4.49E-4	7.06E-4
2-1 6	2680.178	-	-	1.91E-4	9.5E-4
2-1 3	2750.093	1.53E-4		5.75E-4	

*Measured Roh, Heath, and Rao, Ohio State University
Department of Physics, 1975 (to be published).
Accuracy $\pm 0.005 \text{ cm}^{-1}$.

In these experiments the unknown gas is up to 15 torr H_2O in 760 torr artificial air. The calibration samples are up to .2 torr N_2O and up to 2.2 torr CH_4 in 760 torr artificial air or N_2 . All of these gases are assumed to have the same thermal conductivity.

Figures 4-9 show the spectrophone calibration curves for the 2-1 P(6), P(7), P(8) and 3-2 P(6), P(7), and P(8) lines. In each case there is a residual microphone signal at zero absorber concentration which is assumed to be caused by spectrophone window absorption or sample impurities. Thus for each line a least-square fit of the measured data to an expression of the form $S/W = A_0 + A_1p$ was made where p is the concentration of methane or nitrous oxide in ppm.

Thus the desired calibration constant is

$$(2) \quad C = \frac{k}{A_1 p}$$

where k is the absorption coefficient from Table II and A_1p is evaluated at the same concentration (i.e., one ppm). Then for the water vapor-air samples the absorption coefficient is given by multiplying the measured S/W ratio by the constant C .

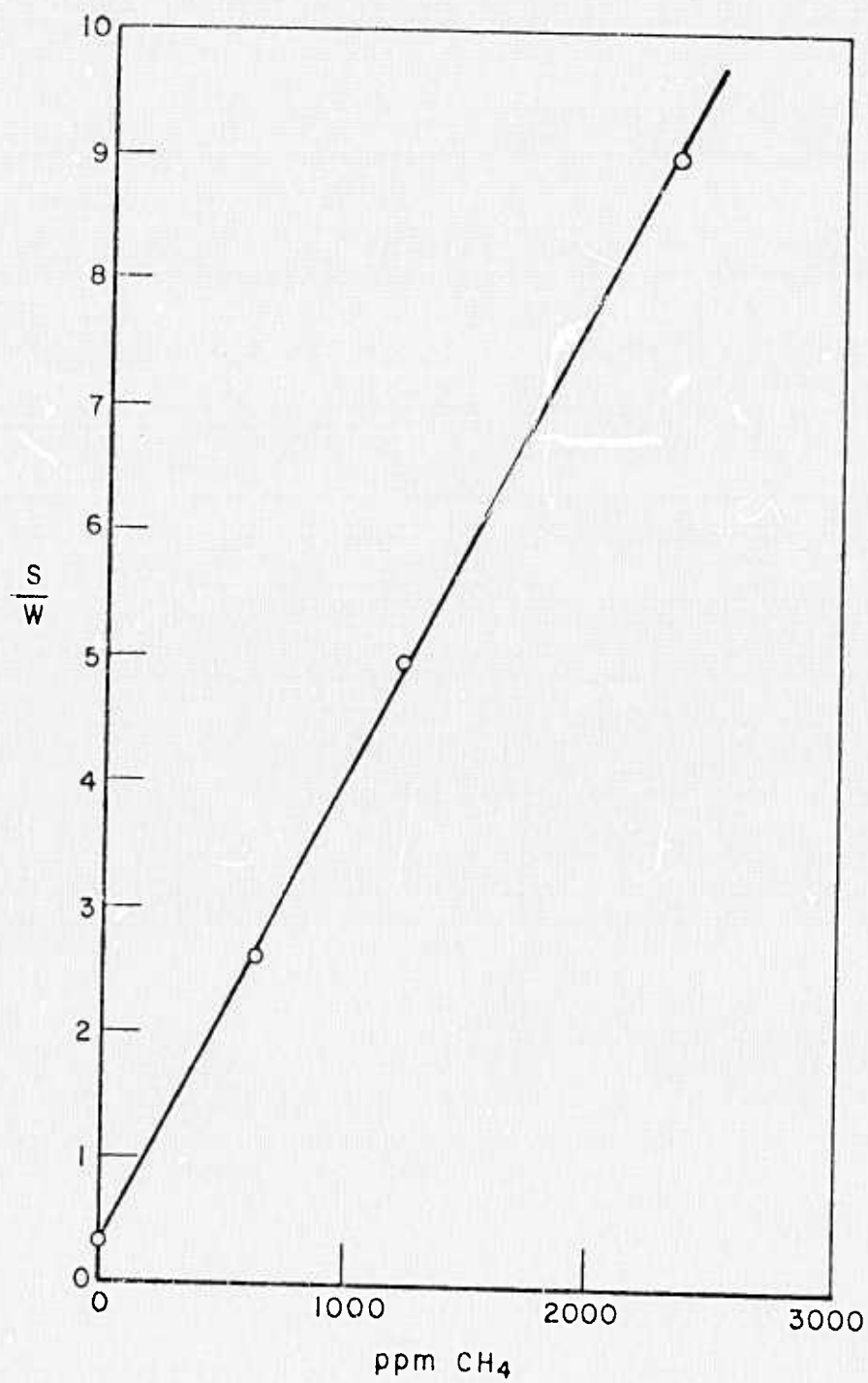


Fig. 4. 2-1 P(6) spectrophone calibration.

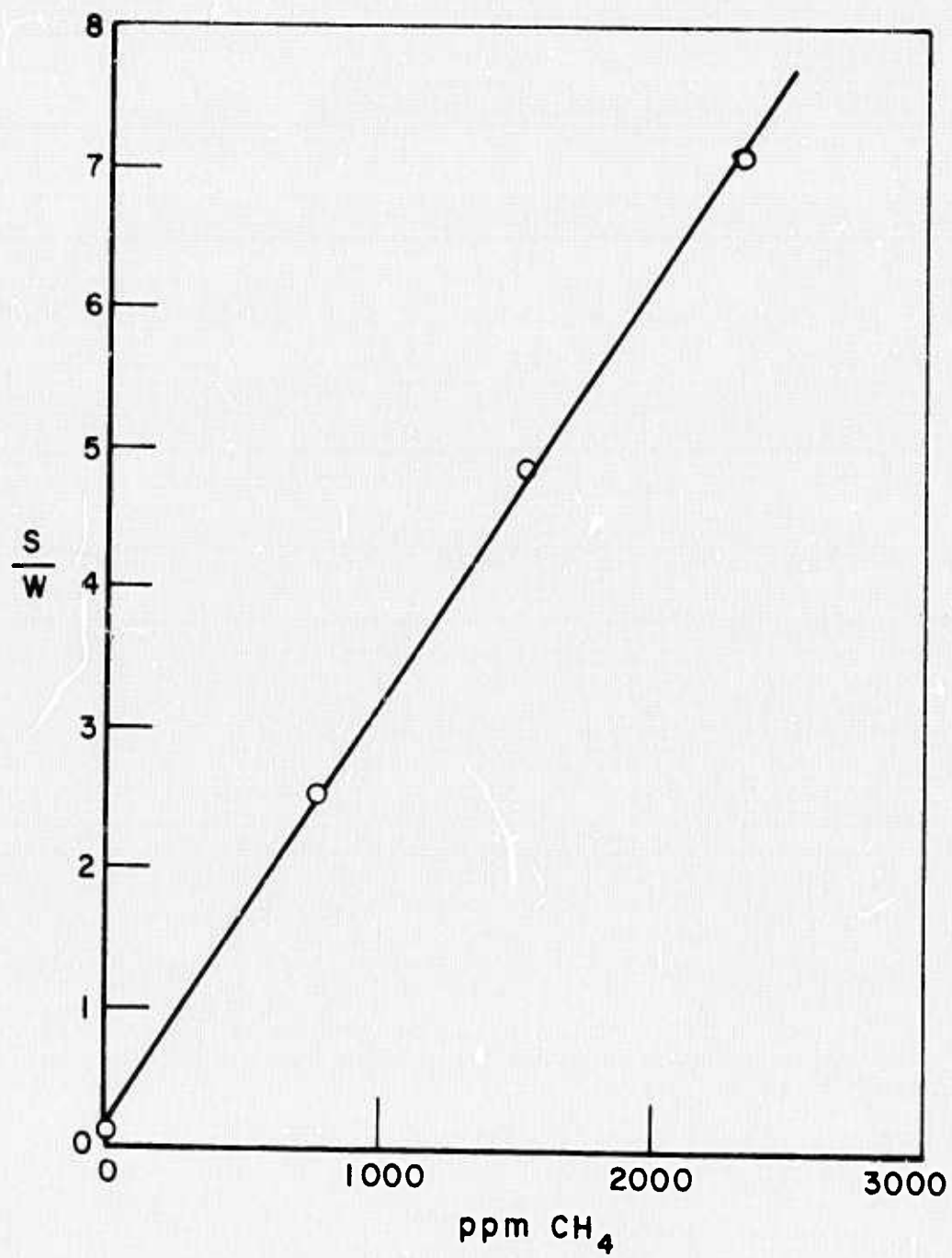


Fig. 5. 2-1 P(7) spectrophone calibration.

