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PROGRESS REPORT

ON

Absorption Spectrum of the Lower Atmosphere

from 2.5 to 4.0 MICRONS

BY

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JOHN STRONG

UNDER CONTRACT WITH

OFFICE OF NAVAL RESEARCH
Contract N5ori-166, Task Order V

JOHNS HOPKINS UNIVERSITY
BALTIMORE 18, MARYLAND

September 15, 1950

Absorption Spectrum of the Lower Atmosphere from 2.5μ to 4.0μ

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Abstract

The work reported here is an extension of our studies of solar radiation with high dispersion. The transmission of the ground layer of the atmosphere has been investigated over path lengths of 112 and 876 feet in the region 2.5μ to 4.0μ, with a high dispersion prism-grating spectrograph and cooled lead telluride detector. The short path records show only water vapor, while those from the longer path show clearly both CH_4 and HDO absorption. Absorption due to N_2O, previously reported in the solar spectrum, was not detected here.

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JOHNS HOPKINS UNIVERSITY, BALTIMORE, MD.

PROGRESS REPORT ON ABSORPTION SPECTRUM OF THE LOWER ATMOSPHERE FROM 2.5 TO 4.0 MICRONS

WILLIAM BENESCH; TAIT ELDER; JOHN STRONG 15 SEPT '50
23PP PHOTOS, GRAPHS

USN CONTR. NO. N5ORI-166

METEOROLOGY (30)
RADIATION AND TEMPERATURE (4)

SOLAR RADIATION
ABSORPTION - SPECTROGRAPHIC MEASUREMENT
ATMOSPHERE - RADIATION

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FIGURE 1. The Searchlight in Operation: In order to complete the experimental work in one week, data were taken both night and day.

This report represents a continuation of the general program of study of the atmosphere at the Johns Hopkins University under contract N5ori-166, Task Order V. Previous work by this group includes the recording of the solar spectrum under low dispersion from an airborne monochromator in the spectral region 2μ to 25μ at various altitudes up to 36,000 feet,[1] and studies of the transmission of solar radiation through the entire atmosphere using a high resolution ground level spectrograph in the spectral region 3.3μ to 4.2μ.[2] Mr. Robert J. Meltzer is currently finishing a study of the effect of foreign gas pressure on water vapor in the region 12μ to 23μ, using the ONR-100-foot absorption tube at the Hopkins. The ultimate purpose of the big tube project is to unravel the roles of the various atmospheric components and the effect of pressure on their absorption. In the big tube it is possible to study controlled synthetic atmospheres. The work by Benesch on the transmission through the total depth of the atmosphere, with the sun at various zenith angles as a light source, pointed up the need for observation under high resolution of the transmission of the lowermost layers of the atmosphere. The present report presents the results of this investigation. In addition to providing further data on the infrared visibility in the sea level air layer, it serves as a supplement to the information to be found in the reports previously mentioned.

The desirability of a carbon arc as the infrared source for these observations was made clear by experiments made last year by the Hopkins group.[3] A 60-inch Army surplus searchlight was loaned to us by Mr. B. A. Wacek of the University Motors Company. This arc, located within a few blocks of the Hopkins campus, was being used for advertising purposes. The arc was in acute disrepair, and we were only able to use it because of the cooperation of Dr. Fred W. Paul, Chief of the Radiation

Branch, Engineering Research and Development Laboratories, Ft. Belvoir, Virginia. Dr. Paul had already helped us with his advice on the best way to proceed, and now made available to us the skilled services of Lt. Claude Orr, Corps of Engineers. After a preliminary survey Lt. Orr joined the Johns Hopkins group on July 10 for six days of intensive work getting the searchlight into operation and carrying out the program.

The searchlight was first set up at a distance of 112 feet from the window of the spectrometer room on the fifth floor of Rowland Hall (Fig. 1). Its sensibly parallel beam was pointed at the 10-inch flat mirror which in the solar investigations[2] had been illuminated by the heliostat. This 10-inch flat could be adjusted in angle by push buttons located at the operator station. With the searchlight at the 112-foot station, it was found possible to locate the optic axis of the searchlight reflector along one side of the 10-inch mirror and eliminate all obscuration by the carbon electrodes and their associated mechanism. Later, when the searchlight was moved to a station 876 feet from the window, on-axis alignment was found to produce the most favorable illumination. It should be noted that for the short path the principal value of the large searchlight reflector was the convenient avoidance of the aforementioned obscuration. However, for the long path even the 5-foot mirror limited the signal intensity to a noticeable extent. This was indeed one of the considerations leading to the choice of such a large mirror for this experiment.

A 4-inch spherical mirror converged the light from the 10-inch flat mirror to a focus on the entrance slit of a Gaertner monochromator, which served as predispersing element for the prism-grating spectrograph. The incoming radiation was chopped at 150 cycles/second by a Plexiglass chopper blade placed in front of the entrance slit of the monochromator. The chopper material is relatively transparent to the visible portion of

the arc spectrum which was accordingly not greatly modulated. However, in the infrared where Plexiglass is opaque, the radiation was completely modulated and was thus suitable for a.c. amplification. The rock salt prism in the Gaertner in conjunction with this selective modulation resulted in ignorance of scattered light and higher orders of the 6-inch plane grating of 7200 lines per inch which was used to disperse the radiation further. A liquid-nitrogen-cooled lead telluride cell served as detecting element; the signal output of this cell was fed into a tuned amplifier, after which it was rectified and finally logarithmically attenuated before being recorded on a Leeds and Northrup Speedomax recorder.

Portions of the data obtained are reproduced in Figure 2 through Figure 16. These figures cover the region 2550 cm^{-1} to 4100 cm^{-1}, or roughly from 4.0 to 2.5μ. Figure 16 is a composite of all the preceding ones on the same page to better display the overall picture of transmission in this spectral region. From 2550 cm^{-1} to 3000 cm^{-1} (Figures 2 - 6) the traces from the long path have been chosen for reproduction, since characteristic lines of CH_4 and HDO which lie in this region do not appear on the short path traces. From 3000 cm^{-1} to 4100 cm^{-1} (Figures 7 - 15) only the short path traces are shown, since the high absorption of water vapor lines in this region leads to complete opacity in many portions of the spectrum.

These figures are essentially graphs of the logarithm of the energy incident on the lead telluride cell as a function of wave number. Curves corresponding to 100 o/o, 50 o/o, and 25 o/o transmission have been drawn in where meaningful, so that the transmission at any point in the spectrum may be estimated easily. Wave number reference marks are given on the figures, which are arranged in order of increasing wave number. For continuity between traces, fiducial marks "o" and "v" indicate corresponding portions of adjacent records. The wave length dispersion is

approximately constant for Figures 2 - 15, being 1 inch = 0.014μ, and under each trace its approximate limits in microns are given for convenience. A resolution of the order of a half wave number was attained.

The runs were made under various atmospheric conditions. The humidity was generally high, with approximately 1/2 cm precipitable water for the long path and 1/2 mm precipitable water for the short path. In at least one instance light rain was actually falling, but this did not appear to change the spectra appreciably. The duration of each spectrum was determined by the lifetime of the liquid nitrogen. Each run lasted approximately twenty minutes. Over such a short time the semi-automatically driven arc was quite steady and served very satisfactorily as a radiation source. For any one run, the attenuator setting and slit widths remained constant, although these were subject to progressive adjustment as the wave length region was changed.

