N69-36380
NASA CR-105672

# INFRARED SPECTRAL STUDIES OF PEROXYACETYL NITRATE (PAN)

by
Inge Fild
D. J. Lovell

## FINAL REPORT

Period Covered: 1 Jan. - 31 Dec. 1969
Principal Investigator: John Strong

*Research sponsored by*
Chemical Physics Branch
Electronics Research Center
National Aeronautics and Space Administration

DEPARTMENT OF PHYSICS AND ASTRONOMY
ASTRONOMY RESEARCH FACILITY
UNIVERSITY OF MASSACHUSETTS, AMHERST
and
THE FOUR COLLEGE OBSERVATORIES

Grant NGR 22-010-042

Contribution # 50/244

# *INFRARED SPECTRAL STUDIES OF PEROXYACETYL NITRATE (PAN)*

---

Inge Fild
D. J. Lovell

Research sponsored by

Chemical Physics Branch
Electronics Research Center
National Aeronautics and Space Administration

FINAL REPORT

NGR 22-010-042

Period Covered: 1 January - 31 December 1969

Principal Investigator: John Strong

Department of Physics and Astronomy
University of Massachusetts
Amherst, Mass. 01002

# ABSTRACT

Through a photochemical reaction of nitrogen dioxide and 2-trans-butene, peroxyacetyl nitrate (PAN) is formed, which plays an important role in polluted air. The decomposition of this has been studied under two conditions: continued irradiation and in the absence of further irradiation. It was found that the rate of decomposition differed markedly in these two conditions. Different reaction mechanisms are postulated to account for this difference.

# INFRARED SPECTRAL STUDIES OF PEROXYACETYL NITRATE (PAN)

by

Inge Fild and D.J. Lovell

## Introduction

Air pollution has become a serious problem today and one of the first tasks of those charged with investigations in this area is to understand the nature of pollutants and their reactions. Air pollutants such as $SO_2$, nitrogen oxides, and organic compounds are directly released into the air by several sources, principally by industry and automobile traffic. Most of the important oxidants in polluted air, however, are formed subsequently by chemical reactions which occur there among the primary pollutants. Photochemical reactions are particularily important in this category.

As a result of many investigations, it is now well established that a photochemical reaction of $NO_2$ and organic compounds, whereby solar energy supplies the necessary irradiation, plays an important rolé in polluted air. Products formed in such reactions are eye irritating and damaging to plant life. In the laboratory, it has been well demonstrated by infrared spectral analysis that peroxyacetyl nitrate (PAN) is one of the more significant pollutants formed in this type of reaction (1, 2, 3).

The present study was undertaken to extend the spectral range of previous studies of PAN as well as to determine the products of decomposition produced by continued irradiation and in the absence of further irradiation.

## Experimental Procedure

PAN at concentrations in the parts-per-million range was studied in a cell of 30 m length. Pfund mirrors, a meter in diameter, one at each end of the cell permit radiation from a globar to traverse the cell three times, as shown schematically in Fig. 1. Relay optics were used to image the far Pfund mirror onto the slits of a Perkin-Elmer Model 210B monochromator. The spectrometer was flushed with dry air. The signal was synchronously detected and amplified with a Brower Model 131 lock-in amplifier (4).

The PAN was formed by irradiating 25 ppm of $NO_2$ and 50 ppm of 2-trans-butene in dry air for 11 hours with black fluorescent lamps. Because of its relatively rapid reaction rate, 2-trans-butene was used as the organic compound for the reaction. The 2-trans-butene (research grade), and $NO_2$ (of 95.5% purity) were obtained from J.T. Baker; and commercial dry air was the gas used in the experiment.

Before every experiment, the cell was evacuated to a pressure of approximately 5 microns Hg and held for several hours to permit degassing of unwanted compounds from the walls. The $NO_2$ and 2-butene of known pressures in calibrated volumes were then expanded into the cell. Following this, dry air was added to produce an atmosphere total pressure in the cell.

The spectral radiant emmission of the 24 4-ft. long Westinghouse BLB 40 watt Black Light Fluorescent lamps in the cell is shown in Fig. 2. The data were supplied by the manufacturer.

