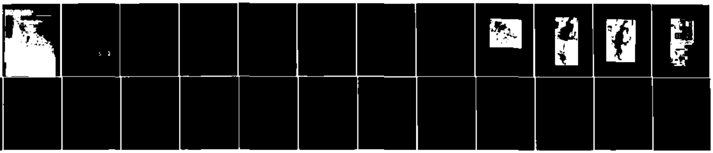
AD-A088 053 NAVAL RESEARCH LAB WASHINGTON DC F/6 7/4
OPTO-ACOUSTIC STUDIES OF METHANE IMPURITIES IN ARGON.(U)
JUL 80 D H LESLIE, G L TRUSTY
UNCLASSIFIED NRL-MR-4283 NL

1 OF 1
AD
A088053



END
DATE
FILMED
9-80
DTIC

[redacted]

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE

9

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER NRL Memorandum Report 4283	2. GOVT ACCESSION NO. AD-A088053	~~3. RECIPIENT'S CATALOG NUMBER~~ Memoran[illegible]
~~4. TITLE (and Subtitle)~~ OPTO-ACOUSTIC STUDIES OF METHANE IMPURITIES IN ARGON		~~5. TYPE OF REPORT & PERIOD COVERED~~ [redacted] Octob~~er 1~~978 — Oct~~ober 1~~979
		~~6. PERFORMING ORG.~~ REPORT NUMBER
7. AUTHOR(s) D.H. Leslie* [redacted] G. L. Trusty	12	8. CONTRACT OR GRANT NUMBER(s) 26
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory ✓ Washington, D.C. 20375		~~10. PROGRAM~~ ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 63754N; 20182AA; 65F204-0
11. CONTROLLING OFFICE NAME AND ADDRESS NAVSEA PMS-405 NC1-11N08 Washington, D.C. 20362	11 30	~~12. REPORT DATE~~ July [redacted]80
		13. NUMBER ~~OF~~ PAGES 25
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) 14 NRL-MR-4283		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

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)*

DTIC
ELECTE
S AUG 20 1980 D
B

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Optoacoustic
Photoacoustic
Spectrophone
Low absorption
Gaseous absorption
Trace-gas
Measurement
Methane
Argon

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

An opto-acoustic detection system has been constructed for detecting absorption of DF laser radiation. Absorption by methane in argon has been observed at 13 DF lines. The system was calibrated using independently measured absorption line parameters for CH_4 broadened by argon at the DF line $P_2(8)$. The spectrophone sensitivity is

$$k = 0.508 \frac{S(\mu V)}{P(W)} \text{ km}^{-1}$$

(Continues)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE i
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. Abstract (Continued)

where S is the spectrophone signal in microvolts and P is the single line laser power in watts. The smallest absorption observed to date is 0.15 km^{-1} for $P_2(10)$ in a 0.1% mixture of CH_4 in argon. Reduction of electrical noise is expected to enable measurement of absorption in the .001 km^{-1} regime. Results at the 3.39 μ HeNe wavelength confirmed gas ghromatograph analysis that a sample of bottled argon contained (2.2 ± .2) ppm CH_4).

TABLE OF CONTENTS

BACKGROUND STATEMENT

In the beam transfer system of a high energy laser it is important that the propagation medium have very low absorption to keep thermal blooming at a minimum. Flowing argon is proposed as the beam conditioning gas for a DF laser. Although argon does not absorb at DF laser wavelengths, the major contaminant in commercial argon, methane, does. In order to determine the design of the gas conditioning system, one must first obtain the proper absorption coefficients for each of the laser output lines. Since the absorptions are small the measurement is difficult. This project uses a procedure especially suited to measuring small absorption levels, the optoacoustic effect, to obtain the required absorption coefficients.

The results will allow the designers to specify the least expensive argon type and the slowest flow rate that will still prevent unacceptable thermal blooming levels, thus avoiding unnecessary operating costs.

OPTO-ACOUSTIC STUDIES OF METHANE IMPURITIES IN ARGON

I. INTRODUCTION

Argon is proposed to be used as the beam conditioning gas for the beam transfer system of a high energy laser. This report discusses results of a measurement program to determine absorption of DF laser radiation by methane impurities in argon. Previous work(1) has indicated the expected absorption to be less than 0.1 km^{-1} (or $10^{-6}cm^{-1}$). At these low absorption levels problems associated with drift of the baseline and 100% transmission levels prohibit the use of traditional multipass cell infrared methods. An opto-acoustic cell (spectrophone) has been designed, constructed, and used to measure DF laser absorption in a 0.1% CH_4 in argon mixture. These results indicate that reducing the electrical noise at the preamplifier stage and optimizing the beam geometry will enable measurement of absorption at the .001 km^{-1} level.

The spectrophone was calibrated against diode laser measurements of argon-broadened methane at the $P_2(8)$ frequency and provided additional information regarding the CH_4-CH_4 and CH_4-argon broadening coefficients.

We first describe the design and construction of the spectrophone. Initial use at 3.39 μm to detect methane is discussed, followed by a description of its present use in the DF spectral region. The calibration and discussion of the electronics is then given. We conclude with a review of other methane measurements in the region and a discussion of how the sensitivity might be improved.

Manuscript submitted June 9, 1980.