The Spectrum of the Long Path

876 Feet

2550 cm^{-1} to 3000 cm^{-1}

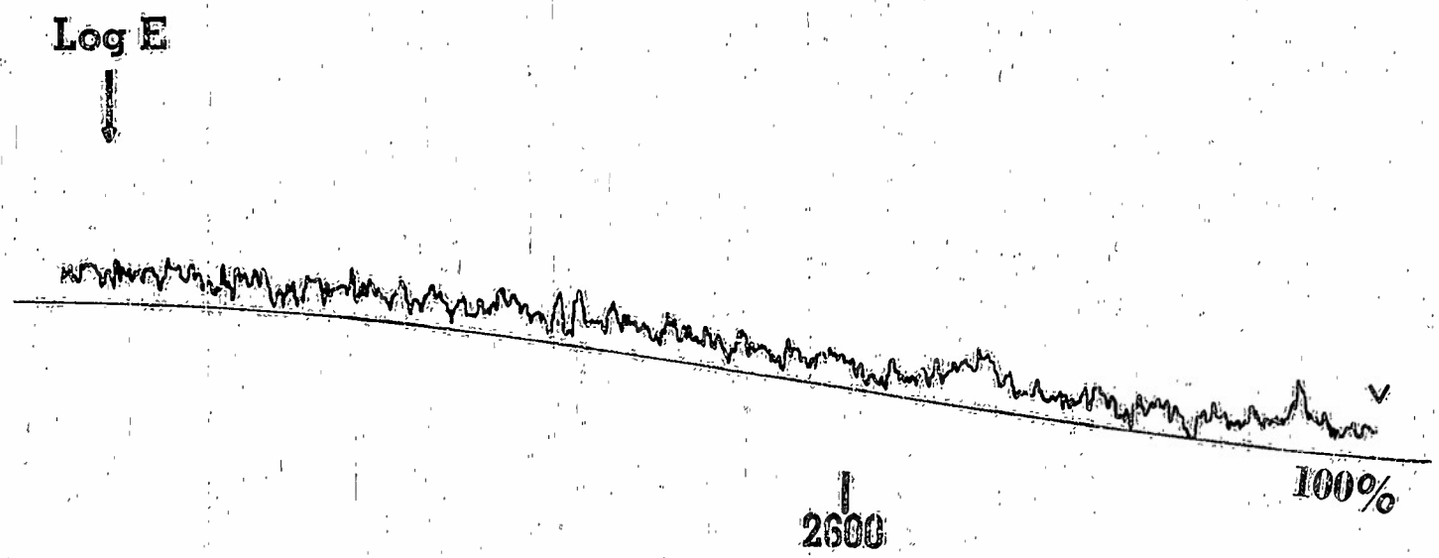

FIGURE 2. The region 3.91 μ to 3.81 μ: At the far left edge of the trace (2560 cm^{-1}) is the region where solar spectra located the relatively strong $2\nu_1$ band of N_2O. No discernable absorption due to this band is to be observed on this or other traces from the searchlight data. However, at this extremity of the spectrum the detecting and dispersing components of our equipment were relatively less efficient than at shorter wave lengths.

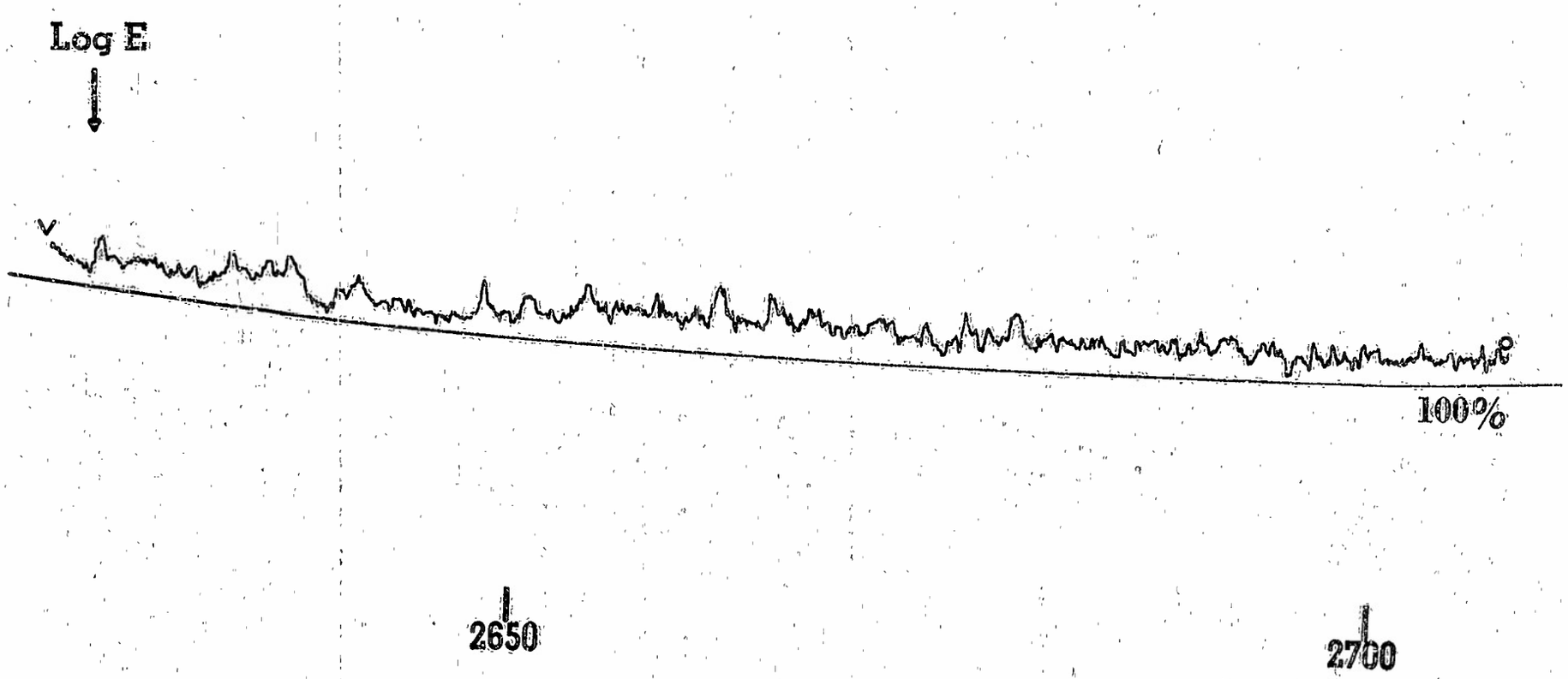

FIGURE 3. The region 3.81 μ to 3.69 μ: Here again is a region of comparatively high transmission. In this space lies the P branch of the HDO fundamental vibration ν_1; only the stronger lines are recognizable due to the small amount of HDO in the path traversed. The Q and R branches, on the following figure, show more conclusively the presence of HDO absorption.

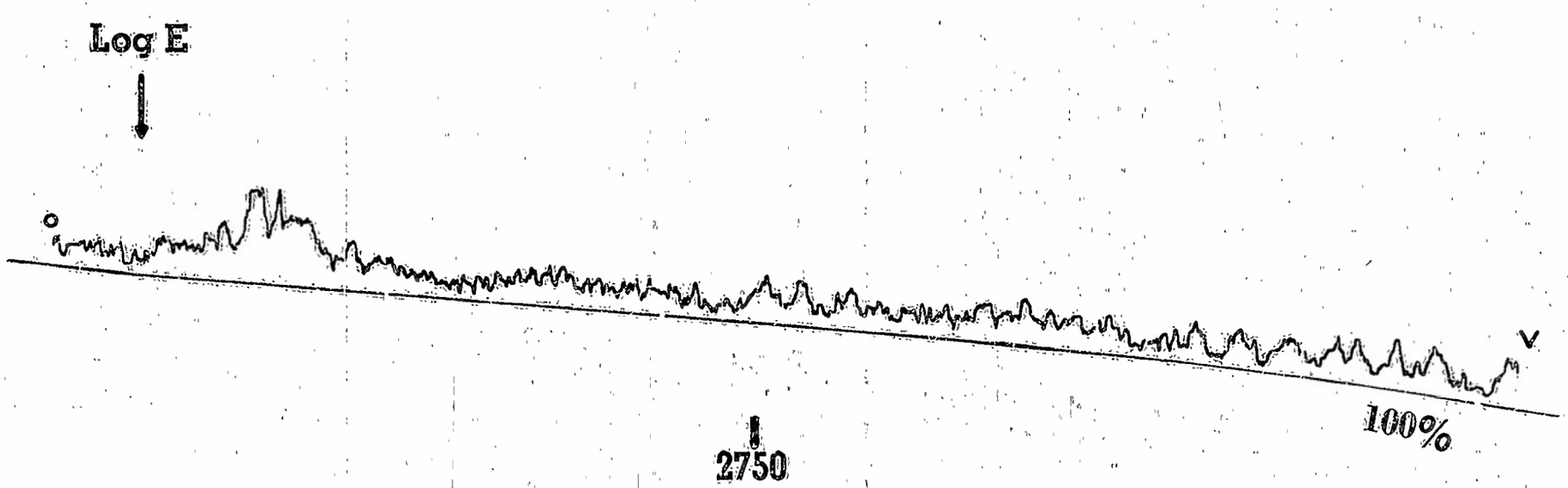

FIGURE 4. The region 3.69 μ to 3.57 μ: The absorption due to the Q branch of HDO stands out clearly on the left at 2719 cm^{-1}. The first group of three lines of the R branch just above 2750 cm^{-1} is also observable, as is the more complicated structure at higher wave numbers.

