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THE ABSORPTION SPECTRUM FROM 0.5 TO 25 MICRONS OF A 1000-FT ATMOSPHERIC PATH AT SEA LEVEL

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ABSTRACT

One infrared absorption spectrum from 0.5 to 25 μ of a 1000-ft-long atmospheric path at sea level is presented. The resolution is between 1 and 2 wave numbers over a considerable portion of this spectral region and is sufficient to allow the identification of structure attributable to some of the rarer constituents of the atmosphere such as N_2O, CH_4, and HDO.

PROBLEM STATUS

This is an interim report. Work is continuing on other phases of the problem.

AUTHORIZATION

NRL Problem N03-05
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OF A 1000-FT ATMOSPHERIC PATH AT SEA LEVEL

INTRODUCTION

The Naval Research Laboratory is currently engaged in a study of the transmission of long atmospheric paths in the infrared region of the spectrum (1,2). The two paths of specific interest are 3.4 and 10.1 statute miles in length. A third path of 1000 ft is used to obtain the wavelength distribution of energy from the light source which in this case is a high-intensity carbon arc searchlight.

Radiation from the source at one end of the path is received by an infrared spectrometer at the other end of the path and recorded in the form of a continuous spectrum from 0.5 μ to 25 μ. Since, as is usual in infrared spectroscopy, the resolution obtainable is primarily dependent on the amount of energy available, it is the most distant of the three sources in this program which determines the minimum slit widths and hence maximum resolution attainable. This follows from the fact that the same slit widths are used in recording spectra both over the two long paths and the 1000-ft control path. If different slit widths were used for the different paths, reduction of the data would be vastly complicated and the results would be less reliable.

The obtainable resolution over the 1000-ft path is never realized when the path is used as the control for the other two paths. However, one spectrum over the 1000-ft path was recorded at maximum resolution and this is reproduced in the present report. The resolution, which is between 1 and 2 wave numbers over most of the region studied, is inferior by a factor of 10 to 20 to that attainable with modern gratings, but it is hoped that this intermediate resolution may prove helpful to those interested in the atmospheric transmission problem. For one thing, it shows the transmission of a specific horizontal path whereas most of the extant grating spectra (3-7) employ the sun as a source and therefore show the transmission of a slant path through the entire atmosphere.

INSTRUMENTATION

The spectra in this report were obtained at the Chesapeake Bay Annex of the Naval Research Laboratory, situated on the west shore of Chesapeake Bay near North Beach, Maryland.

The source of radiation for these measurements was a 60-in. diameter carbon arc searchlight from which the glass front was removed. The spectrometer, a Perkin-Elmer 12-C, was situated in a building 1000 ft away and an image of the searchlight mirror was formed on the entrance slit by a 60-in. focal length, 16-in. diameter mirror. This image was 8 mm in diameter and hence filled 2/3 of the 12-mm-high entrance slit.

Four prisms were used to cover the spectral region as follows: LiF from 0.5 μ to 5.5 μ, CaF_2 from 5.5 μ to 8.3 μ, NaCl from 8.3 μ to 15 μ, and KBr from 15 μ to 25 μ. The detector was a Perkin-Elmer thermocouple, the output of which was amplified by a Perkin-Elmer Model 107 breaker-type amplifier and recorded on a Speedomax Type G recorder.

Wavelength calibration for each prism was carried out immediately following the recording of the spectrum in order to minimize any possible shifts caused by temperature changes. The absorption bands of atmospheric H_2O and CO_2 and of CO, CH_4, NH_3, HCl, HBr, and CH_3OH, along with the emission lines from an H-4 mercury arc, were used for the wavelength calibration and the wavelengths of these bands were taken from the work of Downie et al. (8).

When the NaCl and KBr prisms were used, scattered light was reduced by replacing the metal chopper blade with one made of Plexiglas, the residue being accounted for with CaF_2 and NaCl shutters.

The spectra were recorded on days of great atmospheric clarity (the daylight visual range was in excess of 50 mi) so that attenuation by scattering agents in the atmosphere was negligible. It was then assumed that those regions showing no absorption bands were 100% transparent. The energy distribution in these "windows" agrees well with the calculated distribution obtained using the Planck radiation law and the temperature of the source.

The bandpass of the spectrometer is given beneath the symbol ⊣⊢ in microns and in wave numbers at appropriate places in the spectra. Throughout a good portion of the region covered, the resolution is near the maximum attainable with this prism instrument as borne out by the fact that further reduction in the mechanical slit width produced very slight improvement in the resolution. In the region from 0.5 μ to 2.7 μ reduction of the mechanical slit widths, which were 0.005 mm from 0.5 μ to 1.85 μ and 0.01 mm from 1.85 μ to 2.7 μ, seemed to produce a degradation of the resolving power.

For a more detailed description of the experimental arrangement the reader is referred to Refs. 1 and 2.

DISCUSSION

The spectrum (Figs. 1 through 5) shows a multitude of absorption bands attributable to H_2O, CO_2, HDO, N_2O, O_3, and CH_4. All of these constituents have been observed and reported in the literature where they have in general been studied with grating resolution (3-7). Some differences appear between the concentrations reported by other observers and the concentrations indicated by this spectrum, but those differences cannot be considered quantitatively significant because the reduced resolution, relatively large amount of water vapor, and short path-length in the present work make it difficult to isolate and measure the bands due to the rarer constituents of the atmosphere.