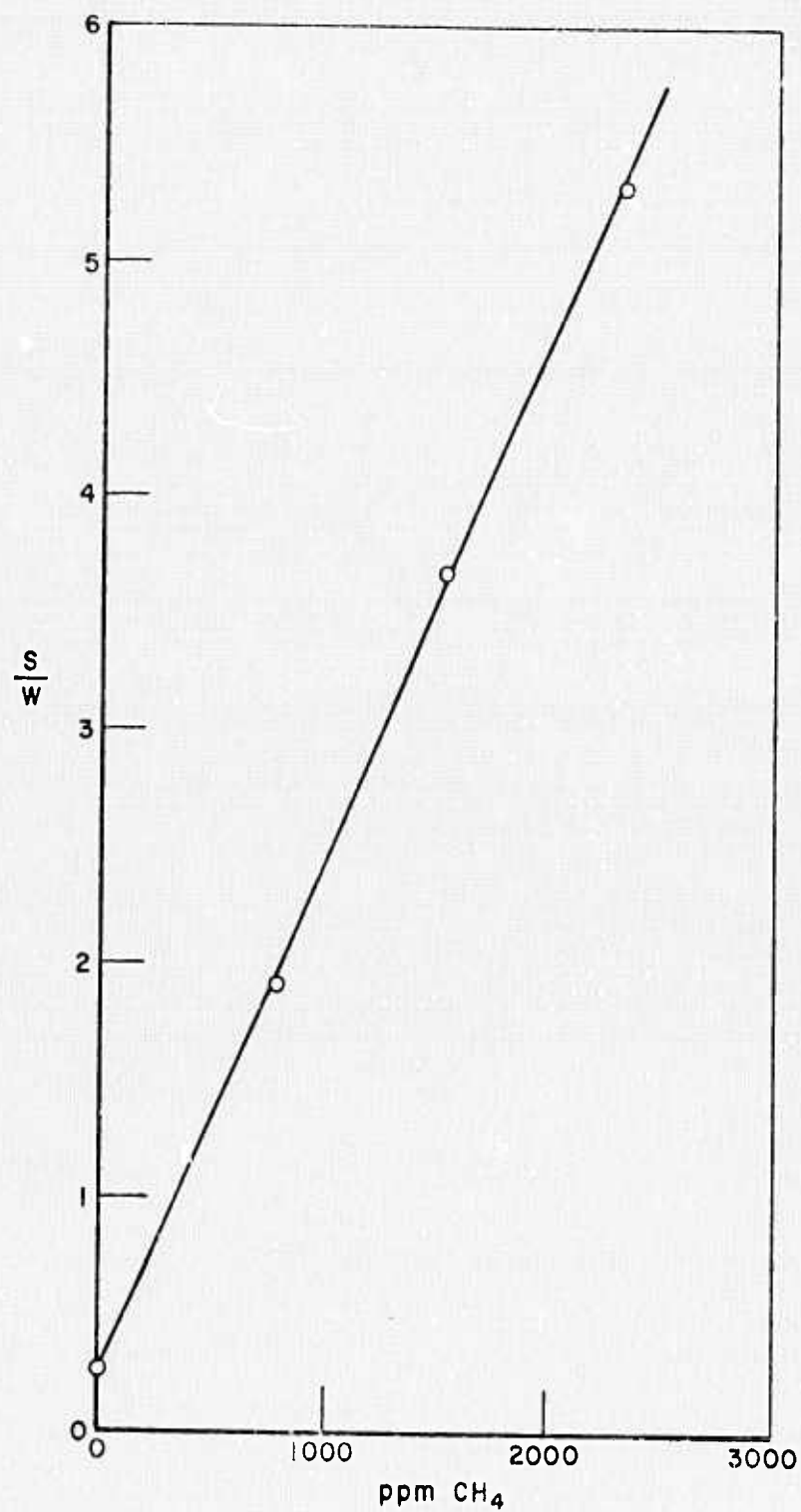


Fig. 6. 2-1 P(8) spectrophone calibration.

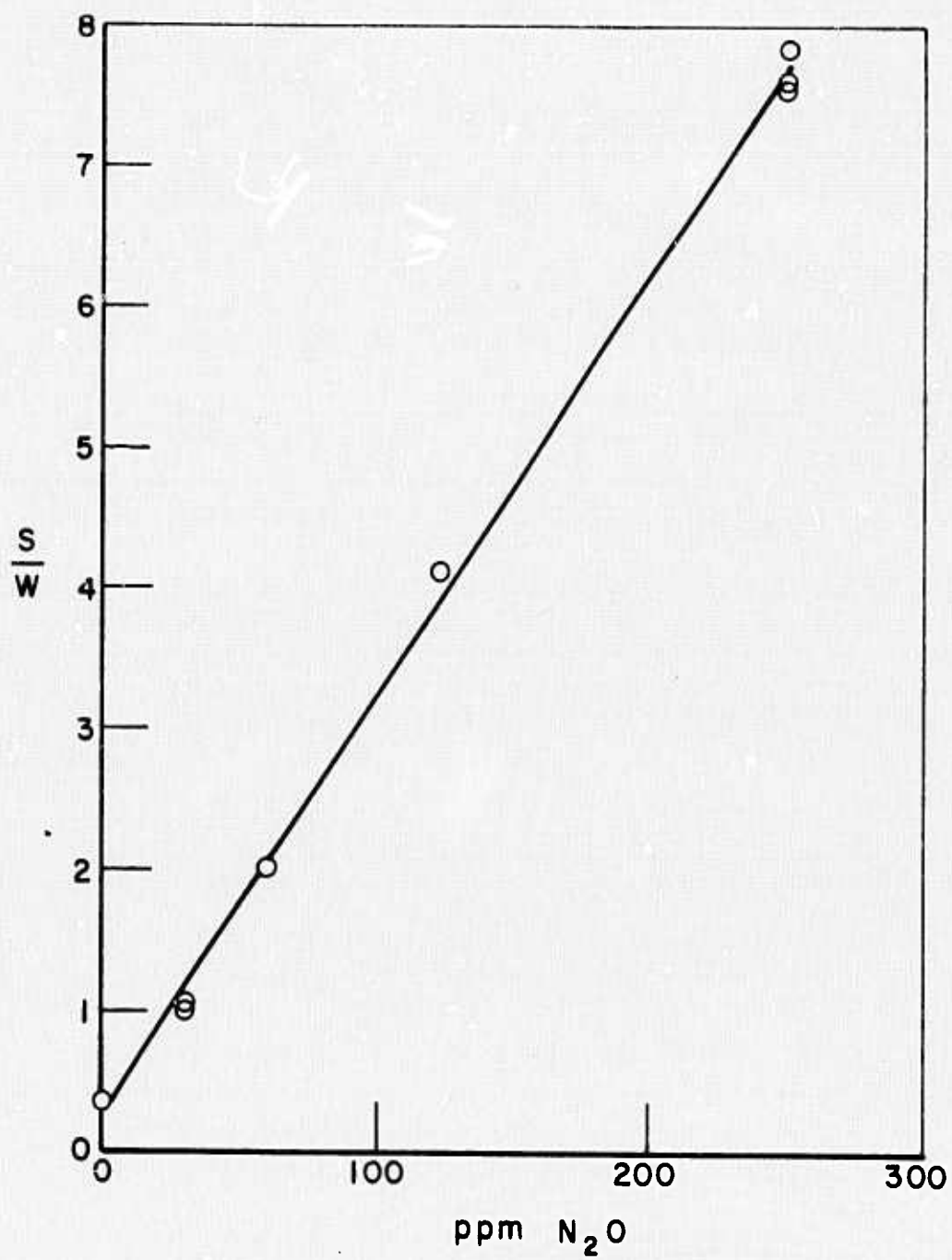


Fig. 7. 3-2 P(6) spectrophone calibration.