II. THE OPTOACOUSTIC CELL (SPECTROPHONE)

A. Background

The modern application of the spectrophone was initiated by Kerr and Atwood(2) and is reviewed by Kreuzer(3). Briefly, a laser beam is modulated at an acoustic frequency and passed through a cell containing the gas in question and a microphone. Absorption is detected at the modulation frequency and amplified using phase-sensitive electronics. The improvement over traditional transmission measurements is that the signal from the spectrophone is directly proportional to the absorption. This is especially important for low level absorption, i.e., $10^{-5}cm^{-1}$ or less.

B. Spectrophone Construction

The cell built for this study employs a non-resonant cavity constructed of a 7 cm piece of K_a band waveguide (3mm x 7mm). Six miniature electret microphones with integral FET preamplifiers (Model 1832, Knowles Electronics, Franklin Park, Ill.) are arranged three each along the 7mm sides of the waveguide, as shown in Fig. 1.

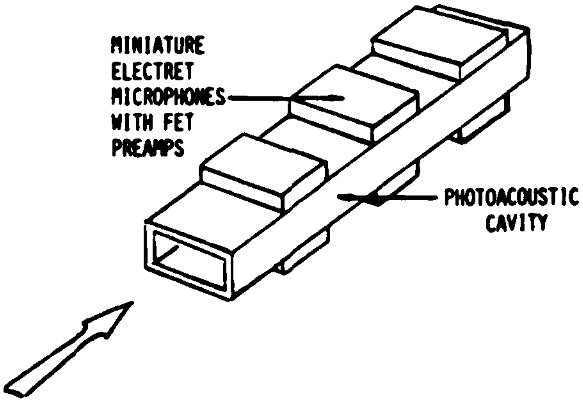


Fig. 1 - Spectrophone geometry (4)

The waveguide is supported at each end by a teflon block which also serves to support each CaF_2 window at its Brewster angle. The optical path through the teflon is a 1" bore with a coarse 8 threads per inch to serve as acoustic baffles. Figure 2 shows the interior of the cell. The waveguide, teflon holders, and electrical connections are contained inside a 1/2" thick x 6" diameter aluminum cylinder as shown in Fig. 3. Micro-dot and epoxy seals allow six coax feed-throughs to the microphones and two to provide 1.35 VDC to power the FET preamps. Also shown in Fig. 3 are two solenoid valves to provide seals to the vacuum line and gas supply. The assembled device, as shown in Fig. 4, is placed in a styrofoam cradle lined with heavy felt, and then placed in a 14" plywood cube. All six interior sides of the cube are covered with 1" of heavy foam padding, 1/8" of lead, and another 1" of light foam padding. Two 3/4" holes in opposite faces provide entrance and exit ports for the laser beam. Another 1" hole allows feed-through for the electrical lines. The extensive acoustic shielding was deemed necessary since the cell was to be placed close to the DF chemical laser, which has a 1500 cfm vacuum pump and a cooling system. Our results to date indicate noises of a purely electrical nature to be the dominant interference, rather than acoustic noise.

A description of the laboratory set-up using a 3.39 μm He-Ne laser is shown in Figure 5, without the acoustic isolation box. A 400 Hz tuning fork placed in front of the laser provided square wave modulation and a reference signal for the PAR 126A lock-in amplifier. Prior to the Model 116 input preamp of the PAR the six microphone

Fig. 2 - Innards of the spectrophone. (The laser beam passes through the inside of the rectangular waveguide.)