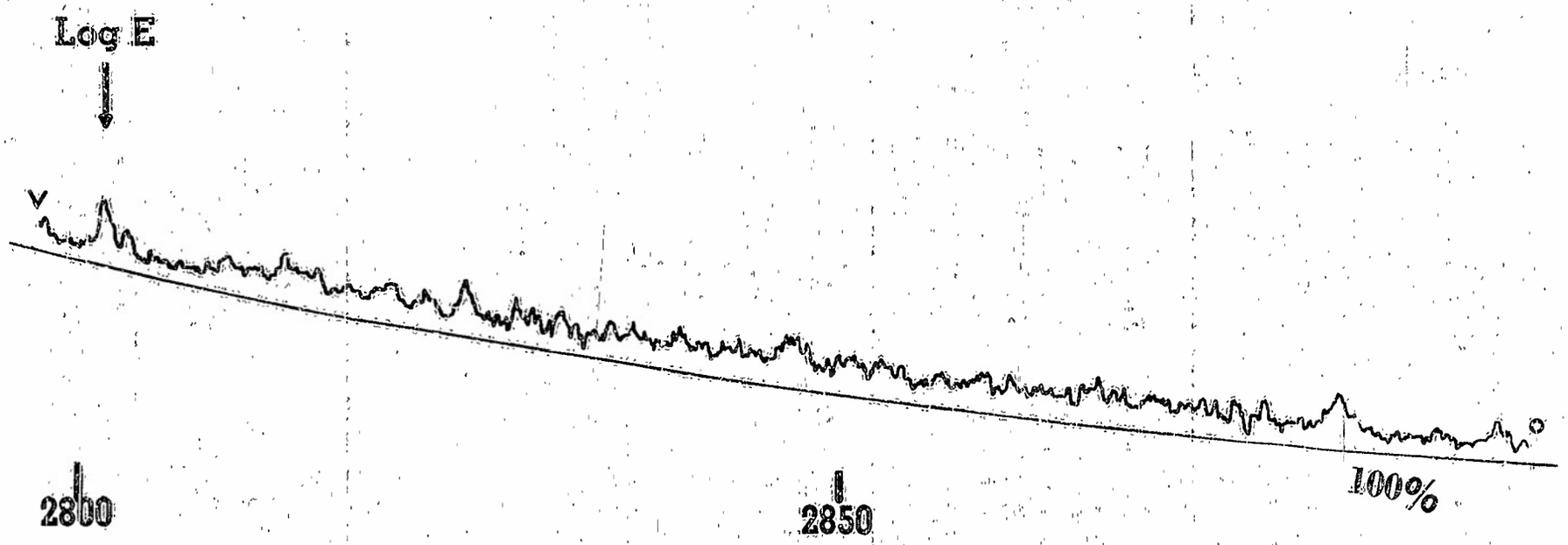

FIGURE 5. The region 3.57 μ to 3.45 μ: This region contains weak absorption due to water vapor and methane. The H_2O line at 2879.8 cm^{-1} and the HDO line at about 2800 cm^{-1} are easily identified, although little detail is manifested.

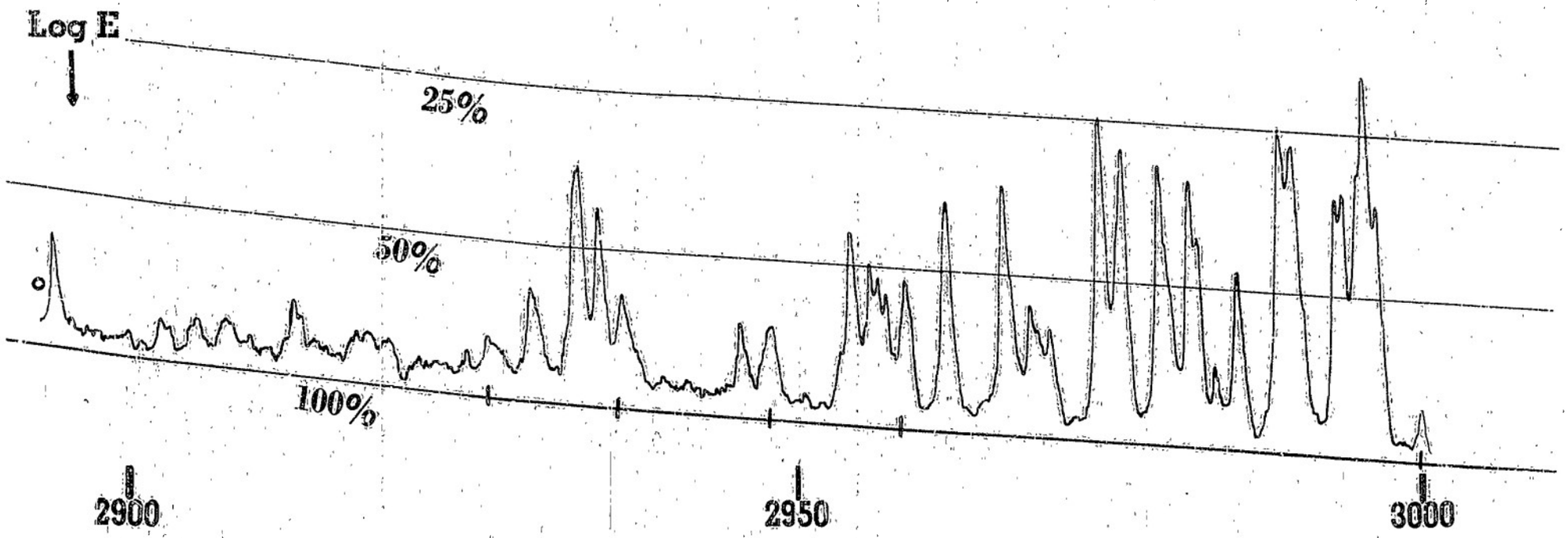

FIGURE 6. The region 3.45 μ to 3.33 μ: This is perhaps the most interesting trace obtained. Small vertical marks along the 100 o/o transmission curve indicate those absorption lines of the P branch of methane (CH_4) which are not masked by known water lines. Since in solar spectra the ratio of the intensities of methane lines to water lines is greater than in the present traces, it may be inferred that the center of gravity of the methane gas in the atmosphere occurs at a greater altitude than that of the water vapor.

A line present in the solar spectra at 2943 cm^{-1} is conspicuously absent in all the searchlight traces. The identity of this line has been the subject of some controversy.