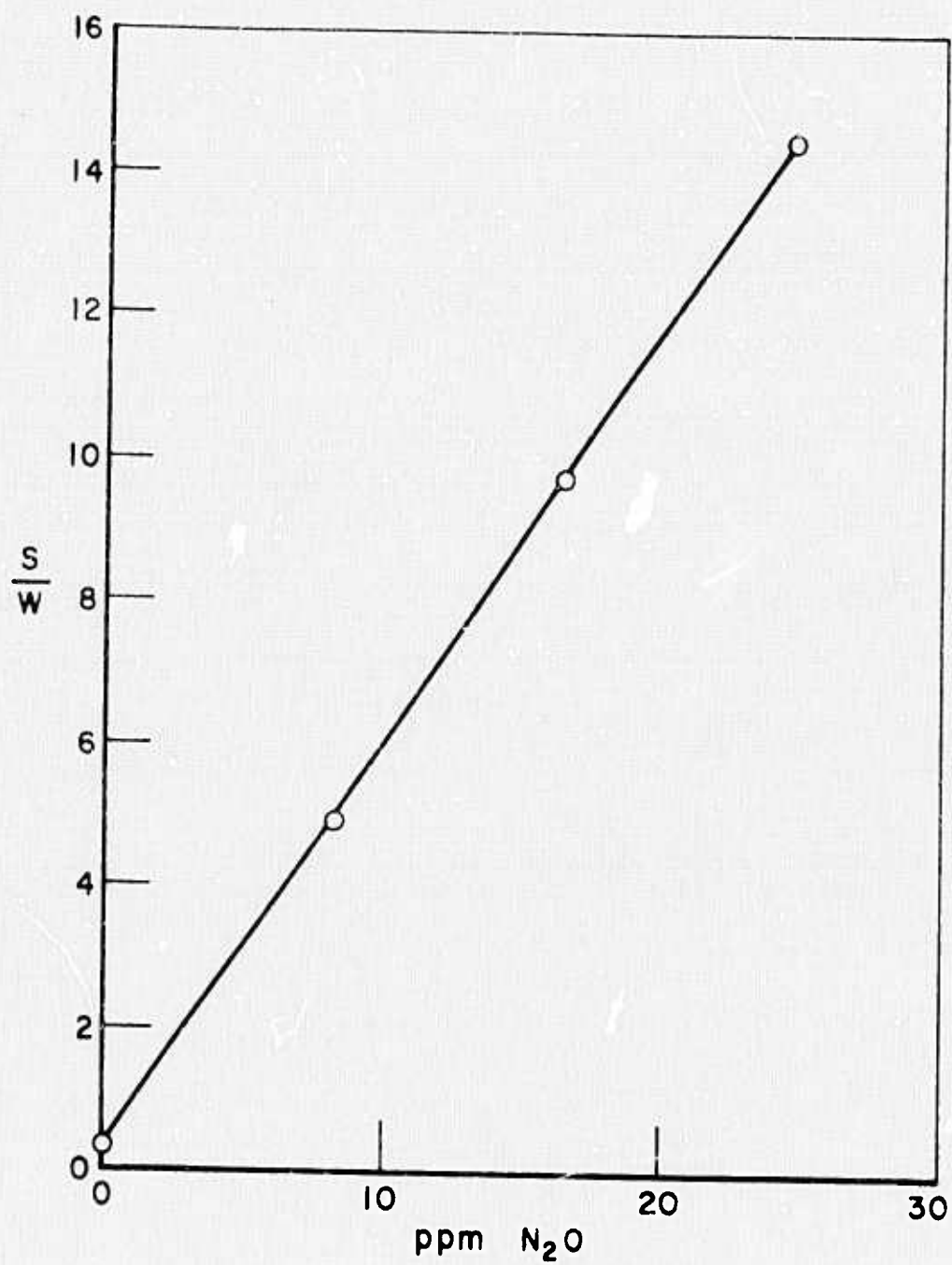


Fig. 8. 3-2 P(7) spectrophone calibration.

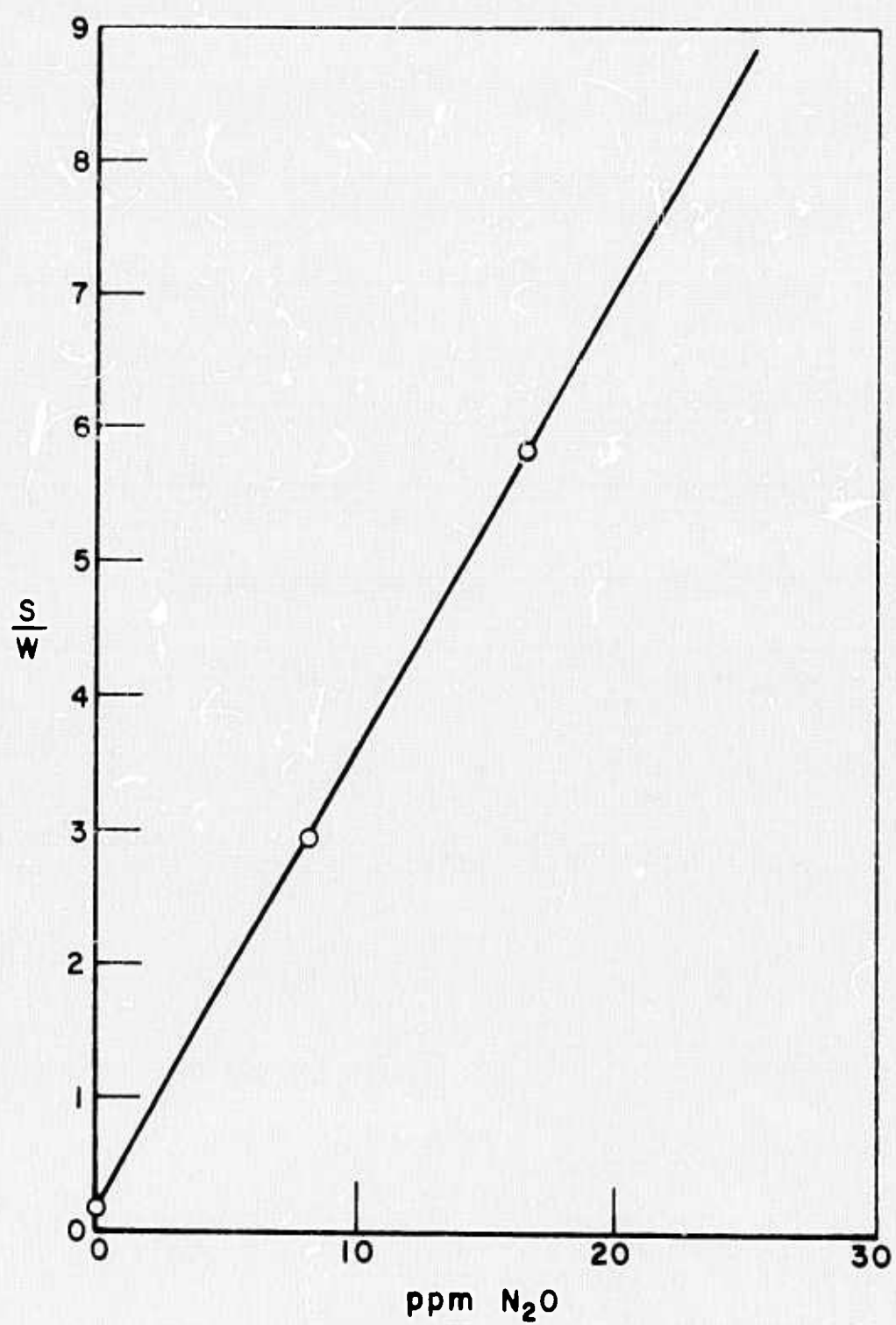


Fig. 9. 3-2 P(8) spectrophone calibration.

As should be clear from the discussion thus far, it has been found necessary to determine C separately for each laser line. Table III gives the values of C. The differences in C may be real, or they may be an indication of measurement repeatability. A larger data base is needed to resolve this.

TABLE III
Spectrophone calibration constants for DF laser lines

Iden.	Freq.*	$A_0 + A_1 p$	C
3-2 8	2546.375	.147 + .346p	.221
3-2 7	2570.522	.161 + .581p	.229
3-2 6	2594.198	.25 + (2.97E-2)p	.273
2-1 8	2631.067	.266 + (2.19E-3)p	.245
2-1 7	2655.863	.179 + (3.01E-3)p	.235
2-1 6	2680.178	.328 + (3.75E-3)o	.253
2-1 3	2750.093	-	.244 [†]

[†]Estimated from the average of the constants for the other 2-1 lines.