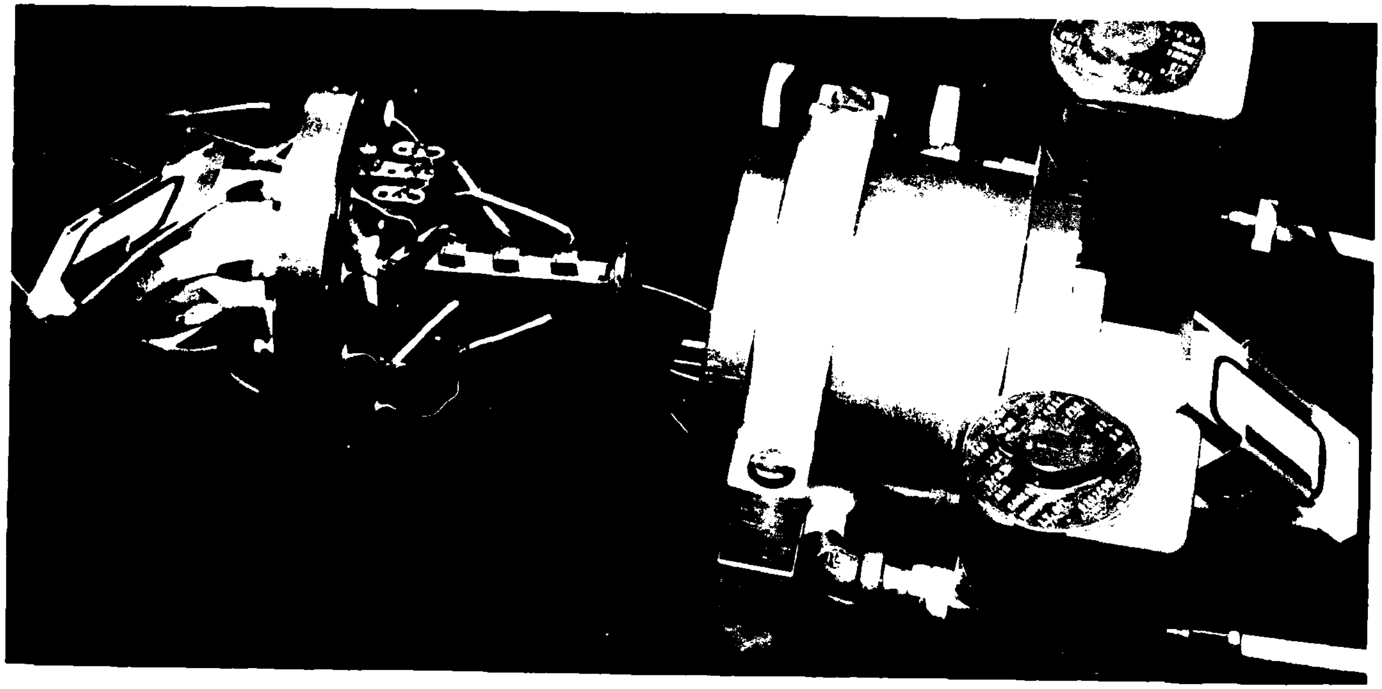


Fig. 3 - Two halves of the spectrophone

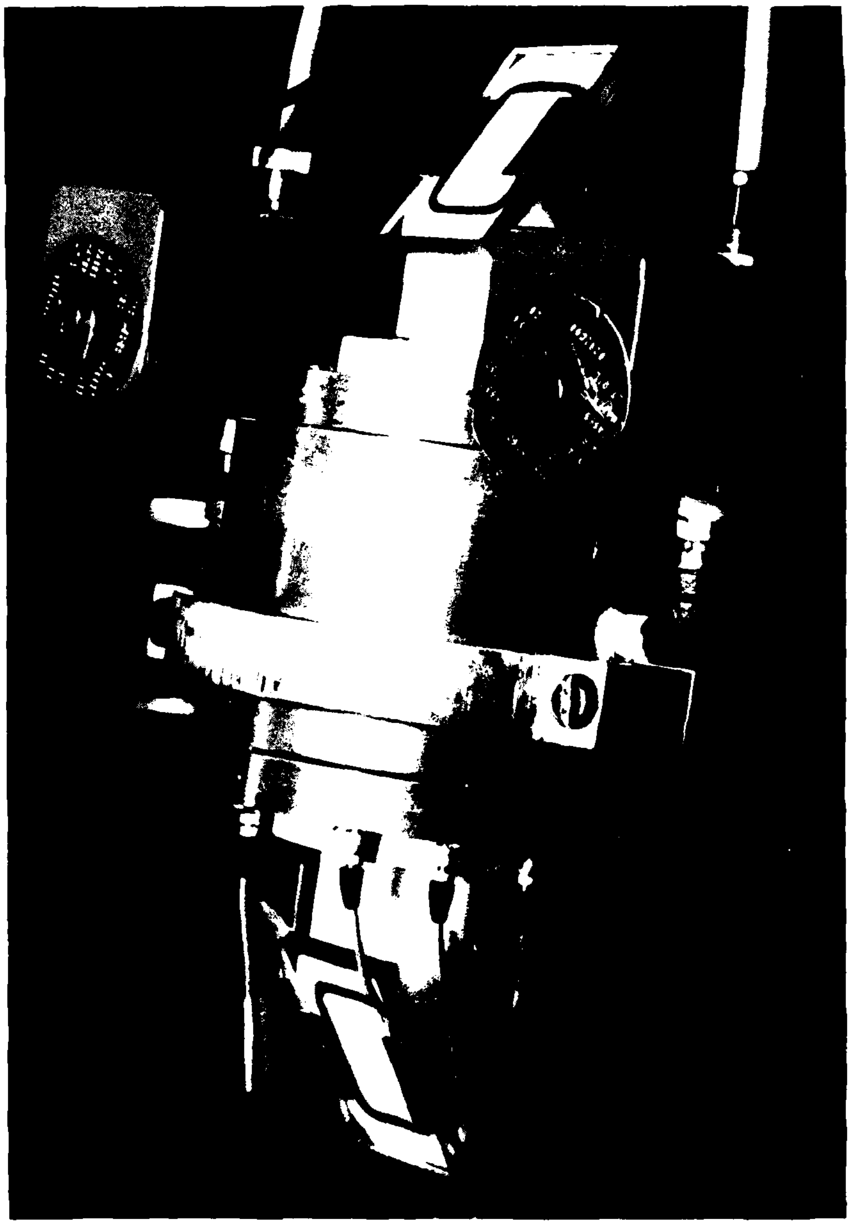


Fig. 4 - The assembled spectrophone

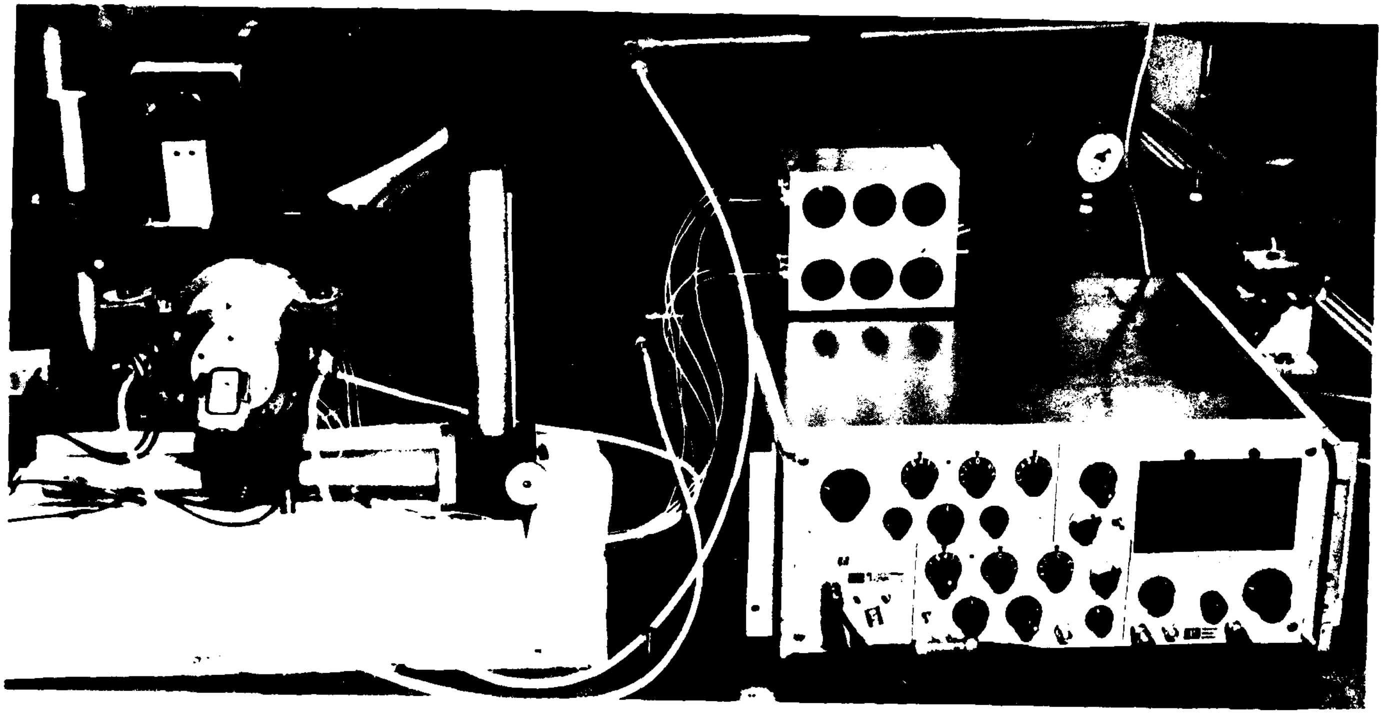


Fig. 5 - Spectrophone system in the lab (prior to installation in the DF laser trailer)

signals are combined in a 6-channel mixer. It is important to point out here that no phase compensation was provided in our initial design. It became clear after phase measurements on each individual channel that compensation is necessary. Our results indicated a phase from 135° to 203°. (One microphone proved to be 90% noise, probably from damage due to an acoustic shock from a sudden release of vacuum.) Hence one improvement we have planned is the construction and use of a six-channel low-noise phase shifter to optimize the mixing of the six microphone signals.

C. Performance at 3.39 μm

Initial performance checks on the cell were made using a 3.39 μm HeNe laser with a rated output of 25 milliwatts. The position of the HeNe relative to methane absorption is shown in Fig. 6 for a 1.6 ppm CH_4 mid-latitude summer atmosphere. The absorption coeficient is 1.4 km^{-1}/ppm, or about 1000 times that expected in the DF laser region.

With the cell filled to one atmosphere of Mil Spec A water-pumped argon we observed a signal of 1.20 μV. A signal of 1.62 μV was recorded for ambient air. Subsequently we concluded the argon tank contained 1.2 ppm CH_4. However, assuming a 1.6 ppm CH_4 concentration at NRL proved to be wrong. Gas Chromatography analysis on the same tank concluded CH_4 presence at 2.26 ppm in the argon tank, and hence the NRL air sample was considerably enriched. What did result from the operation at 3.39 μm was the conclusion that

(1) A sample of Mil Spec A water-pumped argon contained 2.2 ppm CH_4 (± 10%).