In general, the concentrations of water vapor and HDO are larger here relative to the other constituents since water vapor is most concentrated at sea level.

Carbon dioxide is fairly uniformly distributed throughout the vertical atmosphere, its percentage by volume concentration, which is around 0.04%, decreasing slightly with altitude.

Nitrous oxide appears herein to have about the same or slightly larger concentration than the average of 5×10^{-7} fractional volume concentration (NTP) previously reported (9). Figure 6 is an original trace showing the P and R branches of the 4.5-μ band. The band at 3.9 μ hardly shows in this spectrum, but appears strongly in the longer paths (1,2). In Fig. 6 there are also included two spectra showing the effect of adding about 0.7 and 10 atm-cm of N_2O to the path.

Methane, which is generally reported to be about 3 times as abundant as N_2O and to be uniformly distributed throughout the atmosphere, is very difficult to distinguish here through the overriding water vapor structure but the indications are for considerably less than the reported concentrations. Again, a quantitative statement is not reliable, but the two strongest band centers at 7.66 and 3.32 μ are just barely discernable as shoulders on stronger bands of water vapor. The additional absorption by small amounts of CH_4 added to the optical path indicate a concentration less than 1 part per million whereas 1.5 parts per million is the average of the reported values from solar observations, all of which are in good agreement. It is worth noting here that we had expected to find a larger than average concentration of methane since the apparatus is located fairly near some large areas of swampy land. In addition, one of the longer paths, the 3.4-mi path, runs over the west shoreline of the bay between two promontories and the land between these two promontories is largely swampy. No pronounced methane absorption has been found in the 3.4-mi path (which, however, has less resolution by a factor of 5 to 8 than the spectrum in Figs. 1 to 6) even on days of almost no wind when the nose tells you that the swamp's gases are relatively concentrated. This seems to corroborate Hutchinson's assertion (10) that the atmospheric methane is of animal rather than vegetable origin.

No trace whatever of CO has been observed although its low expected concentration (1 part in 10 million) and the overriding structure of N_2O, CO_2, and water vapor make it difficult to discern here.

Ozone has not been observed in the 1000-ft path but has been observed in the 10-mi path (11) where the indicated concentration agrees well with independent observations by chemical means and ultraviolet transmission spectra. The ozone concentration is highly variable being almost undiscernable in several runs made at night while it is usually evident to some extent during the day.

The atmospheric windows, or regions of fairly high transmission between the major absorption bands of water and CO_2, become increasingly contaminated with weaker absorption bands, chiefly of water vapor, as the wavelength increases. These windows and their approximate wavelength limits defined by the centers of the specified absorption bands forming their boundaries are indicated in Table 1.

TABLE 1
Wavelength Limits (microns) and the Atmospheric Constituent Responsible for the Absorption Band Forming the Limits

Window No.	Lower Limit and Constituent	Upper Limit and Constituent
I	0.72 (H_2O)	0.94 (H_2O)
II	0.94 (H_2O)	1.13 (H_2O)
III	1.13 (H_2O)	1.38 (H_2O)
IV	1.38 (H_2O)	1.90 (H_2O)
V	1.90 (H_2O)	2.70 (H_2O and CO_2)
VI	2.70 (H_2O and CO_2)	4.30 (CO_2)
VII	4.30 (CO_2)	6.0 (H_2O)
VIII	6.0 (H_2O)	15.0 (CO_2)
IX	15.0 (CO_2)	25.0 (H_2O)

Window VIII becomes opaque (i.e., its transmission is everywhere less than 0.005 which is the effective limiting sensitivity of our instrumentation) over the 10-mi path when there are 38 cm of precipitable water in the path. Window IX is opaque over the 3.4-mi path for the lowest concentration of water vapor, 1.4 cm, which has been observed in this path during the present program.

REFERENCES

1. Taylor, J. H., and Yates, H. W., "Atmospheric Transmission in the Infrared," NRL Report 4759, July 2, 1956

2. Taylor, J. H., and Yates, H. W., "Atmospheric Transmission in the Infrared," JOSA 47(3):223, March 1957

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REFERENCES

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2. Taylor, J. H., and Yates, H. W., "Atmospheric Transmission in the Infrared," JOSA 47(3):223, March 1957