*Measured Roh, Heath and Rao, Ohio State University Department of Physics, 1975, (to be published).

The calibration constant for the 2-1 P(3) line is taken to be the average of the constants for the other 2-1 lines.

IV. MODEL ATMOSPHERE ABSORPTION MEASUREMENTS WITH THE SPECTROPHONE

After completion of the spectrophone calibration using CH₄-artificial air and N₂O-N₂ samples, a series of model atmosphere absorption measurements were made. The samples contained a variable quantity of water vapor plus analyzed air to 760 torr. The temperature was 24°C. The results of these measurements are given in Figs. 10-15. A least squares straight line of the form $A_0 + A_1 p$ was determined for each laser line. These results are given in Table IV.

It can be seen that the A_0 term is quite variable. This is caused in the first place by the variable N₂O and CH₄ absorption at each laser line. Unfortunately the air analysis, see Table V, does not give the concentration of N₂O. If the N₂O is assumed to be 0.28 ppm, then the data of Table II can be subtracted from the A_0 values. This has been done in Table VI. Now we find that the uniformity of the background signal has been improved. The remaining variability can be due to unknown impurities in the analyzed air, a different N₂O

TABLE IV

Equations of the form $A_0 + A_1p$ which least-square fit the experimental water vapor data. Water vapor pressure is in torr, absorption coefficient in km^{-1} .

LINE	$k \text{ (km}^{-1}\text{)}$
3-2 8	$.0456 + .0022p$
3-2 6	$.018 + .00344p$
2-1 8	$.0166 + .0066p$
2-1 7	$.0173 + .00963p$
2-1 6	$.030 + .0082p$
2-1 3	$.067 + .0073p$

TABLE V

Analyzed Air

O_2	20.95%
N_2	78.08%
CO_2	260 ppm
CO	< 1 ppm
N_2O	< 1 ppm
CH_4	1.4 ppm

TABLE VI

Spectrophone analyzed air measurements.

Estimated Absorption
by $\text{N}_2\text{O}(.28 \text{ ppm})$
& $\text{CH}_4(1.6 \text{ ppm})$

	A_0	$\text{CH}_4(1.6 \text{ ppm})$	$A_0 - \text{N}_2\text{O} + \text{CH}_4$
3-2 8	.0456	.0214	.024
3-2 6	.018	.0027	.016
2-1 8	.0166	.00086	.016
2-1 7	.0173	.00113	.016
2-1 6	.030	.00152	.029
2-1 3	.067	?	?

(3-2 8 analyzed air consistently high; must have had impurity.)

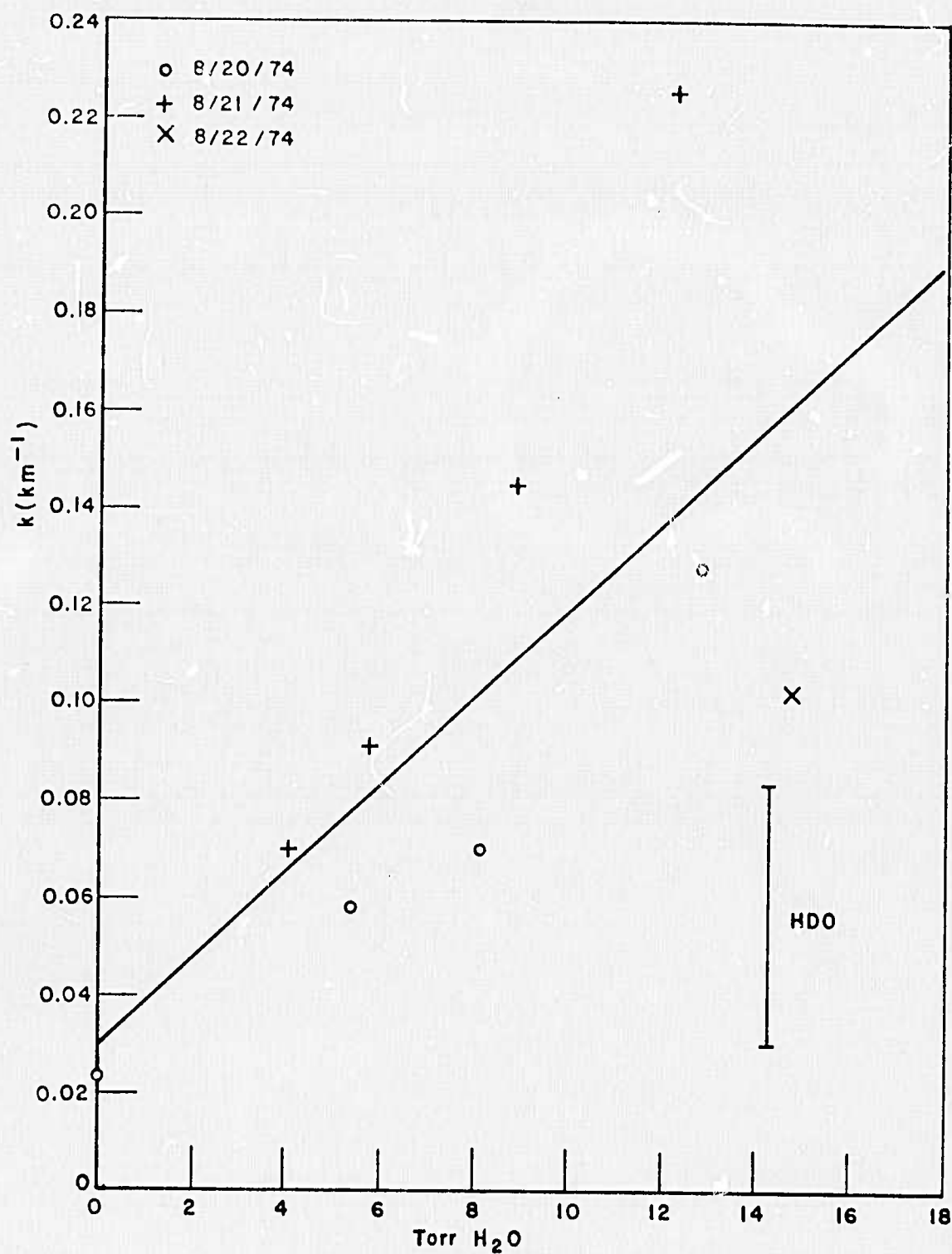


Fig. 10. 2-1 P(6) H_2O + analyzed air.