The spectral region from 2.5μ (4000 $cm^{-1}$ ) to 40μ (250 $cm^{-1}$) was scanned both before and after irradiation by these lamps. The decomposition of the reaction products, including PAN, was observed by periodically recording the absorption in the vicinity of 8.6 and 12.6μ. These are among the stronger absorption bands of PAN (2).

The decomposition of PAN was studied under two different conditions: first, under continued irradiation; second, without further irradiation. When the decomposition of PAN was completed, the entire spectral region from 2.5 to 40μ was monitored again.

## Results of Photooxidation

The identified reaction products of 2-trans-butene and $NO_2$ photooxidation are summarized in Table 1.

TABLE 1

Reaction Products of 2-Trans-Butene
And Nitrogen Dioxide Photooxidation

Peroxyacetyl Nitrate

Acetaldehyde

Methyl Nitrate

Methane

2-Butene Ozonide

Carbon Dioxide

Carbon Monoxide

Water

Ozone was not detected, neither during the irradiation nor after it was completed. Two absorption bands (one at 8.9μ and the other at 11.2μ) have not been completely identified. The band at 11.2μ has been consistently observed. In addition, the absorption at 8.9μ due to acetaldehyde seems to be in excess of that expected by a measurement at 3.7μ. Both the bands at 8.9 and at 11.2μ can be attributed to 2-butene-ozonide as ozonides are expected to absorb at 11.2 - 12.2μ (C-O-O-C stretching) and at 8.3 - 9.5μ (C-O-C stretching). Absorption bands at 8.9 and 11.2μ were observed by other investigators too (5).

In the wavelength region from 15 to 40μ, two new absorption bands (at 16.5μ and 17.25μ) were observed. Since vibrations of the acetyl group ($CO_2$ rocking) as well as of the $NO_2$ group (O-N-O bending) are found in this wavelength region, we attribute both bands to PAN. The band at 17.25μ is referred to as the $CO_2$ deformation, and that at 16.5μ as the $NO_2$ deformation.

## Decomposition Results

Spectra obtained in a typical experiment (under continuous irradiation) are shown in Figs. 3 to 7. In each of these, the upper spectrum was recorded before the irradiation had taken place. The next indicates the photooxidation products after 11 hours of irradiation. The third shows the result of eight days of irradiation. And the lower spectrum was obtained four days later, during which time the irradiation lamps were out. The spectral regions covered in these figures are indicated in each figure. It is thought unnecessary to illustrate the decomposition which occured in the dark, since the products of decomposition obtained this way were less complex, as shown in Table 2.

## TABLE 2

Decomposition Products

| Decomposition with Irradiation | Decomposition in the Dark |
|---|---|
| Methyl Nitrate | Methyl Nitrate |
| Methanol | |
| Methane | |
| Formic Acid | |

In addition, the formation of $CO_2$, CO, and $H_2O$ was observed in both experiments. The concentration of acetaldehyde was found to remain constant during the decomposition period.

Spectra taken after eight days of continuous irradiation indicate that a small amount of PAN persisted. That obtained after a comparable period in the dark indicated that the PAN had completely decomposed. Besides the known absorption bands of PAN, which decreased in both experiments, the bands at 16.5μ and 17.25μ also decreased, lending further credence to their identification as being attributable to PAN.

In the experiment involving continuous irradiation, the absorption bands at 8.9 and 11.2μ, which we referred to as 2-butene-ozonide, completely disappeared. However, no change in these absorption bands were found in the second experiment, where the reaction took place without irradiation. This could possibly be predicted since ozonides are regarded to be instable during prolonged irradiation.

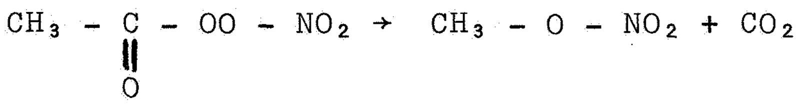
The changes in relative strength with time of the absorption bands attributable to PAN at 8.6 and 12.6μ are shown in Figs. 8 and 9 . The dashed curves indicate the decomposition without irradiation; the solid curves indicate the decomposition with irradiation. The ordinate values were determined by measuring the area of the absorption band with a planimeter.