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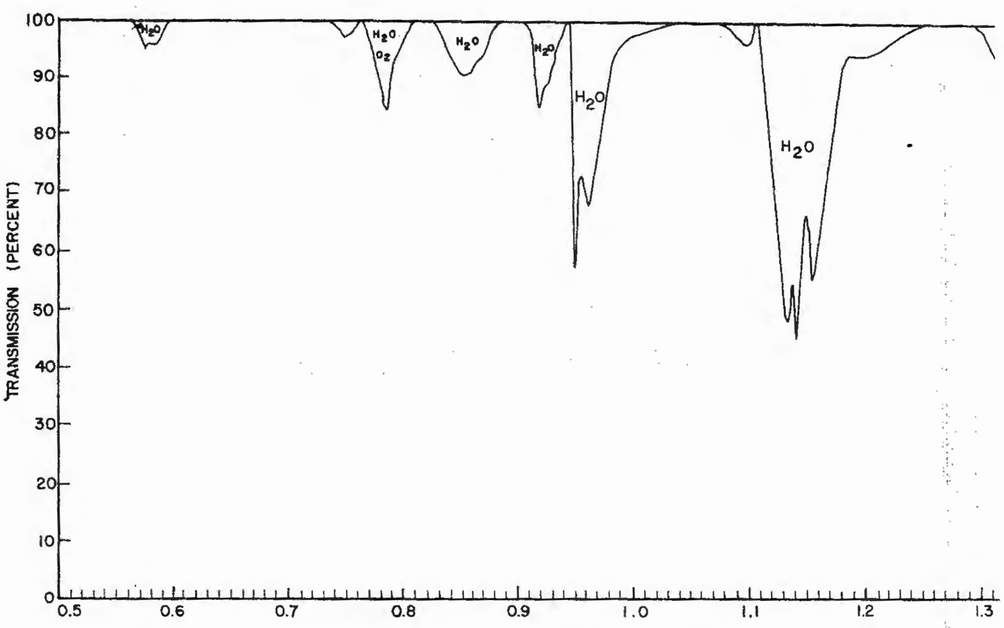
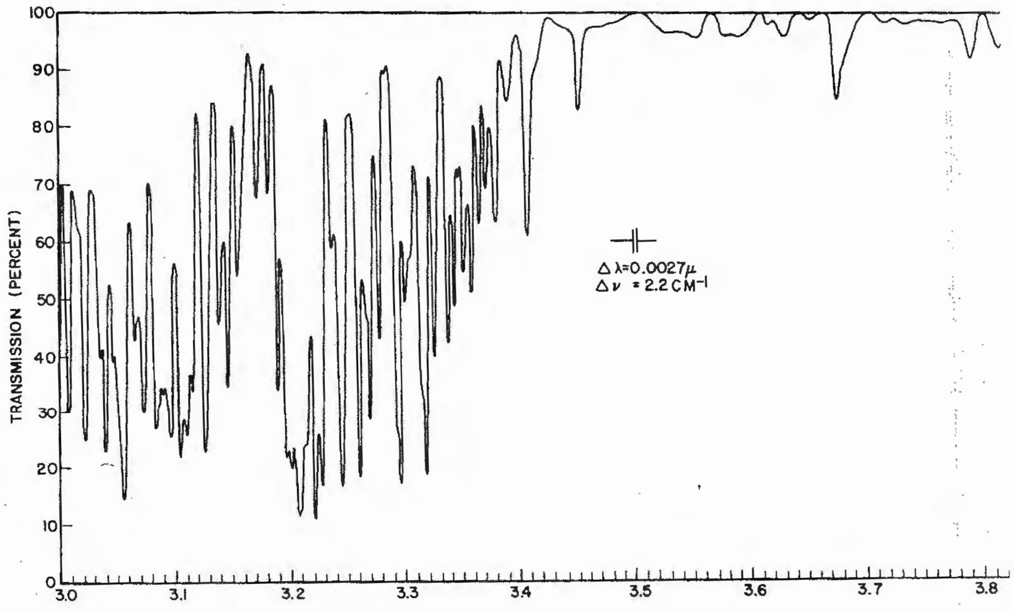


TRANSMISSION (PERCENT)
H_2O
H_2O
O_2
H_2O
H_2O
H_2O
H_2O
100
90
80
70
60
50
40
30
20
10
0
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3



TRANSMISSION (PERCENT)
$\Delta \lambda = 0.0027\mu$
$\Delta \nu = 2.2 \text{CM}^{-1}$
100
90
80
70
60
50
40
30
20
10
0
3.0
3.1
3.2
3.3
3.4
3.5
3.6
3.7
3.8