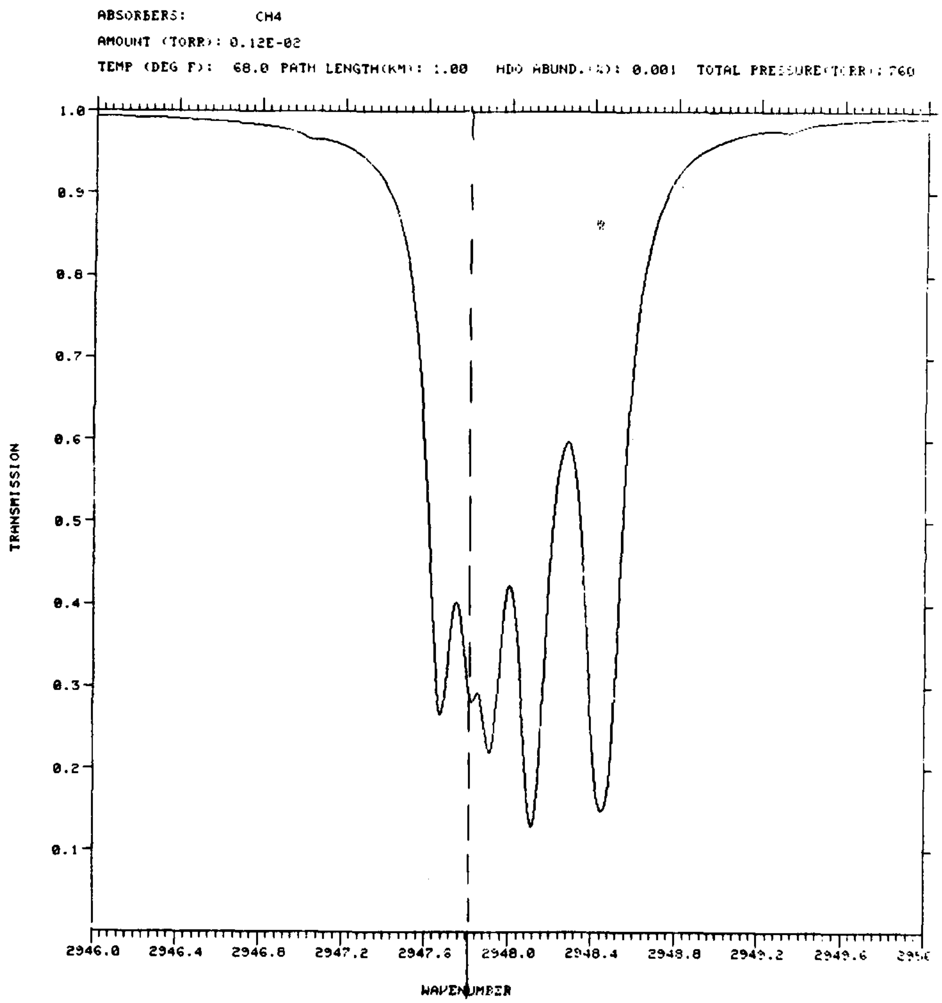


Fig. 6 - 3.39 μm HeNe absorption by CH_4

(2) The spectrophone operated well at an absorption level of 3 km^{-1} with 25 mw of laser power.

III. RESULTS AT THE DF LASER LINES

After return of the NRL DF laser from operations at WSMR, the spectrophone was installed in the transmitter trailer. A 36" focal length spherical mirror was installed on a sliding carriage in front of the power meter. This enabled the mirror to be quickly translated into the system once a steady power level had been determined. Due to divergence of the DF beam, the 36" mirror formed a focus at 60", and the spectrophone was placed as near as possible to the focus. The beam waist (at the output window of the spectrophone) was estimated to be 400 µm in diameter. This insured that the DF beam was capable of passing through the 3mm x 7mm waveguide without touching the walls.

Removal of the rear cavity optic of the laser (mirror for multiline, or grating for single line) allowed a 0.63 µm HeNe beam to propagate collinearly through the laser and the ZnSe output coupler, off the 36" mirror and through the spectrophone. Fine adjustment by watching the diffraction pattern on the trailer door five feet from the cell enabled accurate location of the beam through the spectrophone.

A liquid nitrogen cooled InSb detector was placed at the exit port of the spectrophone to provide a fast measurement of the beam power. The DF power output can fluctuate significantly faster than the power meter. The correlation between power meter reading and InSb detector is given in Fig. 7. Our next series of measurements will incorporate the InSb detector for constant monitoring of the laser power. Figure 8 shows how the power fluctuations will be divided out using a DC ratiometer. This will eliminate the inaccuracy inherent in sliding the mirror in and out of the beam, and will remove much of the error indicated by the data scatter in Fig. 7.

As mentioned previously, it was discovered during the initial DF laser runs that at least one microphone had become very noisy, and that all six were not phased properly. Examination of the signal from each individually with phase adjusted for maximum signal determined that microphone #2 gave the optimum signal-to-noise. All the following measurements refer to data obtained with microphone #2 being the only signal amplified.

Laboratory measurement of the reference frequency provided by the tuning fork indicated that the 400 Hz rating was accurate to less than 0.5 Hz deviation, measured with an HP counter for several hours. Consequently the input filter of the lock-in was set to the maximum filter setting of Q=100 in order to minimize electrical noise. The only other parameter that need be mentioned here is the iris setting within the DF optical cavity. It was set at 5mm diameter to insure that the TEM_{00} mode dominated and hence the smallest beam waist possible was obtained. Circular thermofax paper burns were obtained only for this diameter or smaller. A 1-second time constant at the post-detection stage was used. Future plans include use of 10- or 30-second time constants at both spectrophone and InSb detectors to obtain maximum noise reduction prior to division at the ratiometer.