Significant variances between the decomposition of PAN under the conditions of these experiments are noted. Both observations began after an 11 hour period of irradiation, which was required to form PAN. With continued radiation, the concentration of PAN stays constant for a day, and then decomposes at approximately a constant rate to an amount of about one third the original concentration. On the other hand, when the decomposition is done in the absence of irradiation, the concentration of PAN decreases at the start of the observations. After nine days, PAN could no longer be detected.

## Conclusions

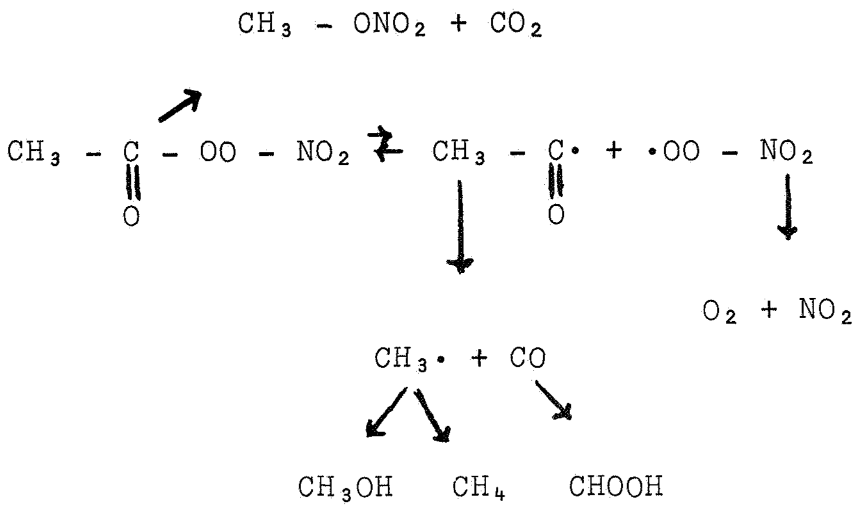
We note that after the 11 hour irradiation period $NO_2$ and some 2-trans-butene remain. These are thus still available to form more PAN if the irradiation is continued. Since, however, the PAN concentration is not observed to increase further, we conclude that the decomposition has commenced,and the rate of formation and decomposition must be approximately the same. After continued irradiation, the 2-butene supply is exhausted and the rapid decomposition of PAN is observed. As the reaction proceeds, the reformation of PAN from intermediate decomposition products starts. However, this is at a rate low enough so that the total concentration of PAN continues to decrease, and so the rate of decomposition also decreases. In fact, at the end of our experiment the rates of PAN reformation and decomposition appeared to become the same again, as the concentration stayed approximately constant. It actually decreased slightly because such side products as methyl nitrate and methanol were being formed.

Since only methyl nitrate was found after decomposition in the dark (see Table 2), it is necessary to postulate a different reaction mechanism for the irradiated and dark reactions. In the dark, the main decomposition reaction of PAN is a simple rearrangement:



$$CH_3 - \underset{\displaystyle O}{\underset{\|}{C}} - OO - NO_2 \rightarrow CH_3 - O - NO_2 + CO_2$$

The variety of reaction products after the prolonged irradiation indicates a more complicated mechanism, involving radicals at various steps. One possibility might be simplified in the following way:



Methyl radicals as intermediate reaction products may lead to methanol and methane, involving $H_2O$ or radicals like H and OH. Formic acid is probably formed of carbon monoxide in the same way.

## Acknowledgment

We are indebted to P. Hanst for discussions about the PAN problem, and to John Strong for guidance in the experimental procedure. This work was supported by NASA, Electronics Research Center, Cambridge, Massachusetts, under Grant NGR 22-010-042; the 100-ft. absorption cell was provided by ONR (Contract N00014-67-A-0230-0002).