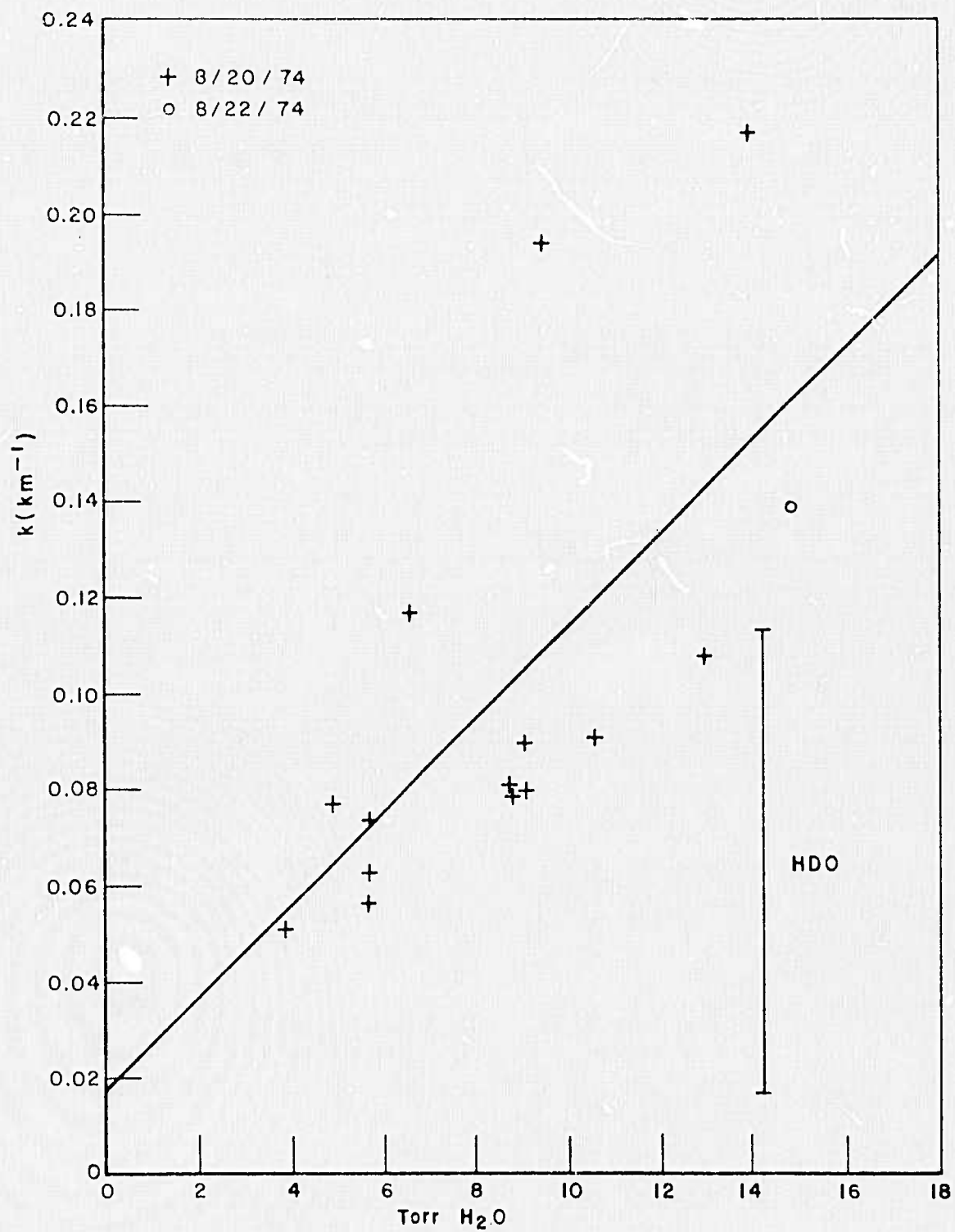


Fig. 11. 2-1 P(7) H_2O + analyzed air.

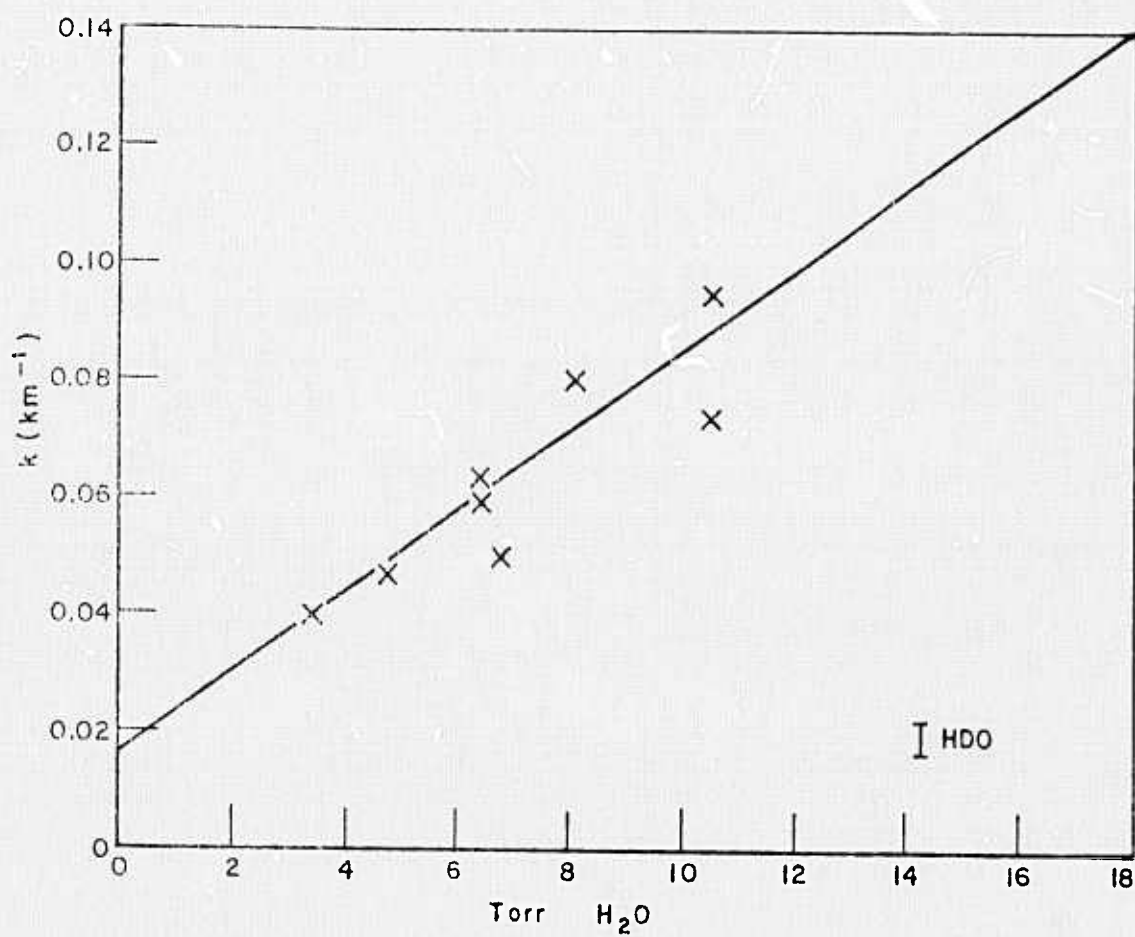


Fig. 12. 2-1 P(8) H_2O + analyzed air.

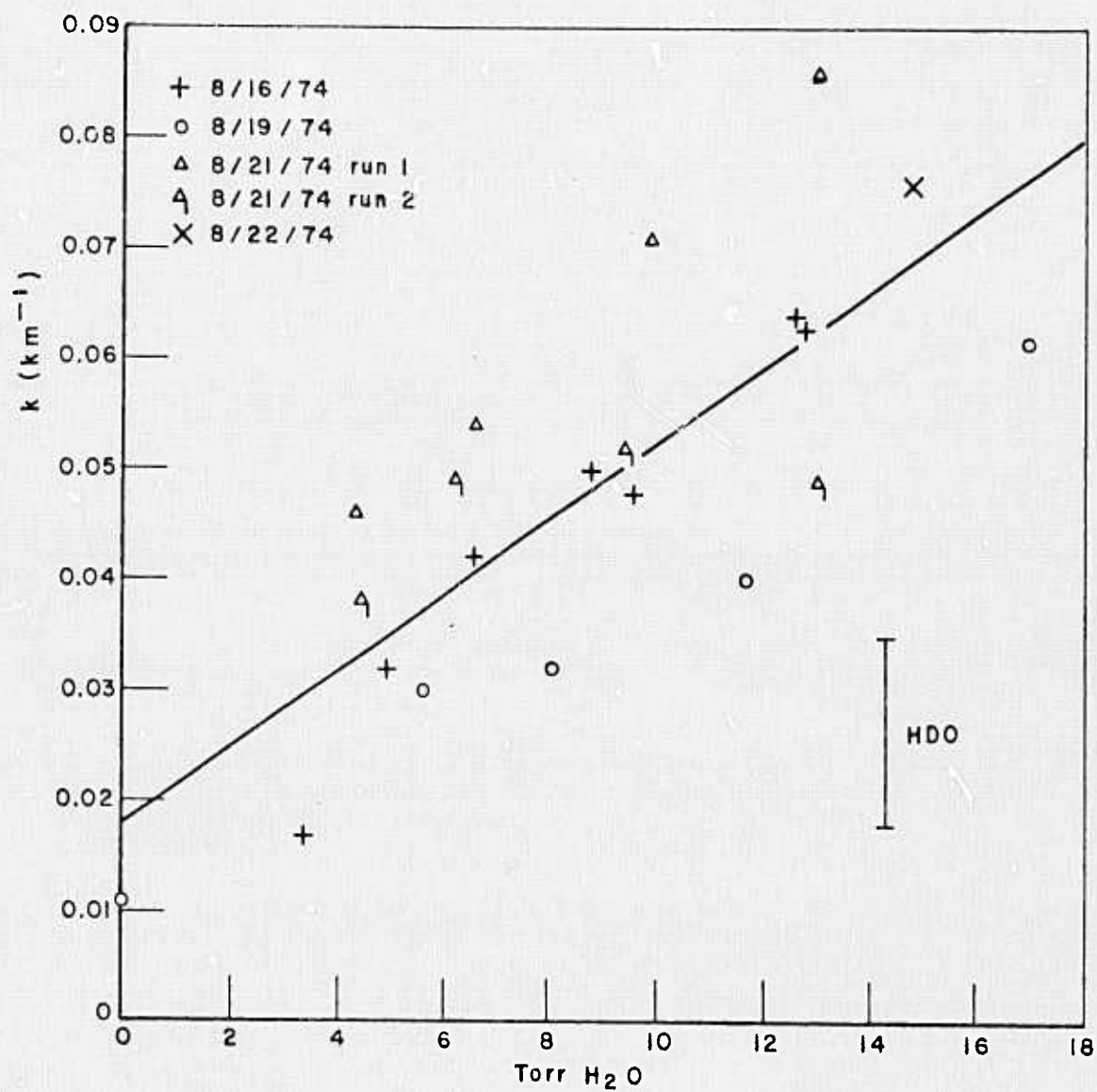


Fig. 13. 3-2 P(6) H_2O + analyzed air.