The Spectrum of the Short Path

112 Feet

2900 cm^{-1} to 4100 cm^{-1}

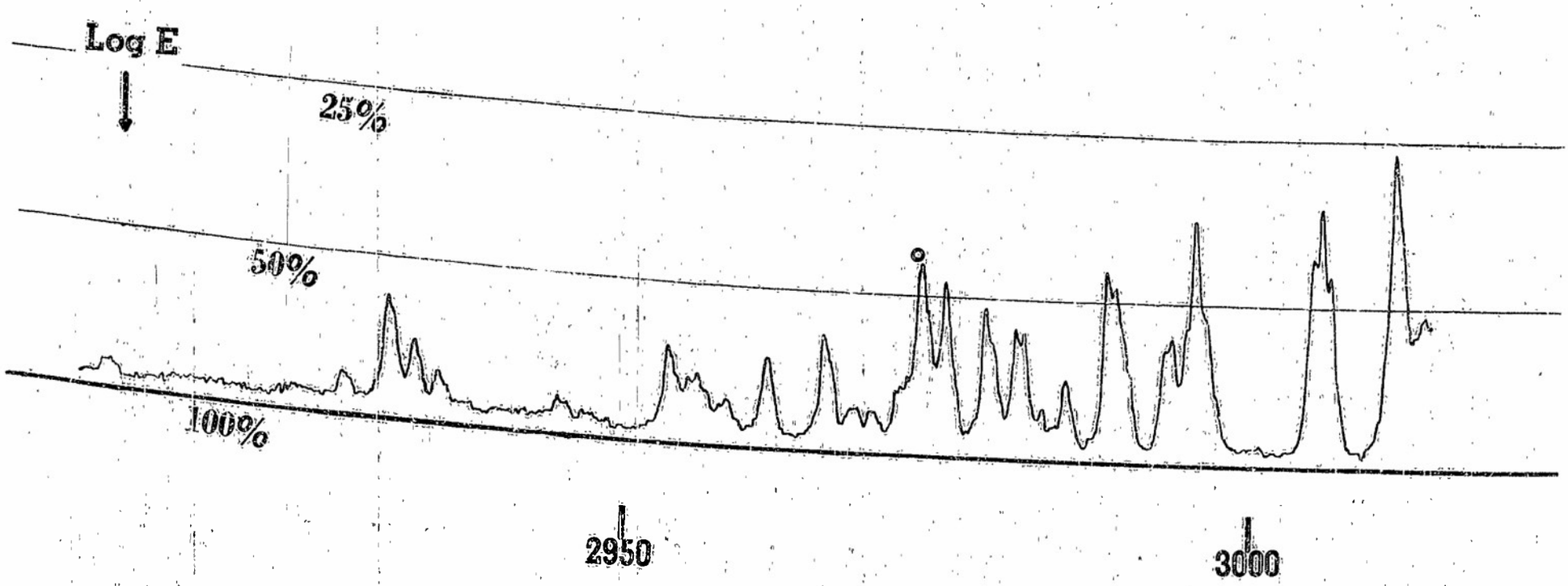

FIGURE 7. The region 3.44 μ to 3.32 μ: This figure almost completely overlaps the spectral region of the preceeding figure, and thus a qualitative comparison of the absorption due to the long and short paths is possible. It is to be noted that the heights of the absorption lines do not increase with length of path in a simple manner. This is due to the rather complicated curve of growth for absorption lines observed under finite resolving power. The variations in absolute humidity during the course of the experiment preclude precise quantitative comparison.

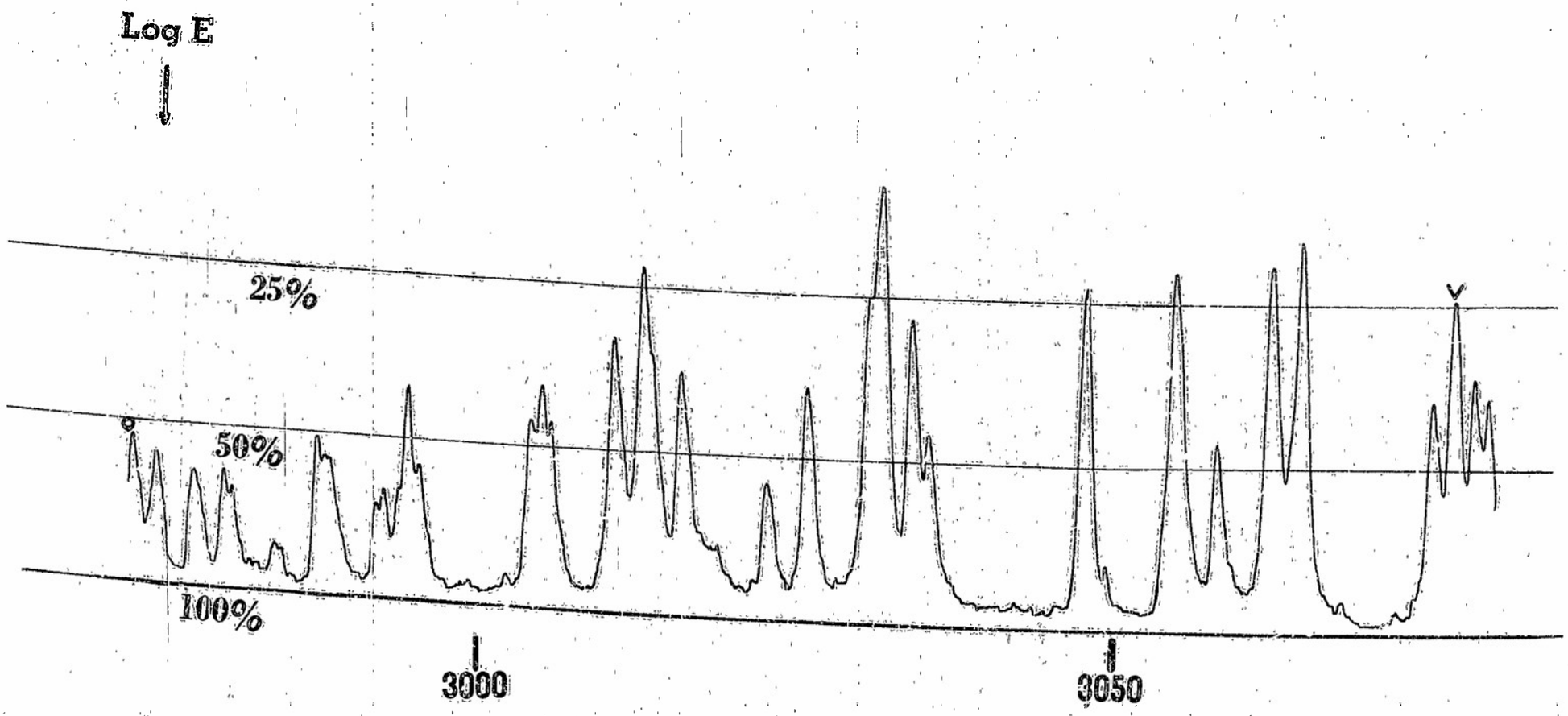

FIGURE 8. The region 3.36 μ to 3.24 μ: The P branch of the overtone band $2\nu_2$ of water vapor is responsible for virtually all the absorption on this trace. The group of three lines near 3015 cm^{-1} is not observed in solar spectra because of the masking effect of the Q branch of methane, here quite weak.