## References

1. E.R. Stephens, P.L. Hanst, R.C. Doerr, W.E. Scott. *Ind. Eng. Chem.*, 48, 1498 (1956).
2. E.R. Stephens, E.F. Darley, O.C. Taylor, W.E. Scott. *Proc. Am. Petrol. Inst.*, Div. of Refining, 40, III (1960).
3. N.A. Renzetti, R.J. Bryan. *J. Air Poll. Contr. Association*, 11, 421 (1961).
4. D.J. Lovell, John Strong. "Long-Path Study of Infrared Absorption and Emission," *Appl. Opt.*, to be published.
5. C.S. Tuesday. "Chemical Reactions in the Lower and Upper Atmosphere," *Proc. Intern. Symp.*, San Francisco, Calif., 15, 1961.

Fig. 1: Schematic diagram of the long-path infrared cell.

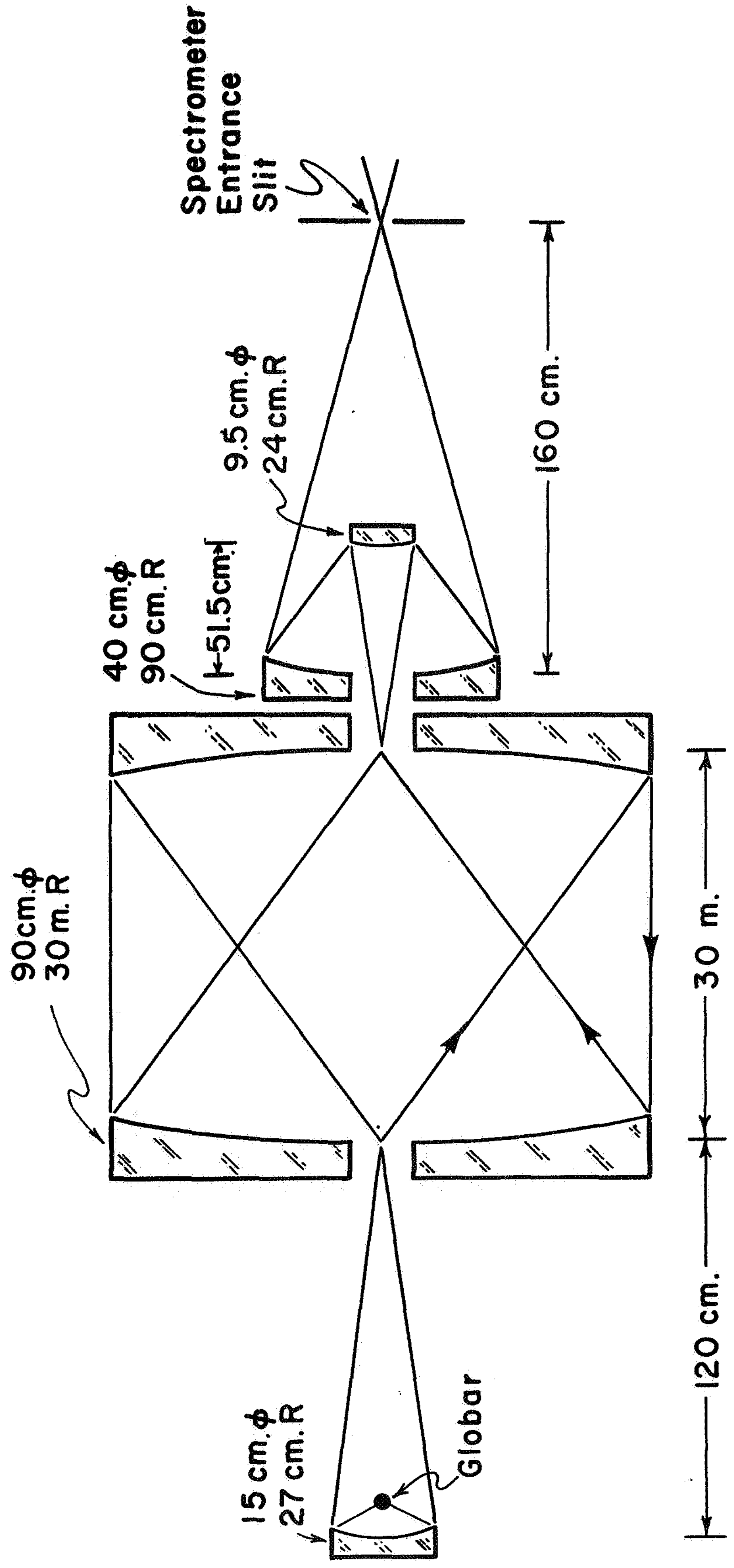


Fig. 2: Spectral radiant emmission of the Black Light Fluorescent Lamps used.