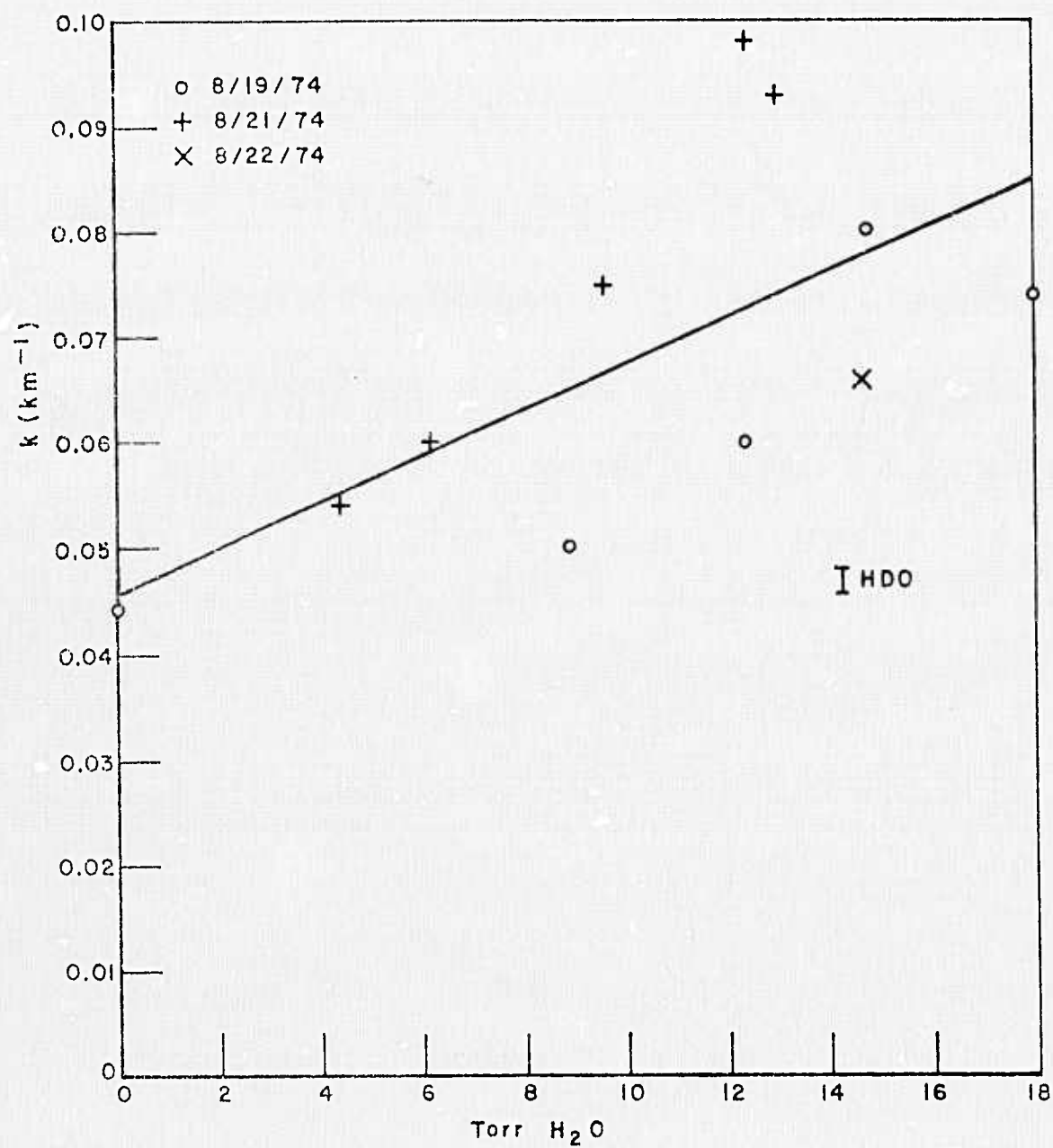


Fig. 14. 3-2 P(8) H_2O + analyzed air.

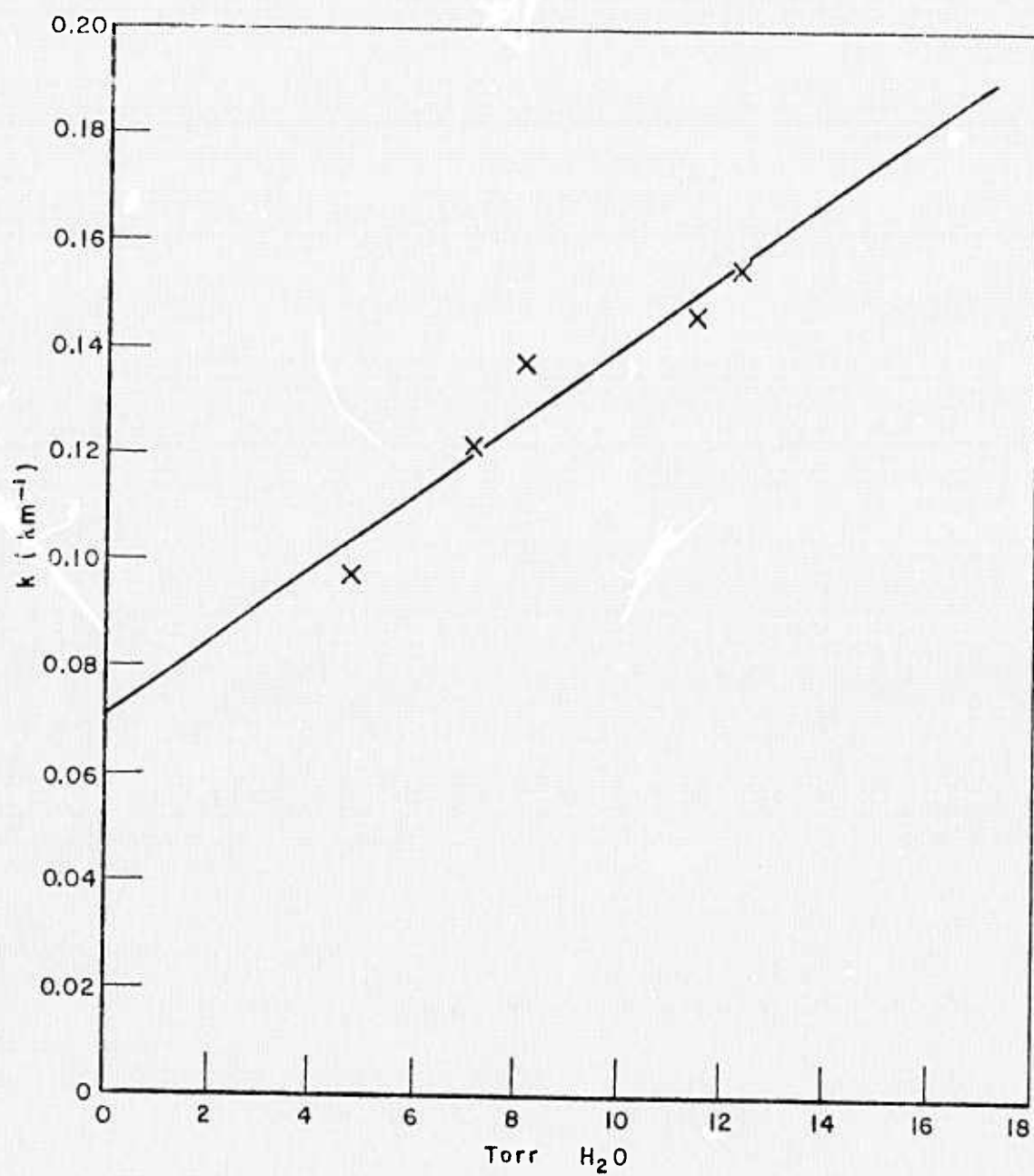


Fig. 15. 2-1 P(3) H_2O + analyzed air.

concentration; or variable window effects. It is noted that the 3-2 P(8) background measurement was repeated several times and was consistently high. This line is affected most by N₂O. Also an impurity may absorb at that frequency.