Typical data for 0.1% CH_4 in argon (Air Products certified at 0.105%) is given in Table 1. Alteration of the flow ratios of

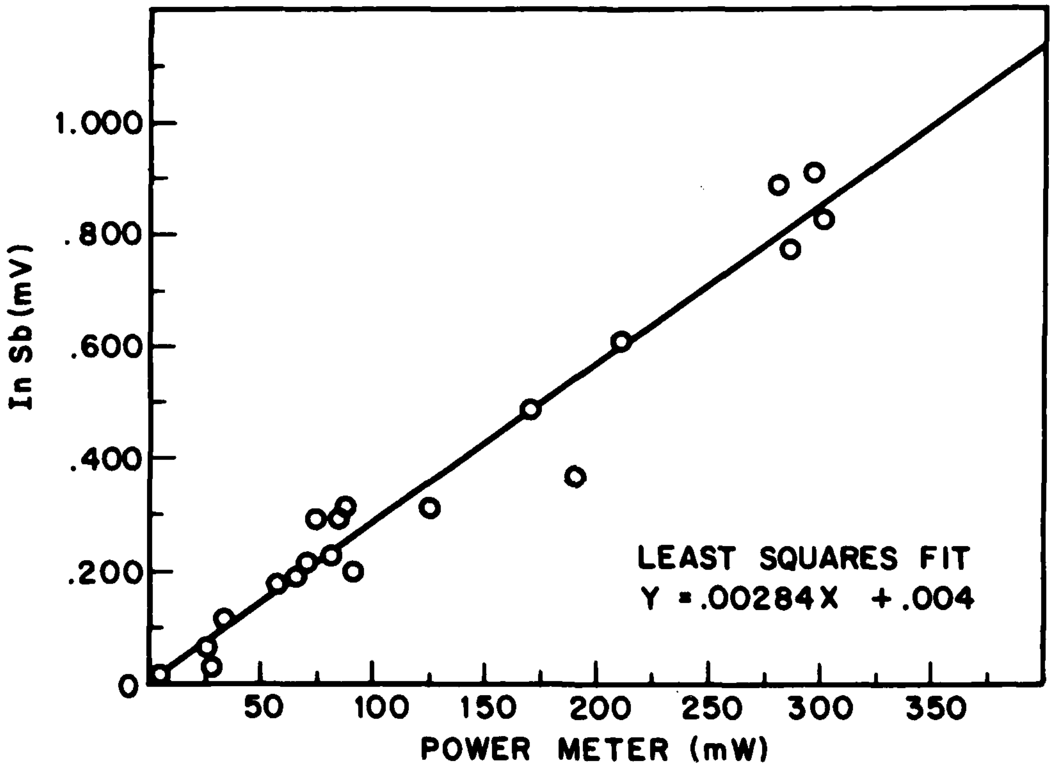


Fig. 7 - InSb and power meter correlation

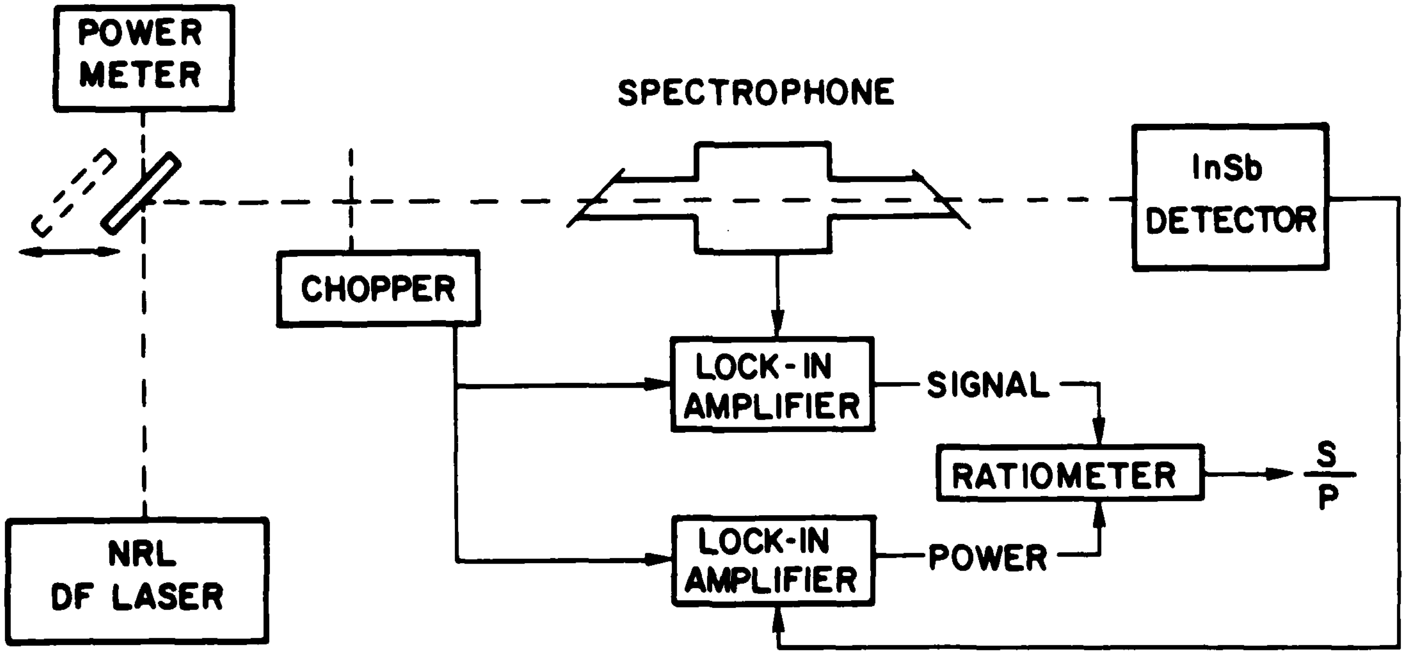


Fig. 8 - Optical and electronic layout

TABLE 1. RAW DATA AT 0.1%

DF Laser	Signal at Microphone #2	Laser Power
$P_2(3)$	0.30 μVolts	90 mW
$P_1(7)$	0.38	70
$P_2(4)$	0.62	170
$P_1(8)$	0.18	80
$P_2(5)$	0.24	210
$P_1(9)$	0.73	65
$P_2(6)$	0.62	280
$P_2(7)$	0.51	295
$P_2(8)$	0.37	285
$P_2(9)$	0.23	190
$P_2(10)$	0.13	125
$P_3(7)$	0.13	84
$P_3(8)$	0.45	73
$P_3(9)$	0.08	33
$P_3(10)$	0.10	5

TABLE 2. DF ABSORPTION BY $CH_4 \left[\frac{km^{-1}}{ppm} \times 10^{-3} \right]$

DF LINE	NRL	SPENCER (c)	ENG	AFWL (d)	SAI - (e) ECS
$P_1(6)$	b	2.13		2.81	2.3
$P_2(3)$	1.16	1.77			
$P_1(7)$	1.55	2.34		2.26	2.2
$P_2(4)$	1.43	1.91			
$P_1(8)$	.523	.515		.214	0.5
$P_2(5)$	.282	.364		.314	
$P_1(9)$	4.79	4.70		15.3	4.9
$P_2(6)$	.797	1.24		.688	1.0
$P_1(10)$	a,b	2.65			1.9
$P_2(7)$	.662	.805		.713	0.9
$P_1(11)$	a	.302	.283		0.5
$P_2(8)$	.452*	.555	.452*	.612	0.5
$P_1(12)$	a	.057	.038		
$P_2(9)$	.378	.598		.794	0.6
$P_3(6)$	a	.168		.093	0.1
$P_1(13)$	a	.872			
$P_2(10)$	.150	.139		.111	0.1
$P_3(7)$	.218	.213		.154	0.2
$P_2(11)$	b	.131			0.4
$P_3(8)$	2.27	2.34		.257	2.3
$P_3(9)$	0.0	.043		.037	
$P_3(10)$	0.0	.061		.029	

(a) We may be able to study these lines with the NRL tunable diode laser.
(b) Tuning of gas flow may bring these lines up to power.
(c) Pure CH_4 (no foreign broadener).(6)
(d) N_2 and Argon broadener with no observable difference.(7)
(e) Dry air broadener. (8)
(*) Calibration

fluorine and deuterium, and alteration of the laser head total pressure can allow more lines than shown in Table 1 to lase. Lines such as $P_1(10)$, $P_1(6)$, $P_2(11)$, $P_3(5)$, etc. have been encouraged to lase at elevated fluorine pressures, but considerable time and fuel are consumed during the time required to obtain stable output.