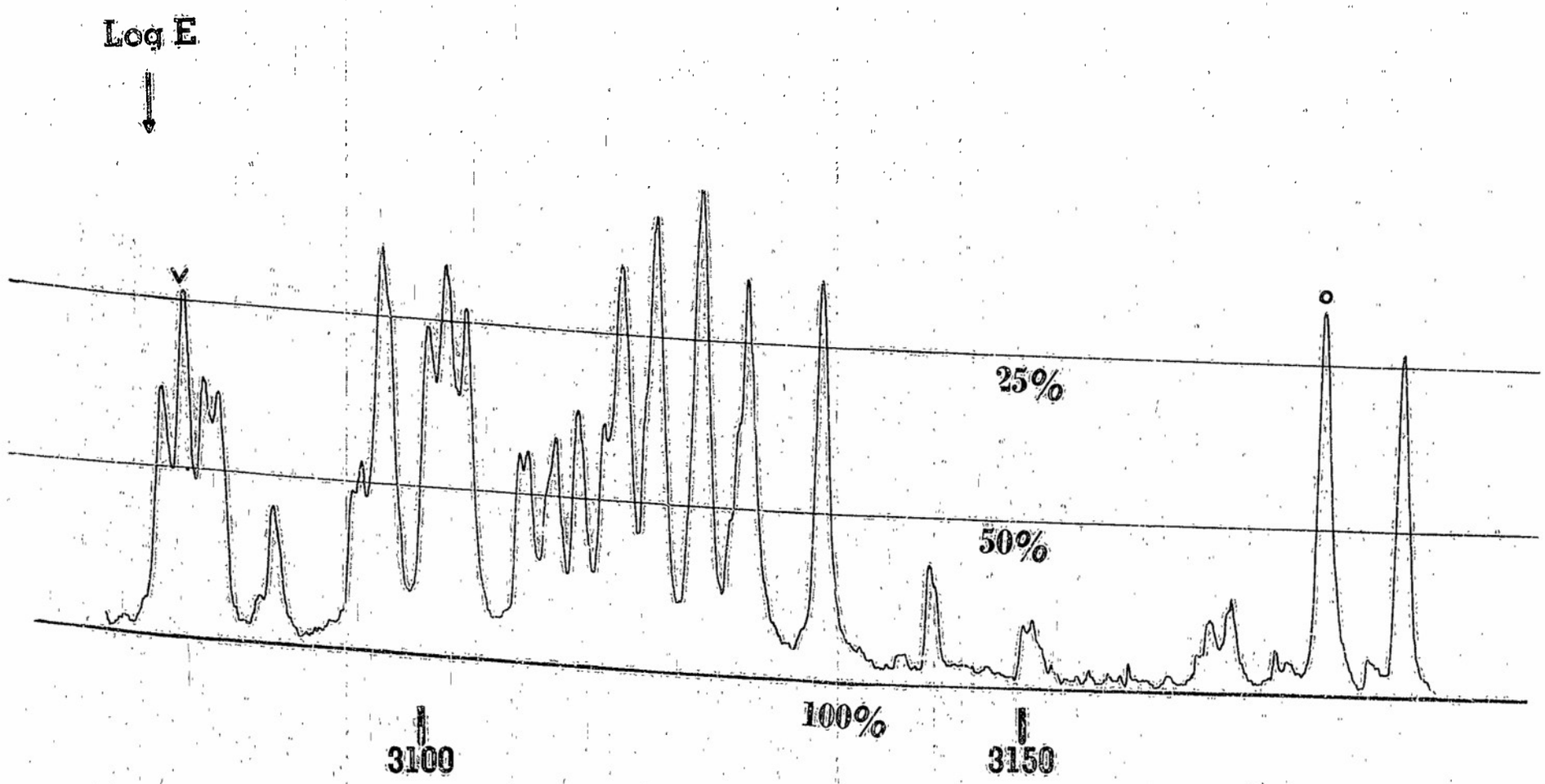

FIGURE 9. The region 3.26 μ to 3.14 μ: The 40 wave-number-wide window at 3160 cm^{-1} is the only such large clear space on our traces above 2950 cm^{-1}. This window is an obvious feature of the long path traces as well, although of course the weak water lines inside the window absorb more strongly there.

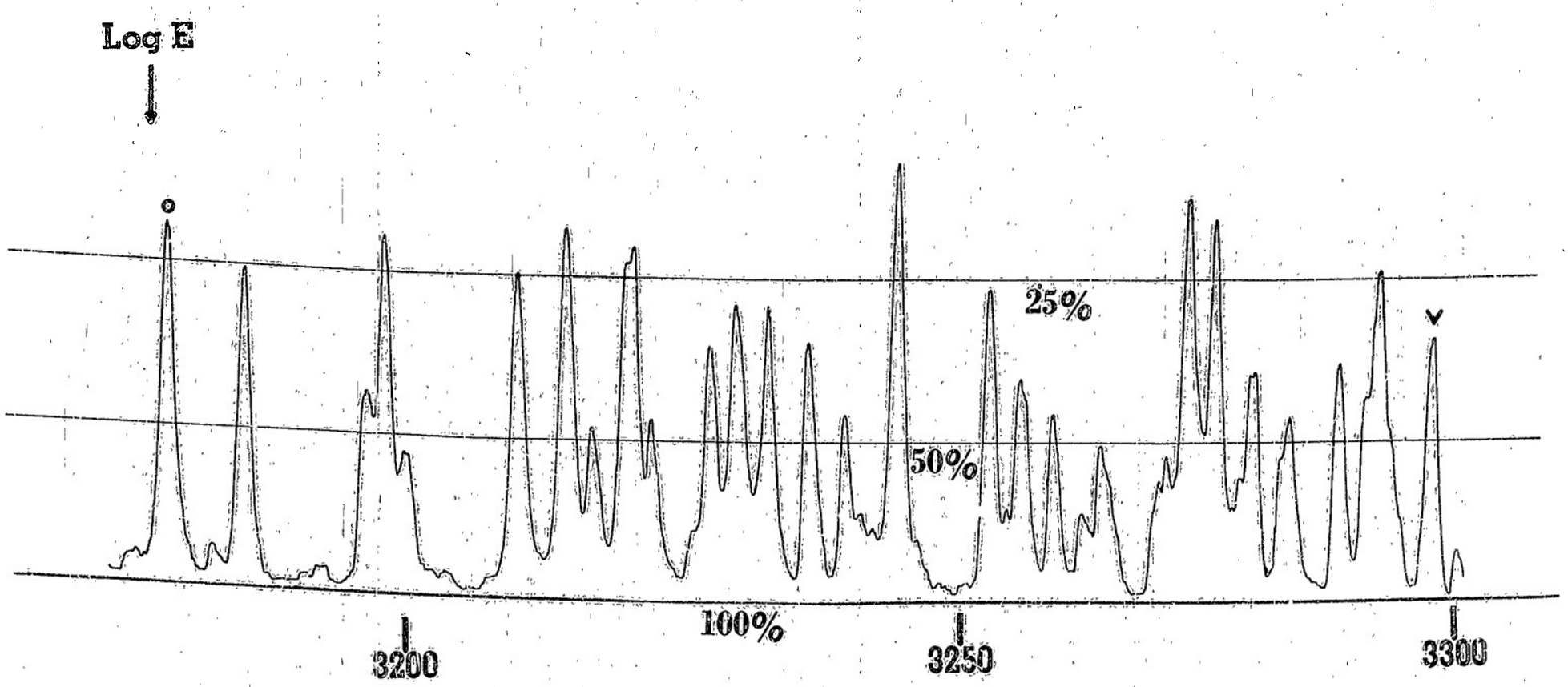

FIGURE 10. The region 3.15 μ to 3.03 μ: In this region the P branch lines of water vapor absorption have largely given way to those of the Q and R branches, R branch lines being roughly twice as frequent as Q branch lines. On all of these curves, for transmissions less than 25 o/o the logarithmic scale rapidly becomes compressed. For example, the strong line at about 3245 cm^{-1} is closer to saturation than might be inferred from a linear extrapolation of the per cent transmission lines drawn on the graph.