The water vapor absorption for the DF laser frequencies consists of three components - selective absorption by H₂O¹⁶; selective absorption by H₂O¹⁸; and continuum absorption. We have separately measured the HDO absorption for each laser line using samples with enhanced HDO concentration (see RADC-TR-74-295). Using this information plus calculated coefficients for the H₂O¹⁶ selective absorption, we may arrive at an estimate of the continuum absorption. The following comparisons will be made at 14.3 torr (the AFCRL Mid-latitude sea level summer model).

Table VII gives certain results which will be referred to below. It gives calculated H₂O and HDO absorption coefficients plus the measured H₂O and N₂ continuum coefficients from Burch [12].

TABLE VII

Calculated absorption coefficients for 14.3 torr H₂O, 760 torr total at 24°C (Mid-Latitude Sea Level Summer Model). Continuum water vapor derived from pure H₂O data of Burch [12]; continuum N₂ from measurements of Burch [12].

Iden.	Freq.*	TOTAL				
		H ₂ O (161)	HDO (162)	SELECTIVE WATER (161+162)	Contin. H ₂ O (Burch)	Contin. N ₂ (Burch)
3-2 8	2546.375	4.67E-5	1.15E-3	1.20E-3	1.86E-2	8.0E-3
2-1 11	2553.951	5.03E-6	5.19E-4	5.24E-4	1.82E-2	7.1E-3
3-2 7	2570.522	4.93E-5	4.63E-3	4.68E-3	1.75E-2	5.0E-3
2-1 10	2580.095	5.64E-6	2.67E-3	2.67E-3	1.70E-2	3.6E-3
3-2 6	2594.198	3.68E-4	7.23E-3	7.60E-3	1.68E-2	2.6E-3
2-1 8	2631.067	5.05E-3	9.14E-3	1.42E-2	1.78E-2	1.9E-3
1-0 11	2638.391	7.96E-4	2.46E-1	2.47E-1	1.82E-2	1.6E-3
2-1 7	2655.863	4.61E-6	7.25E-2	7.25E-2	1.93E-2	-
2-1 6	2680.178	2.44E-4	3.71E-2	3.73E-2	2.12E-2	-
2-1 3	2750.093	4.73E-5	1.19E-2	1.20E-2	2.75E-2	-

*Measured Roh, Heath, Rao, Ohio State University Department of Physics, 1975 (to be published). Accuracy $\pm 0.005 \text{ cm}^{-1}$.

A word about the Burch continuum measurements. In these experiments the absorption by high pressure, high temperature water samples were measured at frequencies that appeared to be free of selective absorption. Using data obtained at several temperatures,

an extrapolation to ambient (24°C) was made. Next a measurement of a broadened sample (2 atm H₂O; 4.5-10 atm total) at 428 K was used to evaluate the ratio of self to foreign broadening. If one assumes this ratio to be constant with temperature, the values in Table VII can be obtained.

One of the purposes of this study was to determine the validity of Burch's results and the subsequent assumptions which have been used to estimate the sea level continuum coefficients. This is discussed more fully in Appendix I.

In Table VIII we have subtracted for 14.3 torr the OSU measured HDO coefficient and the calculated (AFCRL tape) H₂O coefficient from the results measured in the current study. For the 2-1 P(3) line calculated HDO data was used since a measurement is not available. The results of Table VIII are plotted in Fig. 16. It is noted that the residual absorption is much greater than had been expected (Burch continuum, of order .02 km⁻¹). There is an indication that selective absorption effects have not been entirely accounted for by the procedure just described.

TABLE VIII

Table uses calculated H₂O(161) and measured H₂O(162) numbers

		Calc. 14.3 torr H ₂ O (161)	Meas. 14.3 torr H ₂ O (162)	Σ	Meas.	Diff.
3-2	8	.0000467	.00246	2.51E-3	3.15E-2	.029
3-2	6	.000368	.0174	1.78E-2	4.92E-2	.031
2-1	8	.00505	.00599	1.10E-2	9.44E-2	.083
2-1	7	4.61E-6	.0955	9.55E-2	1.38E-1	.043
2-1	6	2.44E-4	.0524	5.26E-2	1.26E-1	.073
2-1	3	4.74E-5	-	-	1.04E-1	.092

We had not attempted, prior to these experiments, to measure a sample of ordinary water in the White cell believing that the transmittance would be too near 1.0 for accurate measurement. However, very recent improvements in the pulsed DF laser used for the White cell studies and improvements in the cell itself including improved alignment and longer path length (1.34 km) have made water vapor measurements possible. For 14.3 torr water vapor in 760 torr (total) N₂ we have obtained a value of .038 ± .005 for the 201 P(8) line and .103 ± .01 for the 201 P(7) line. Comparing to the spectrophone measurements given in Table VIII for the same conditions we see that there are significant differences. For 2-1 P(8) the spectrophone result was .0944, 2.5 times greater than the White cell. For the 2-1 P(7) the spectrophone result was .138 versus .103, or one third larger.

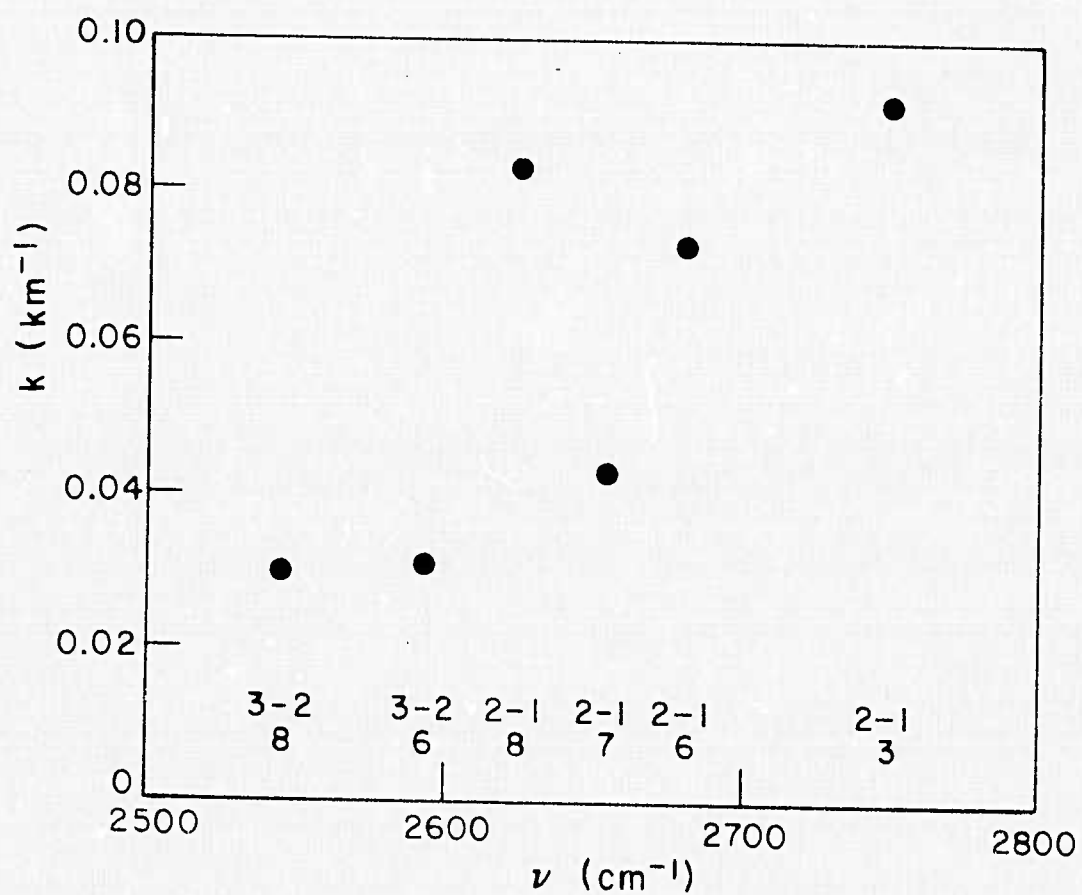


Fig. 16. Water continuum absorption coefficients versus wave number.