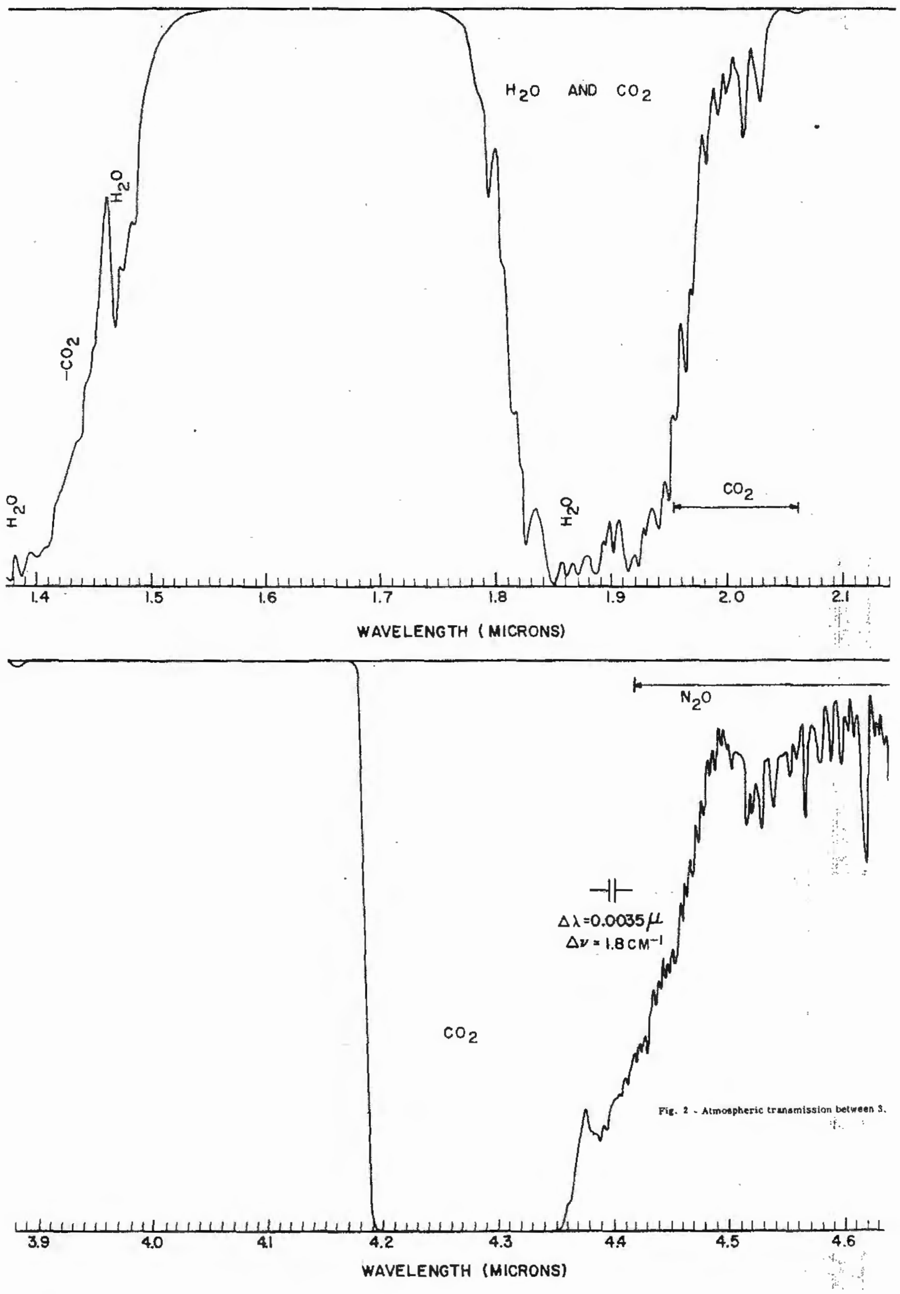
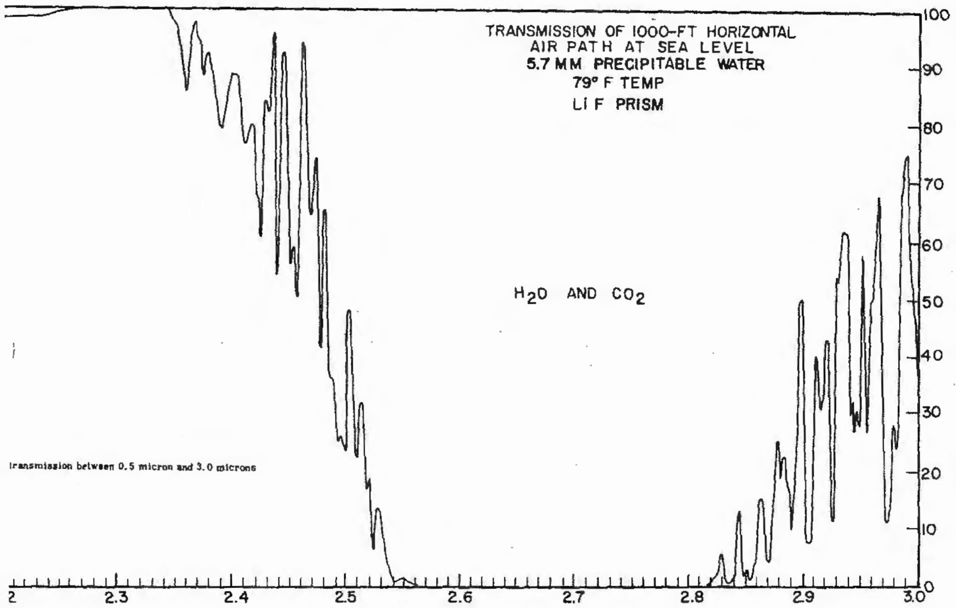
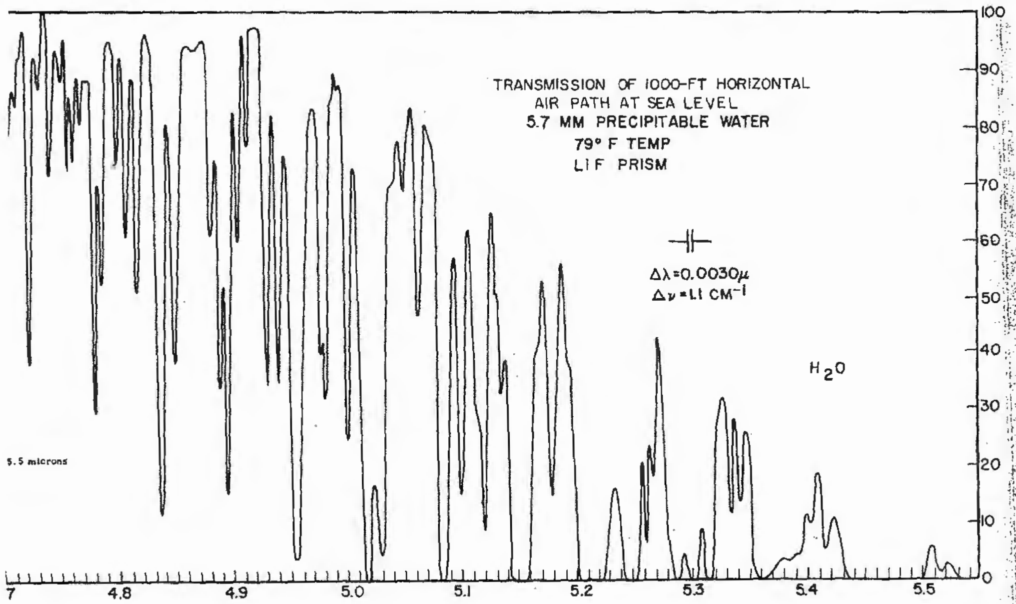