A DC signal level of 0.1 μV ± .03 μV was observed with the laser beam blocked, after having maximized the spectrophone signal with the laser beam passing through the spectrophone. Since weakly absorbed lines showed no change between the beam blocked and -unblocked conditions, zero absorption was inferred and so we subtracted the DC signal from the observed spectrophone signal, prior to dividing by the beam power.

Table 2 summarizes our results for averages of two different days' results, using different fills of the spectrophone from the same bottle of Air Products Certified 0.105% CH_4 in argon. The asterisk at $P_2(8)$ refers to the calibration of our device with the results of Eng (5). Our result of 0.89 μVolt/Watt for $P_2(8)$ at 0.1% was set equal to Eng's result of 0.452 $km^{-1}/ppm \times 10^{-3}$ for CH_4 broadened by argon at the $P_2(8)$ frequency. The spectrophone calibration of $k = 0.508 \frac{S(\mu V)}{P(W)} km^{-1}$ follows from these two measurements. Eng also found the CH_4-CH_4 broadening coeficient to be 0.0767 cm^{-1}/atm, where as the CH_4-argon broadening coefficient was 0.0567 cm^{-1}/atm. He used the isolated $2\nu_4$ R(0) methane line at 2618.27 cm^{-1} and obtained a self-to-foreign broadening ratio of 1.35 ± .02. This agrees well with the results of Pine(9) and Varanasi, et.al.,(10) who both used the ν_3 R(0) line at 3028.7 cm^{-1}.

The self-to-foreign broadening difference requires that the results of Spencer, et.al.(6), not be too closely judged against our results. Since the integrated absorption coefficient is independent of line-width, a narrow line will have more peak absorption and less wing absorption relative to a wide absorption line of the same integrated intensity. We hope to examine lineshape subtleties such as these, by comparing our argon-broadened data with the self-broadened results of Spencer. Such study, however, awaits the reduction of noise and several immediate improvements in our system.