The 2-1 P(8) spectrophone data was obtained on only one day and subsequent to these measurements a problem was discovered with one of the spectrophone windows. In the spectrophone if a window changes after the calibration run then the calibration is lost and all data measured will be in error.

V. CONCLUSIONS

Extinction coefficients were measured on six DF lines for air samples with varying amounts of water vapor. The prime objective was to measure the contribution due to the water vapor continuum, for which the only available information involved considerable extrapolation.

The results of the measurements, after correcting for air and H₂O absorption, indicate a water continuum coefficient of $.04 \text{ km}^{-1}$ with an estimated accuracy of $\pm 50\%$.

It is recommended that additional measurements should be made, with particular care paid to system and sample stability and to gas purity to eliminate the experimental data scatter. It is believed that with improved procedures it should be possible to measure the N₂ pressure-induced absorption.

Power levels used for the experiments ranged from 0.1 to 1 watt at the spectrophone. The power level appeared to be ample for the measurements, and future measurements may be performed on a lower power laser, allowing more running time and a quieter experimental environment.

The outstanding cooperation of the United Aircraft Research Laboratories in making the POSM laser available and in operating the system is gratefully acknowledged.

APPENDIX 1 DESCRIPTION OF HDO WHITE CELL CALIBRATION AND CLARIFICATION OF BURCH WATER CONTINUUM EXPERIMENTS [12]

Water vapor absorption in the 3.8μ region is caused by individual absorption lines of HDO and H₂O and wing absorption from remote lines of the 2.7μ and 6.3μ water vapor bands.

At any frequency the absorption coefficient can be written as [12]:

$$(A-1) \quad k(\nu, p, P, T) = k_L(\nu, p, P, T) + C_S(\nu, T)p + C_F(\nu, T)P_b$$

where

- k = absorption coefficient ($\text{mol}^{-1}\text{cm}^2$)
- ν = frequency
- p = water vapor pressure (atm)
- P_b = broadener pressure (atm)
- T = temperature ($^{\circ}\text{K}$)
- C_S = wing absorption coefficient for pure water ($\text{mol}^{-1}\text{cm}^2\text{atm}^{-1}$)
- C_F = foreign broadening wing absorption coefficient
- k_L = local absorption coefficient caused by lines near frequency ν ($\text{mol}^{-1}\text{cm}^2$).

In absorption measurements with the DF laser one is constrained to measurement at a set of fixed frequencies. Further in general, since the pressure dependence of k_L may be complex and unknown, it may not be possible to separately determine the quantities C_S , C_F , and k_L . However, for many frequencies in the 3.8 region the largest contribution to C_S and C_F comes from H₂O wing absorption whereas the dominant contribution to k_L is HDO absorption. Hence by making measurements on two samples having different HDO concentrations one can determine the individual quantities in Eq. (A-1).

The procedure used was as follows. First a measurement was made with a sample of normal water (.03% HDO) at 15 torr and 0.73 km path length. The transmittance was found within experimental error to be 100%. This confirmed that the continuum absorption coefficients were too small to be reliably observed in this path length. Next a sample containing 6.22% HDO was prepared and admitted to the cell at 15 torr and the k_L coefficients measured for each laser line. The data from this experiment was linearly extrapolated to 0.03% HDO to obtain values for k_L applicable to the normal atmosphere.

In the third experiment a sample of normal water was placed in the acoustic spectrophone and the total absorption coefficient determined for each line. By subtraction of k_L from this result, the wing coefficient was determined as shown in Table VIII of the main report.

It is useful to describe and compare the only other available 3.8 μ water continuum measurements, Burch et.al. [12]. In this work a black body source and tunable spectrometer were employed so that it was possible to select frequencies which appeared to have little influence from local absorption. The continuum absorption was made observable by increasing the temperature and hence the allowable water vapor concentration. Pure water vapor and water vapor-nitrogen mixtures were studied separately.

For the pure water vapor samples measurements of the absorption coefficient were plotted against pressure for a given temperature. The following relation was assumed:

$$(2) \quad k(\nu, p, T) = k_L(\nu, T) + C_S(\nu, T)p.$$

Note that here k_L is not a function of p . Thus C_S is the slope of the measured line and k_L is its y-axis intercept.

It is important to investigate under what conditions k_L can be independent of pressure. In the Burch experiments observation frequencies were selected which were not coincident with strong local lines. It is not possible to separate absorption caused by lines "within a few cm^{-1} " of ν from that caused by remote lines if they both have the same pressure dependence. That is, for Lorentz lines one is very quickly in the $|\gamma - \nu_0| \gg \alpha$ region where $k = C_p$. The one additional factor in Burch's experiment is the spectral resolution ($0.2\text{--}0.3 \text{ cm}^{-1}$) which is greater than the absorption line widths. In this case there might have been weak absorption lines near the measurement frequency whose absorption would appear independent of pressure due to the finite spectral resolution [12].

It is perhaps equally likely that the non-zero observed intercepts were due to experimental error, a possibility which Burch discusses at some length [12]. Measurements of $C_S(\nu, T)$ for three temperatures are then extrapolated, for each frequency, to $T = 296 \text{ K}$.

In the second half of the Burch study the influence of nitrogen broadening was investigated by measuring the transmittance of a sample of 2 atm H_2O (at 428 K) broadened with N_2 to total pressure of 4.5-10 atm. The slope of a plot of $k_T - k_p$ vs. P_{N_2} is the coefficient C_B where k_T is the absorption coefficient of the broadened sample and k_p is the previously determined pure water vapor coefficient. Burch determined an average value of the ratio C_B/C_S for all frequencies to be $0.12 \pm .03$. It was assumed that, although data for C_B was only available at 428 K, the ratio C_B/C_S was independent of temperature and thus the desired result for 296 K was available.

It was the purpose of the experiments described in this report, to obtain continuum absorption coefficients for the DF laser frequencies using a procedure which did not involve the temperature extrapolations of Burch's method.

REFERENCES

1. McClatchey, R.A. and J.E.A. Selby, "Atmospheric Attenuation of HF and DF Laser Radiation," AFCRL-72-0312, 23 May 1972.
2. Long, R.K., 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 No. F30602-72-C-0016 for Rome Air Development Center. (AD 775373) (RADC-TR-73-389)
3. Mills, F.S. and R.K. Long, "Absorption Coefficient Measurements of CO₂, HDO-N₂, and CH₄-Air Using a DF Laser," Report 3271-10, August 1974, The Ohio State University ElectroScience Laboratory, Department of Electrical Engineering; prepared under Contract No. F30602-72-C-0016 for Rome Air Development Center. (AD A001097) (RADC-TR-74-295)
4. Ford, D.L., F.S. Mills and R.K. Long, "Laser Absorption in the 5 Micron Band," Report 3271-3, July 1972, The Ohio State University ElectroScience Laboratory, Department of Electrical Engineering; prepared under Contract No. F30602-72-C-0016 for Rome Air Development Center. (AD 748437) (RADC-TR-72-195)
5. Mills, F.S. and R.K. Long, "Measured N₂O-N₂ Absorption at Five DF Laser Frequencies," Report 3271-9, March 1974, The Ohio State University ElectroScience Laboratory, Department of Electrical Engineering; prepared under Contract No. F30602-72-C-0016 for Rome Air Development Center. (AD 778949) (RADC-TR-74-89)
6. Bell, A.G., Proc. Am. Assoc. Advanced Scie. 29, (1880), p. 115.
7. Bell, A.G., Phil Mag 11, (1881), p. 510.
8. Tyndall, J., Proc Roy Soc (London) 31, (1881), p. 307.
9. Roentjen, W.C., Phil Mag 11, (1881), p. 308.
10. Delany, M.E., Science Progress 47, (1959), p. 459.
11. Trusty, G.L., "Absorption Measurements of the 10.4 Micron Region Using a CO₂ Laser and a Spectrophone," Report 2819-4, January 1973, The Ohio State University ElectroScience Laboratory, Department of Electrical Engineering; prepared under Contract No. F33615-69-C-1807 for Air Force Avionics Laboratory. (AD 907549) (AFAL-TR-72-413)

12. Burch, Gryvnak and Pembroke, "Investigation of the Absorption of Infrared Radiation by Atmospheric Gases: Water, Nitrogen, Nitrous Oxide," AFCRL-71-0124 or Ford Aeronutronic Corp. U-4897, January 1971.