Fig. 2 - Atmospheric transmission between 3.


TRANSMISSION OF 1000-FT HORIZONTAL
AIR PATH AT SEA LEVEL
5.7 MM PRECIPITABLE WATER
79° F TEMP
LiF PRISM
H_2O AND CO_2
transmission between 0.5 micron and 3.0 microns
2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3.0
100
90
80
70
60
50
40
30
20
10
0


TRANSMISSION OF 1000-FT HORIZONTAL
AIR PATH AT SEA LEVEL
5.7 MM PRECIPITABLE WATER
79° F TEMP
LiF PRISM
$\Delta\lambda = 0.0030\mu$
$\Delta\nu = 1.1$ CM^{-1}
H_2O
5.5 microns
7
4.8
4.9
5.0
5.1
5.2
5.3
5.4
5.5
100
90
80
70
60
50
40
30
20
10
0

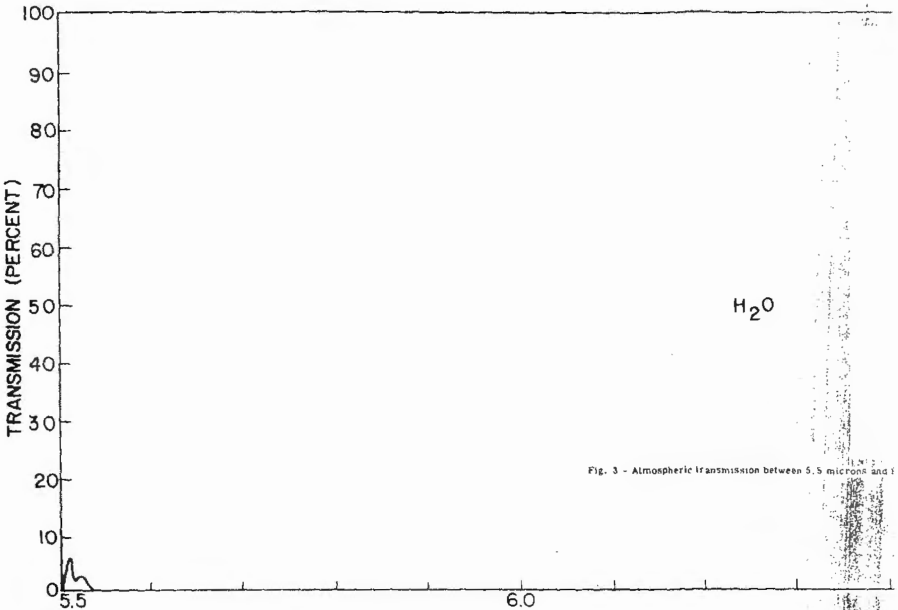


Fig. 3 - Atmospheric transmission between 5.5 microns and

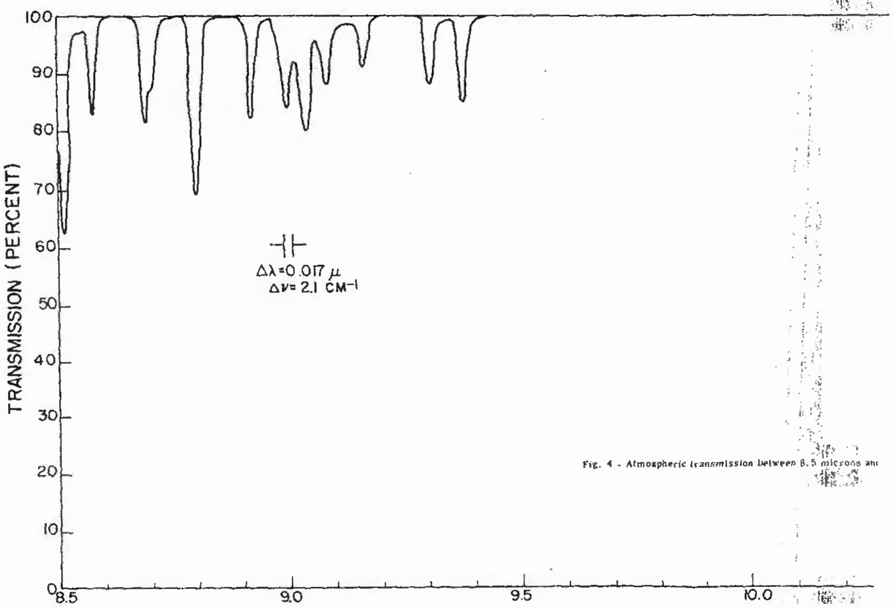
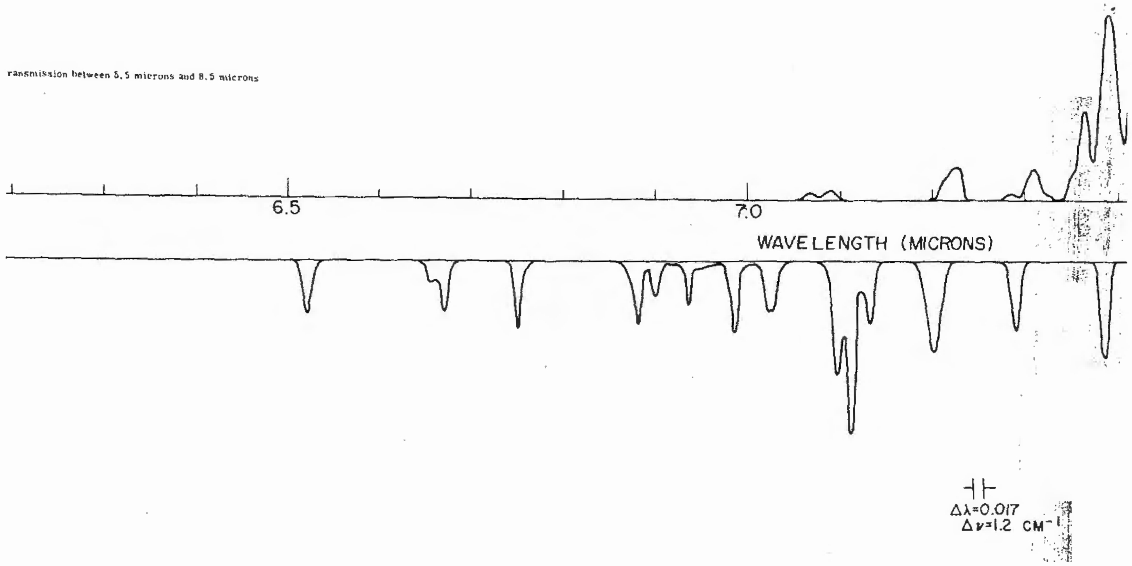


Fig. 4 - Atmospheric transmission between 8.5 microns an

TRANSMISSION OF 1000-FT HORIZONTAL
AIR PATH AT SEA LEVEL
5.7 MM PRECIPITABLE WATER
79° F. TEMP.

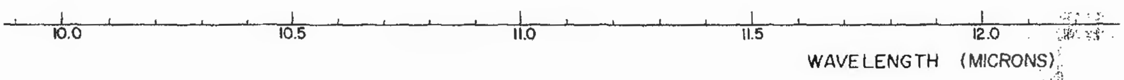
H_2O

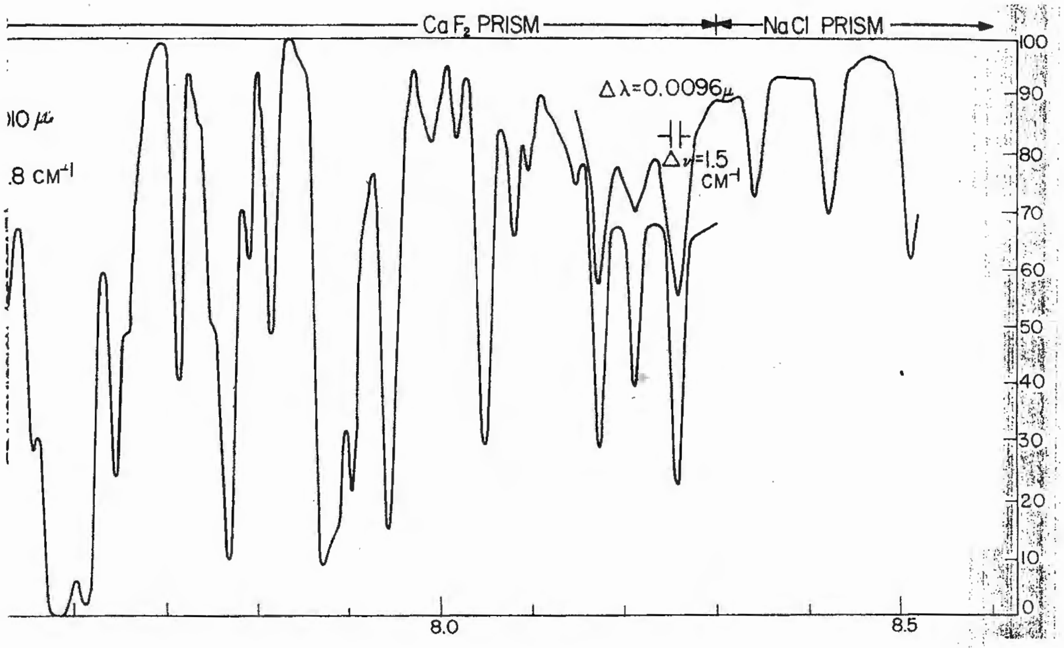
ransmission between 5.5 microns and 8.5 microns