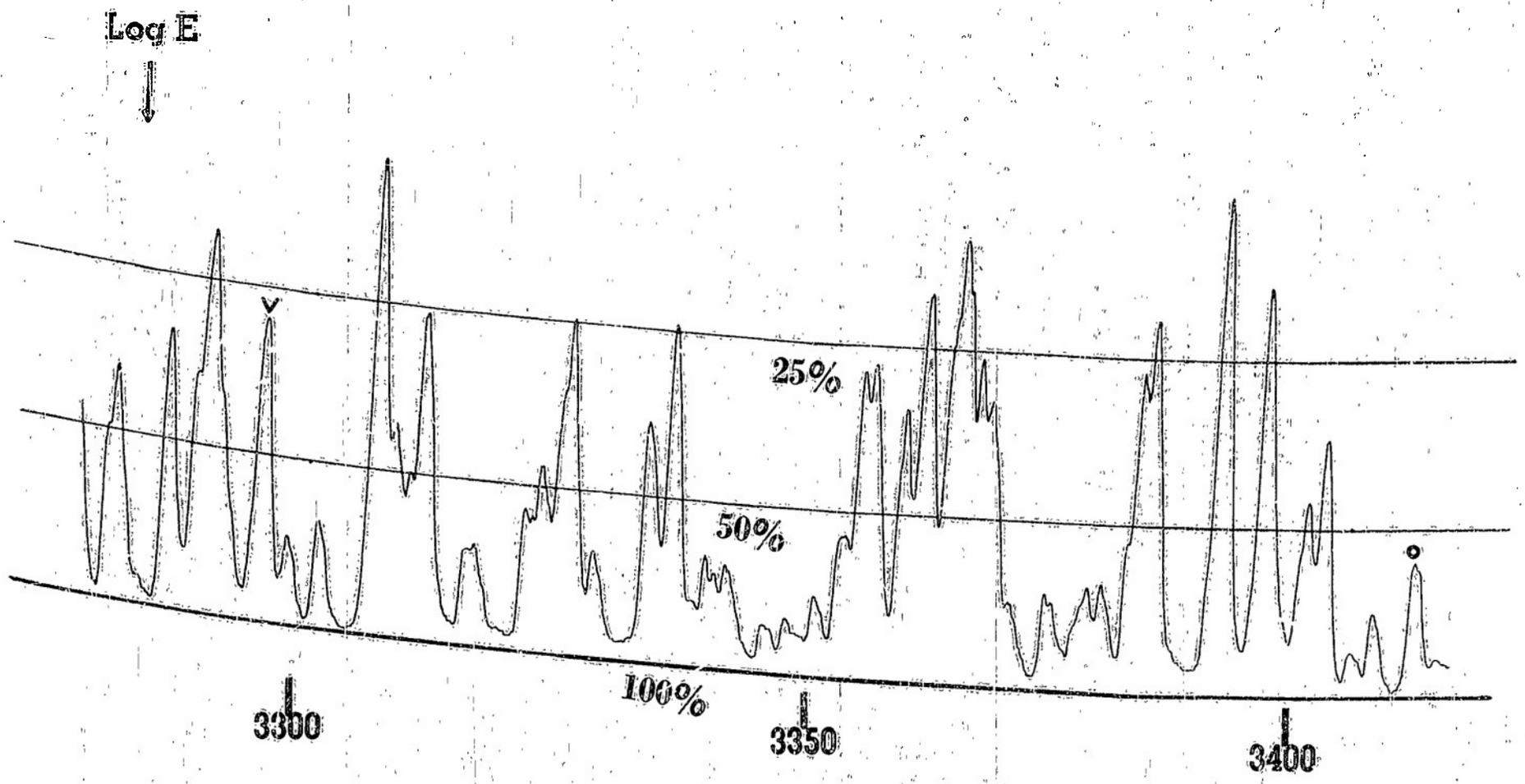

FIGURE 11. The region 3.04 μ to 2.92 μ: This trace and the succeeding ones illustrate the difficulty of identifying foreign substances in the air by their spectra in this region, because of the combination of many dense water lines with increasing line widths. Indeed, the accurate analysis of water vapor itself, even in areas where complete opacity is not present, becomes difficult, as for example in the clump of lines centered at 3365 cm^{-1}.

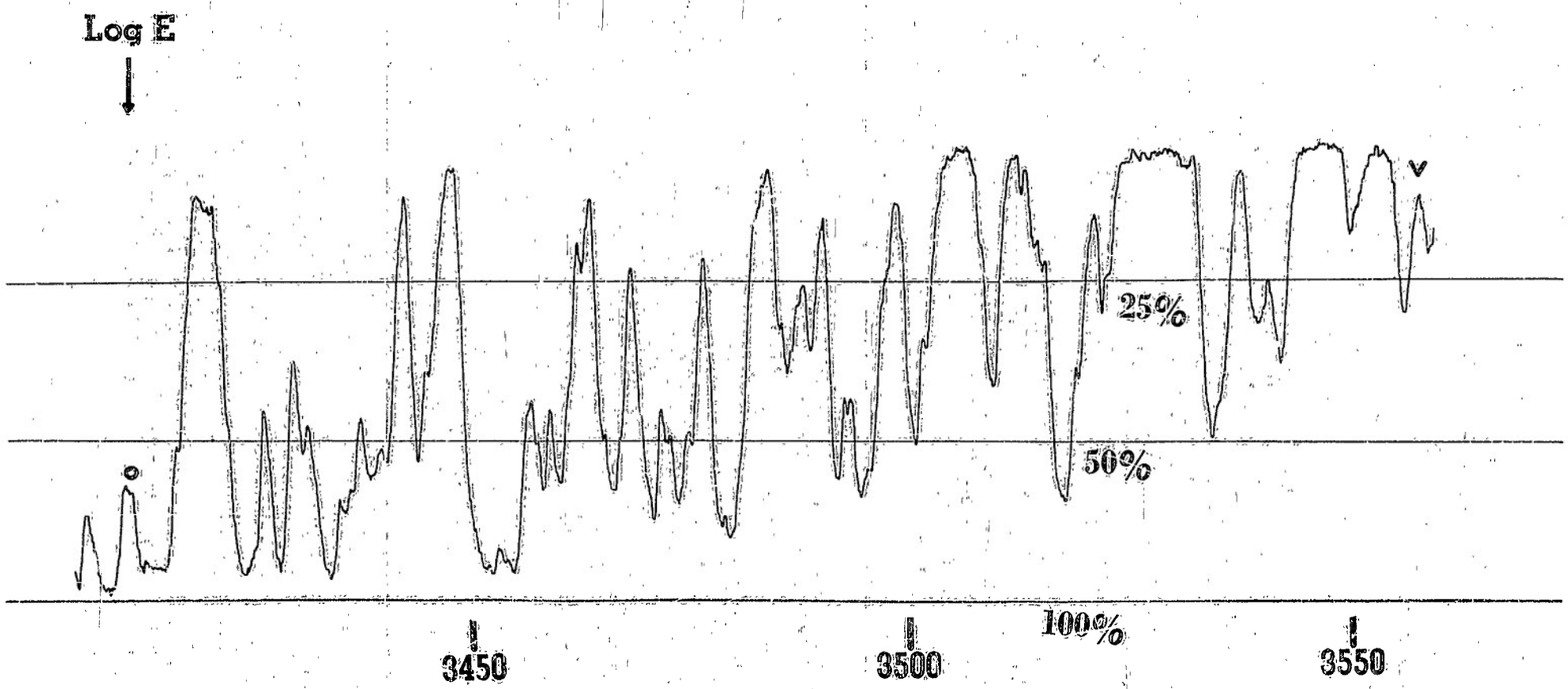

FIGURE 12. The region 2.93 μ to 2.81 μ: On this trace, nearly two hundred wave numbers from the center of the 2.7 μ band of water there are already intervals of complete opacity up to 10 wave numbers in extent. For example, due to the effect of their mutual masking, over ten known water lines in the black region near 3530 cm^{-1} are inseparable.