IV. CONCLUSIONS AND RECOMMENDATIONS

We have designed and constructed a state-of-the-art device for the measurement of extremely small absorption coeficients. Operation in the strong absorption region of CH_4 at 3.39 μm successfully determined that the methane concentration in a sample of Mil Spec A bottled argon was twice the rated level of 1 ppm. The device has been used at 13 DF laser lines to measure absorption as low as 0.15 km^{-1} in a 0.1% CH_4 in argon mixture at $P_2(10)$. The device has been calibrated with an independent measure of absorption at $P_2(8)$ by CH_4 in argon. The stronger absorption values compare well with previous studies, considering differences in broadening gas, technique, and calibration between the various experiments.

Our sensitivity can be improved by the following methods:

1. Replace the broken microphone and adjust the phase of each signal prior to mixing. This could give improvement by a factor of $\sqrt{6}$ in Signal/Noise. The construction

of a six channel phase adjustor does not seem out of the ordinary.

2. Optimize the geometry of the laser beam in the waveguide. A circular cross section waveguide would best match the circular beam distribution. This would eliminate the dead regions now present in the rectangular waveguide. A telescope could be constructed with two spherical mirrors to allow variation of the focal spot size. The optimum ratios beam diameter to waveguide diameter could then be found. A circular cross section waveguide would also reduce the possible absorption by the walls of the device, and hence reduce the amount of false signal.
3. Multipass the cell. A factor of two is possible using a plane mirror at the spectrophone exit, as we have seen ourselves. This would require some rearrangement of the power meter. Improvement of greater than two could be investigated using properly chosen spherical mirrors in a White-type cell arrangement.
4. Operate at an acoustically resonant frequency. We now chop at 400 Hz. The lowest funtamental resonance is 3.07 kHz for $\lambda/2$ in a 7 cm cell with argon gas. The only modification required is to chop at resonance. An improvement factor of at least ten is possible at resonance (11).

Implementation of suggestions 1-4 can, in principle, provide an increase of at least fifty in sensitivity, i.e., 0.003 km^{-1}.

Suggestion (2) above will also reduce alignment problems and hence reduce the possibility of false signal from cell wall absorption.

A final consideration is placing the spectrophone inside the DF laser optical cavity. Here the single-line power is on the order of 50 watts. The absorption we are measuring is small, and hence would not tend to degrade the cavity Q. The spectrophone windows are already mounted in Brewster mounts for the DF wavelength and with identical CaF_2 windows. Some cavity optics modification, however, may be necessary to achieve a proper beam size. This intracavity technique has been used, for example, for ethylene detection using a windowless spectrophone and a CO_2 laser.(12)

REFERENCES

1. J. L. Griggs, P. R. Carlson, F. G. Smith, "Use of Argon in the Sea Lite Beam Transfer System", Final Report 30 October 1978 to NSSC PMS-405 Contract M00024-78-C-4305, SAI Report 78-33.
2. E. L. Kerr and J. G. Atwood, "The Laser Illuminated Absorptivity Spectrophone: A Method for Measurement of Weak Absorptivity in Gases at Laser Wavelengths", Appl. Optics 7, 915-21 (1968).
3. L. B. Kreuzer, "Ultra Low Gas Concentration Infrared Absorption Spectroscopy", J. Appl. Phys. 42, 2934-43 (1971).
4. C.K.N. Patel and R.J. Kerl, "A New Optoacoustic Cell with Improved Performance", Appl. Phys. Lett. 30, 578-79 (1977).
5. R. S. Eng and A. W. Mantz, "Tunable Diode Laser High Resolution Absorption Parameter Measurements", Final Report 2 November 1979 to NRL Contract N00173-79-M-E606.
6. D. J. Spencer, G. C. Denault, and H. H. Takomoto, "Atmospheric Gas Absorption at DF Laser Wavelengths", Appl. Optics 13, 2855-68 (1974).
7. T. F. Deaton, D. A. Depatie, T. W. Walker, "Absorption Coefficient Measurements of N_2O and CH_4 at DF Laser Wavelengths," Appl. Phys. Lett. 26, 300-303 (1975).
8. D. R. Woods, R. E. Meredith, F. G. Smith, T. W. Tuer, "High Resolution Spectral Survey of Molecular Absorption in the DF Laser Region; Measurements and Calculations" SAI Report for DARPA Contract F30602-75-C-0028 RADC-TR-75-180 July 1975.
9. **A. S. Pine, 1979 Symposium on Molecular Spectroscopy, Ohio State University.**

10. P. Varanasi, L. A. Pugh, B. R. P. Bangaru, "Measurement of Multiplet Intensities and Noble Gas-Broadened Line Widths in the ν_3-Fundamental of Methane," J.Q.S.R.T. 14, 829-838 (1974).

11. K. Frank and P. Hess, "Accurate Measurement of Relaxation Times With An Acoustically Resonant Optoacoustic Cell", Chem. Phys. Lett. 68, 540-543 (1979).

12. S. Shtrikman and M. Slatkine, "Trace-gas Analysis with a Resonant Optoacoustic Cell Operating Inside the Cavity of a CO_2 Laser," Appl. Phys. Lett. 31, 830-831 (1977).

END

DATE
FILMED

9-80

DTIC