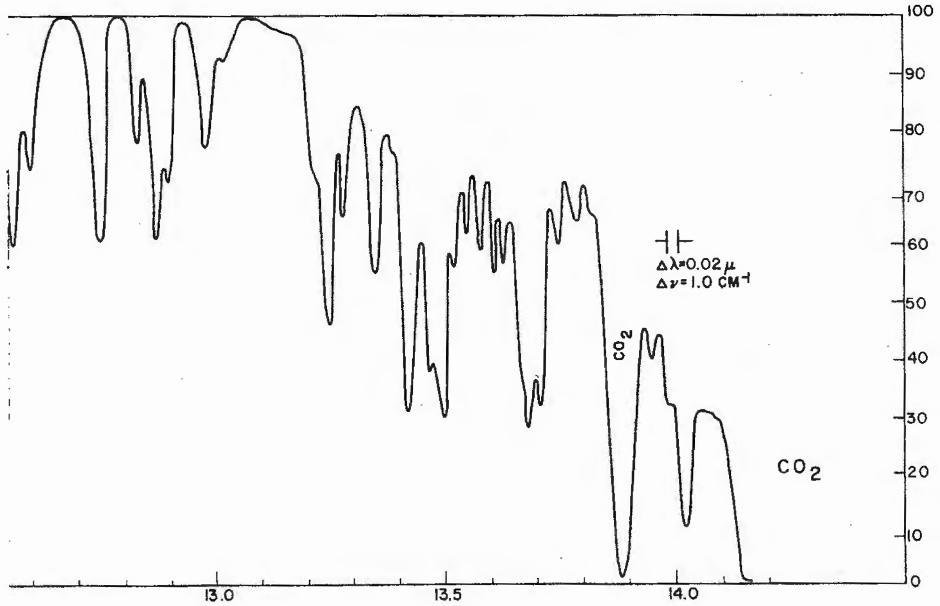
TRANSMISSION OF 1000-FT HORIZONTAL
AIR PATH AT SEA LEVEL
5.7 MM PRECIPITABLE WATER
77° F. TEMP.
Na CL PRISM

ransmission between 8.5 microns and 15 microns





CaF2 PRISM
NaCl PRISM
Δλ=0.0096μ
Δν=1.5 CM⁻¹
)10 μ
.8 CM⁻¹
100
90
80
70
60
50
40
30
20
10
0
8.0
8.5