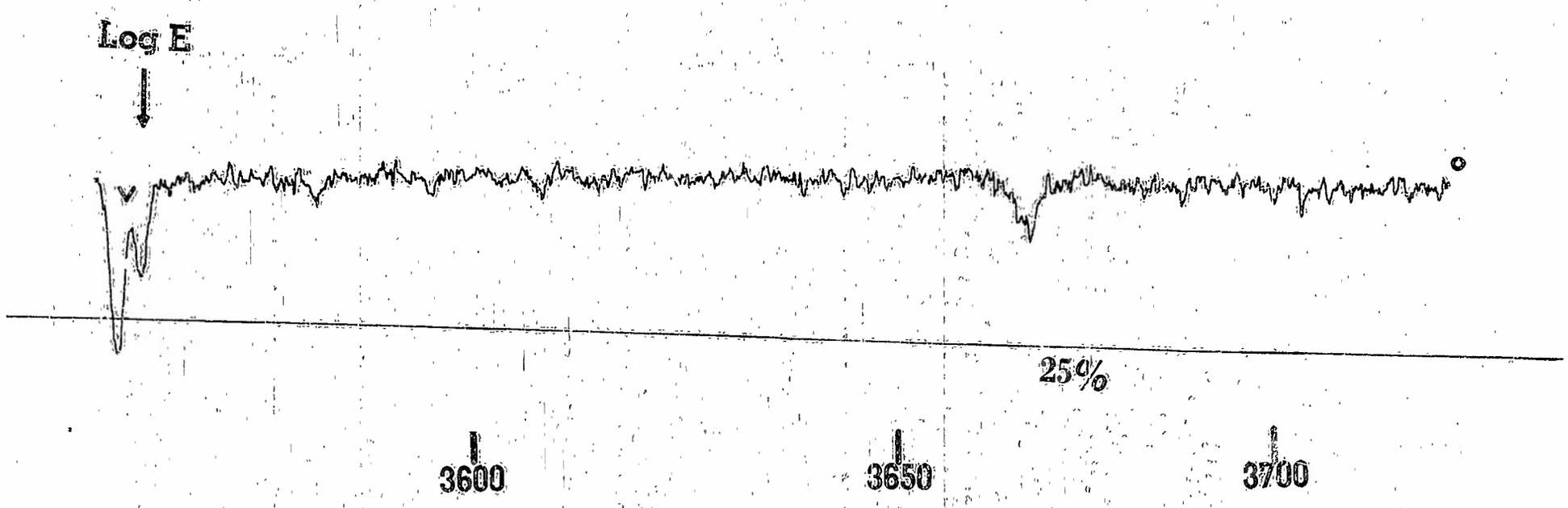

FIGURE 13. The region 2.80 μ to 2.68 μ: Here in the body of the 2.7 μ absorption band there is only the slight transmission at about 3662 cm^{-1}, representing a decrease in absorption between the 3668.82 cm^{-1} and 3656.13 cm^{-1} lines.

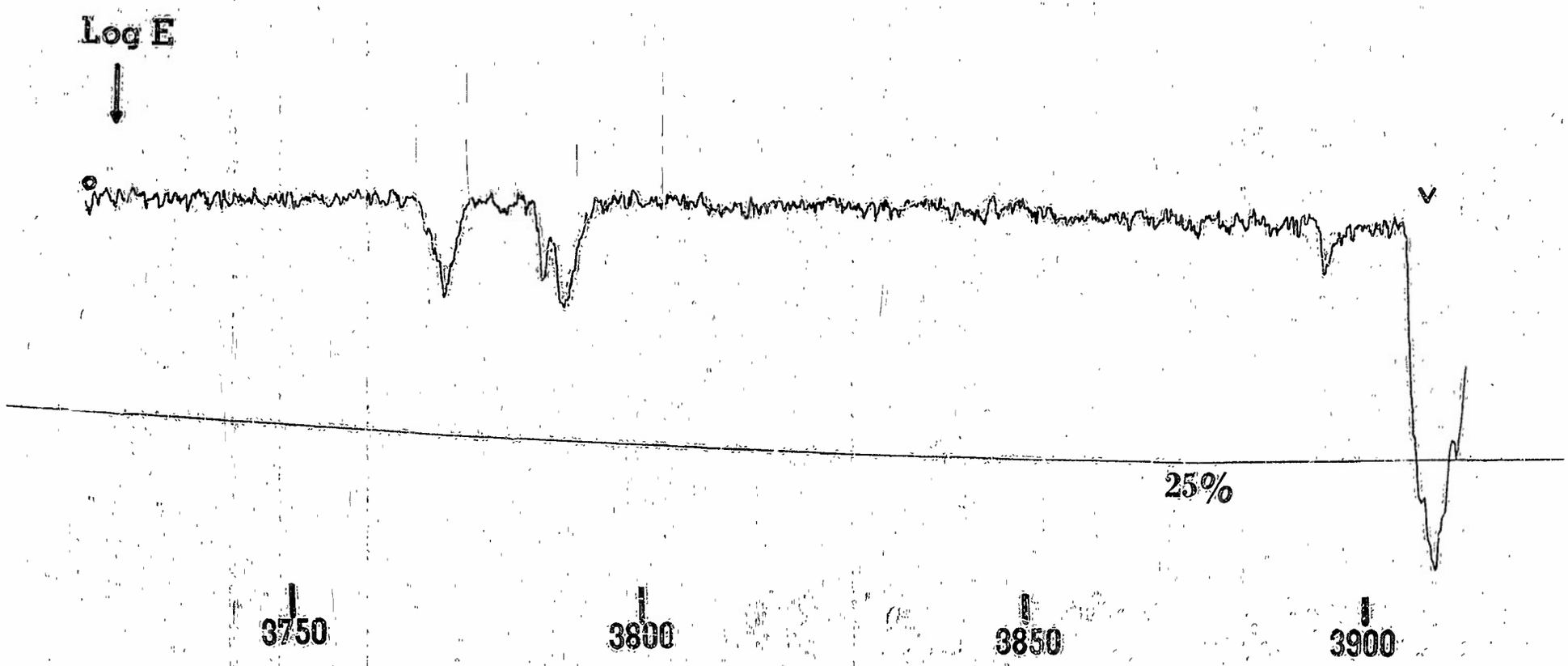

FIGURE 14. The region 2.67 μ to 2.55 μ: Except for the transmissions shown by the curve at about 3770 and 3790 cm-1, this region is also opaque. The 3909 cm-1 region presages the return to individual lines on the next trace.

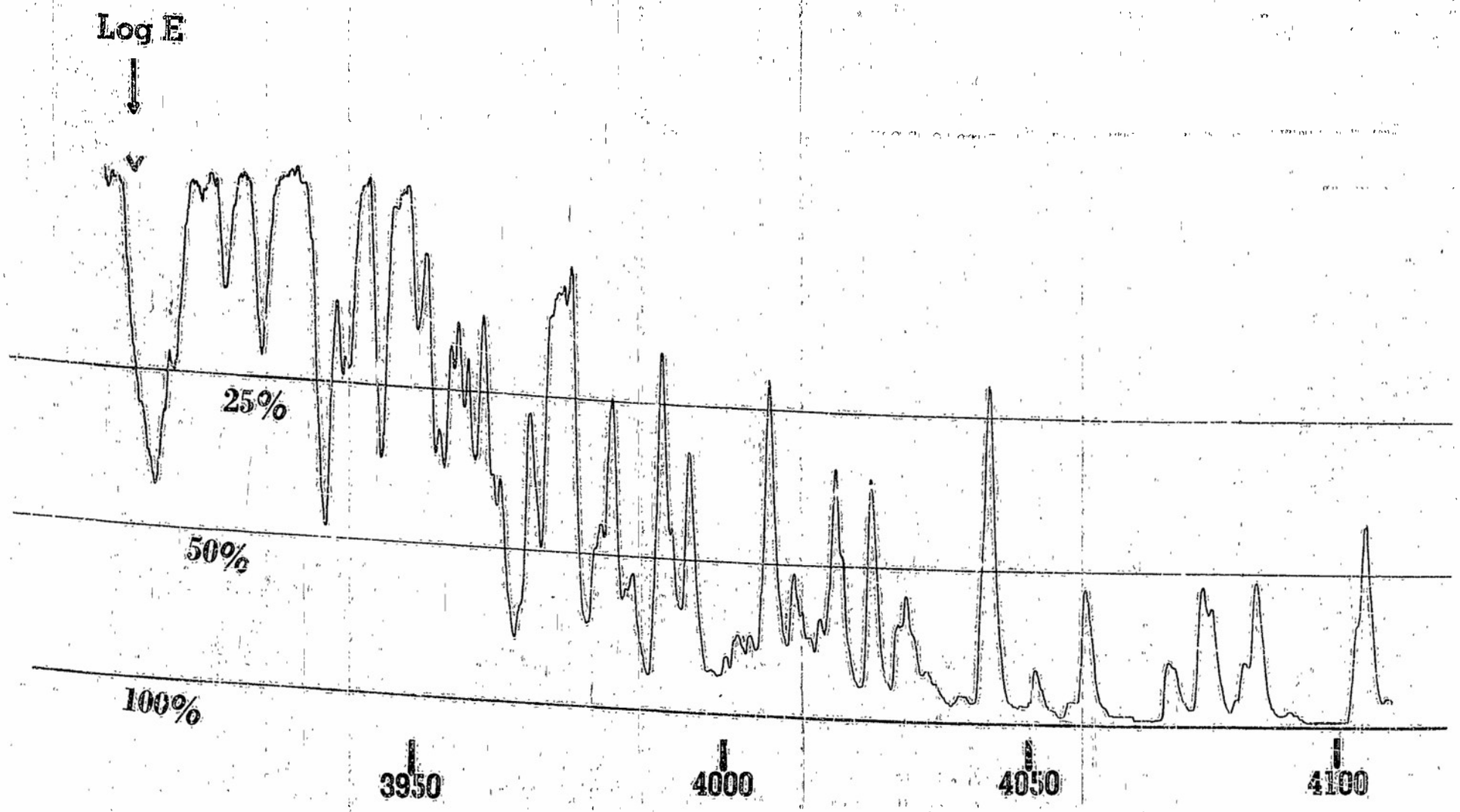

FIGURE 15. The region 2.55 μ to 2.43 μ: At this short wave length extremity of our observations a host of water vapor absorption lines are again found.