Δλ=0.02 μ
Δν=1.0 CM⁻¹
CO2
CO2
100
90
80
70
60
50
40
30
20
10
0
13.0
13.5
14.0

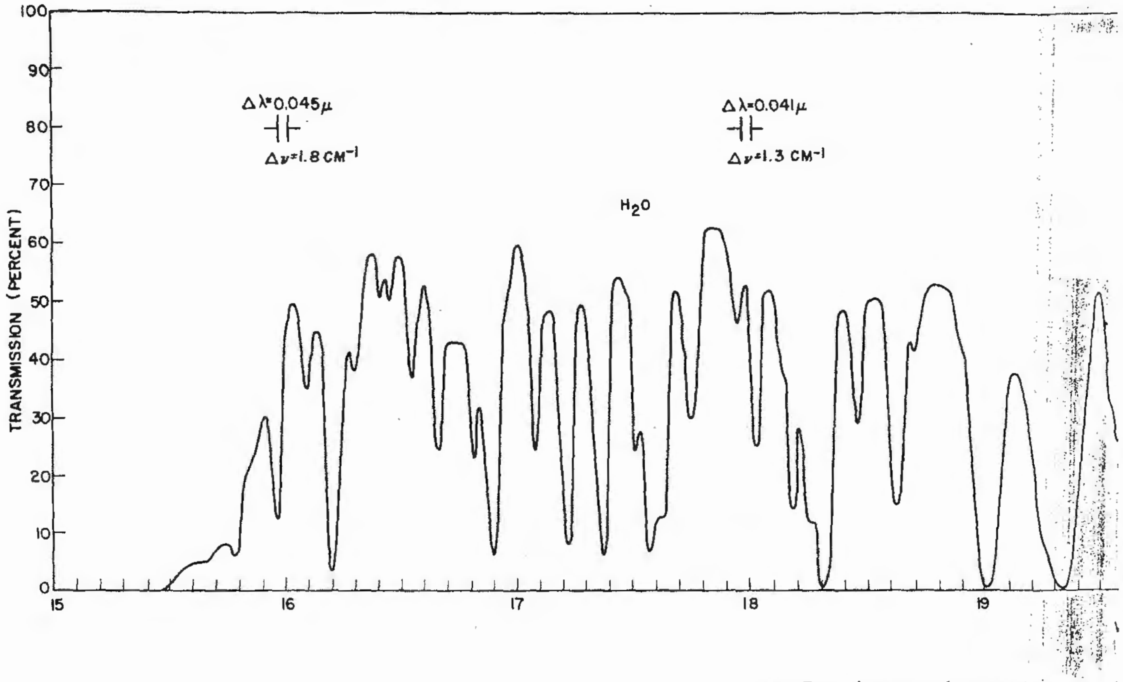


Fig. 5 - Atmospheric transmi

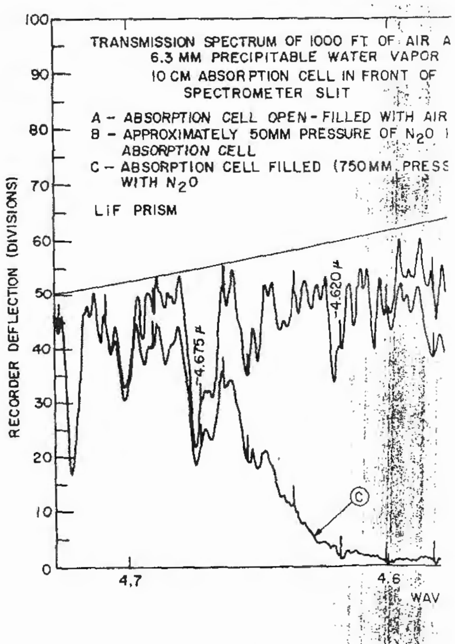


Fig. 6 - Atmospheric t
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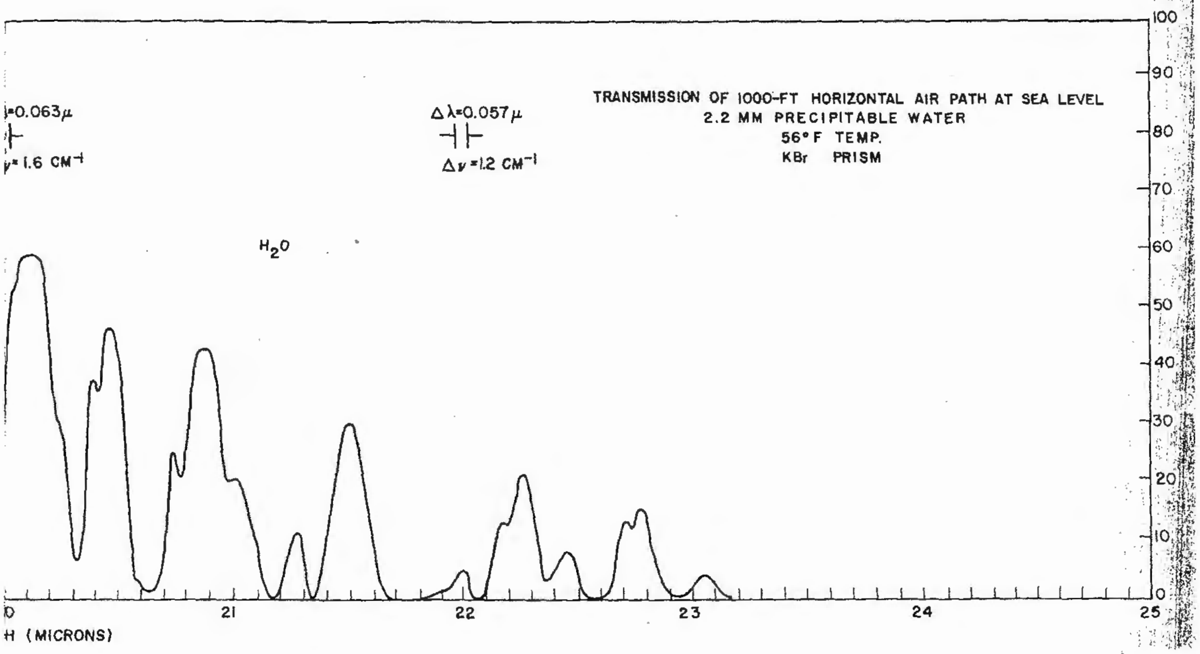
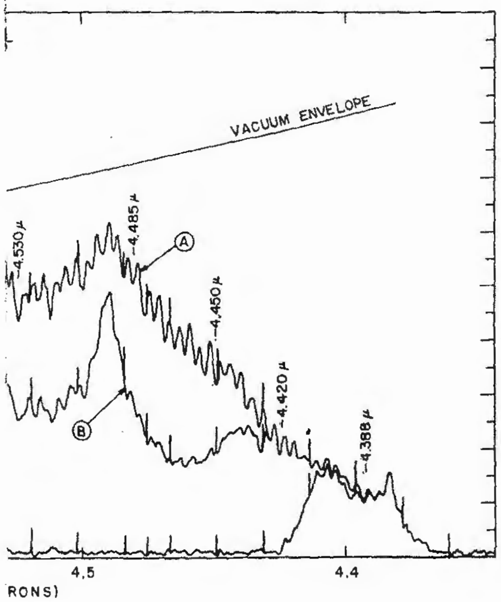


etween 15 microns and 25 microns



ion in the 4.5-micron region
sorption by N_2O

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