No attempt was made to scan to the 1.8 μ water band, since before that region is reached the Plexiglass chopper becomes ineffective.

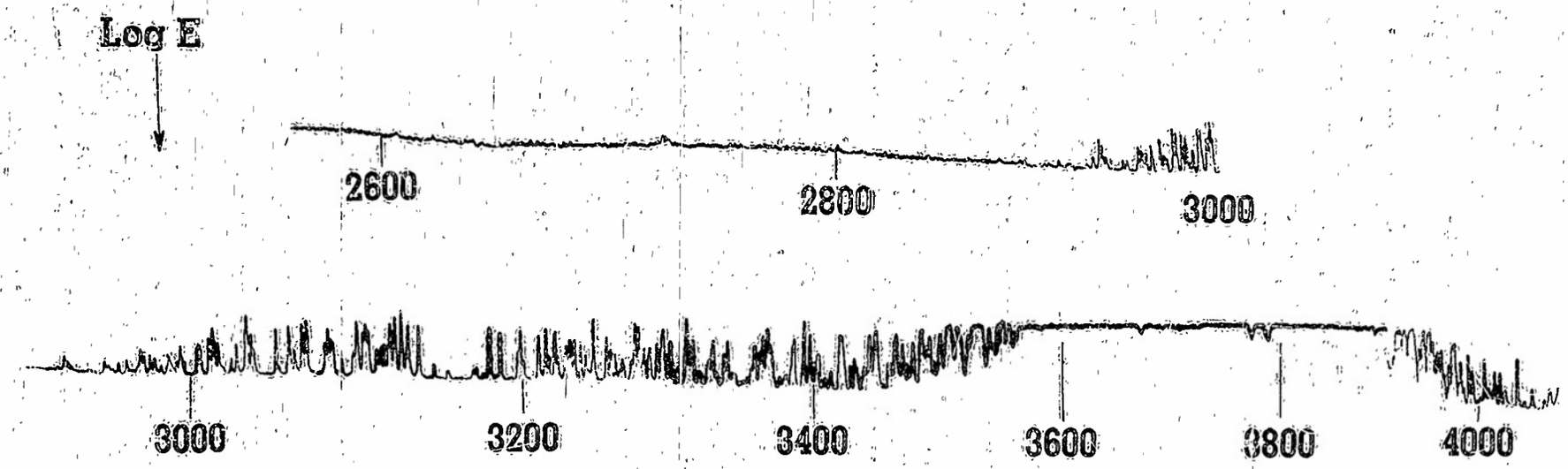

FIGURE 16. The region 4.0 μ to 2.5 μ: This trace reviews the entire spectral region observed. The HDO Q-branch absorption is evident at 2719 cm^{-1}; the incidence of appreciable water vapor line absorption shows at about 2900 cm^{-1}; and, the window at 3160 cm^{-1} and the 2.7 μ absorption band at 3700 cm^{-1} are depicted with a somewhat better perspective than on the preceeding traces. The upper curve here is a composite of all the long path traces, the lower curve of the short path traces. It is to be pointed out that nearly all of the absorption observed in this infrared spectrum of the lower atmosphere is due to ordinary water vapor.

In conclusion it is a pleasure to acknowledge the valuable technical assistance and enthusiastic cooperation of Lt. Orr.

We also are pleased to acknowledge the help of Dr. William S. Benedict, of the National Bureau of Standards, who has continued his interest in our work and advised on the interpretation of the obtained spectra, as he has done on former occasions.

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1. Progress Report dated January 10, 1949, ONR Contract N5ori-166, Task Order V, on High Altitude Infrared Transmission of the Atmosphere.

2. Progress Report dated August 1, 1950, ONR Contract N5ori-166, Task Order V, on The Solar Spectrum from 3.3 to 4.2 Microns.

3. J.O.S.A. 40, 455, (1950), C. S. Rupert and J. Strong.

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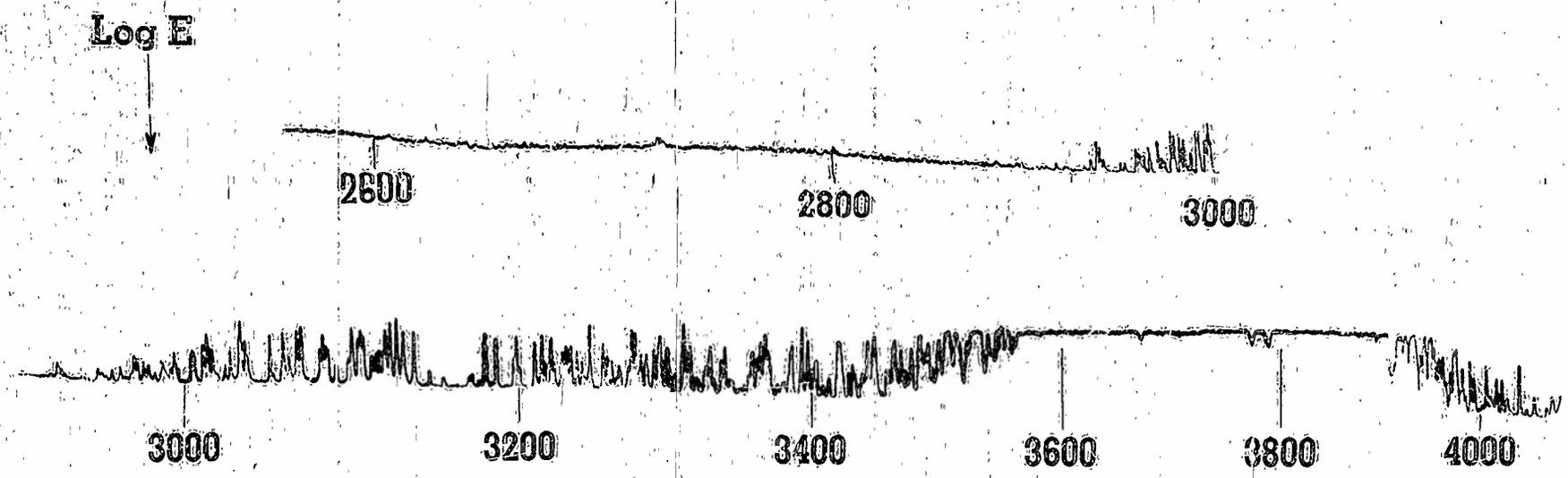

FIGURE 16. The region 4.0 μ to 2.5 μ: This trace reviews the entire spectral region observed. The HDO Q-branch absorption is evident at 2719 cm^{-1}; the incidence of appreciable water vapor line absorption shows at about 2900 cm^{-1}; and, the window at 3160 cm^{-1} and the 2.7 μ absorption band at 3700 cm^{-1} are depicted with a somewhat better perspective than on the preceeding traces. The upper curve here is a composite of all the long path traces, the lower curve of the short path traces. It is to be pointed out that nearly all of the absorption observed in this infrared spectrum of the lower atmosphere is due to ordinary water vapor.