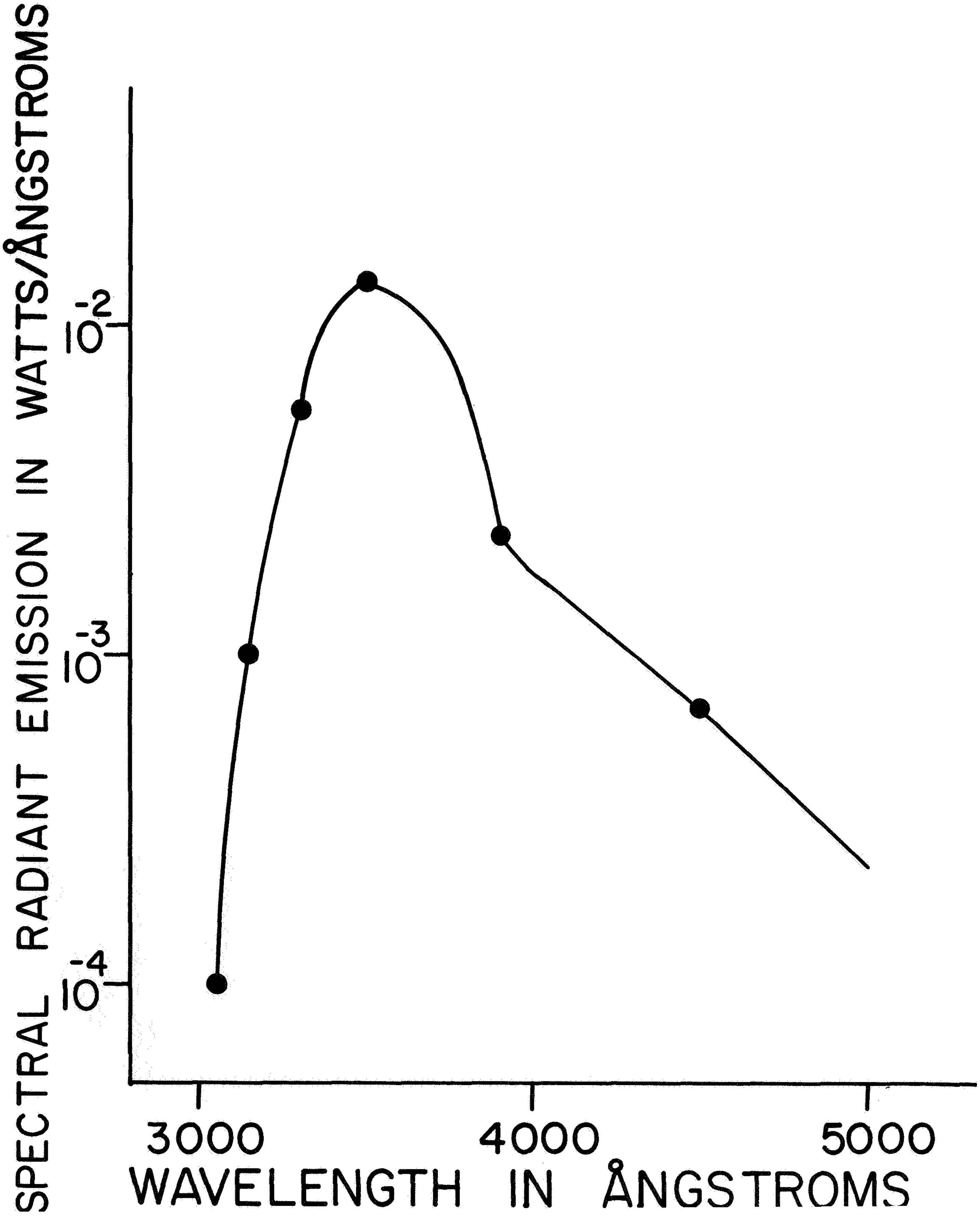


Fig. 3: Spectral region 6.3 to 8.4μ.

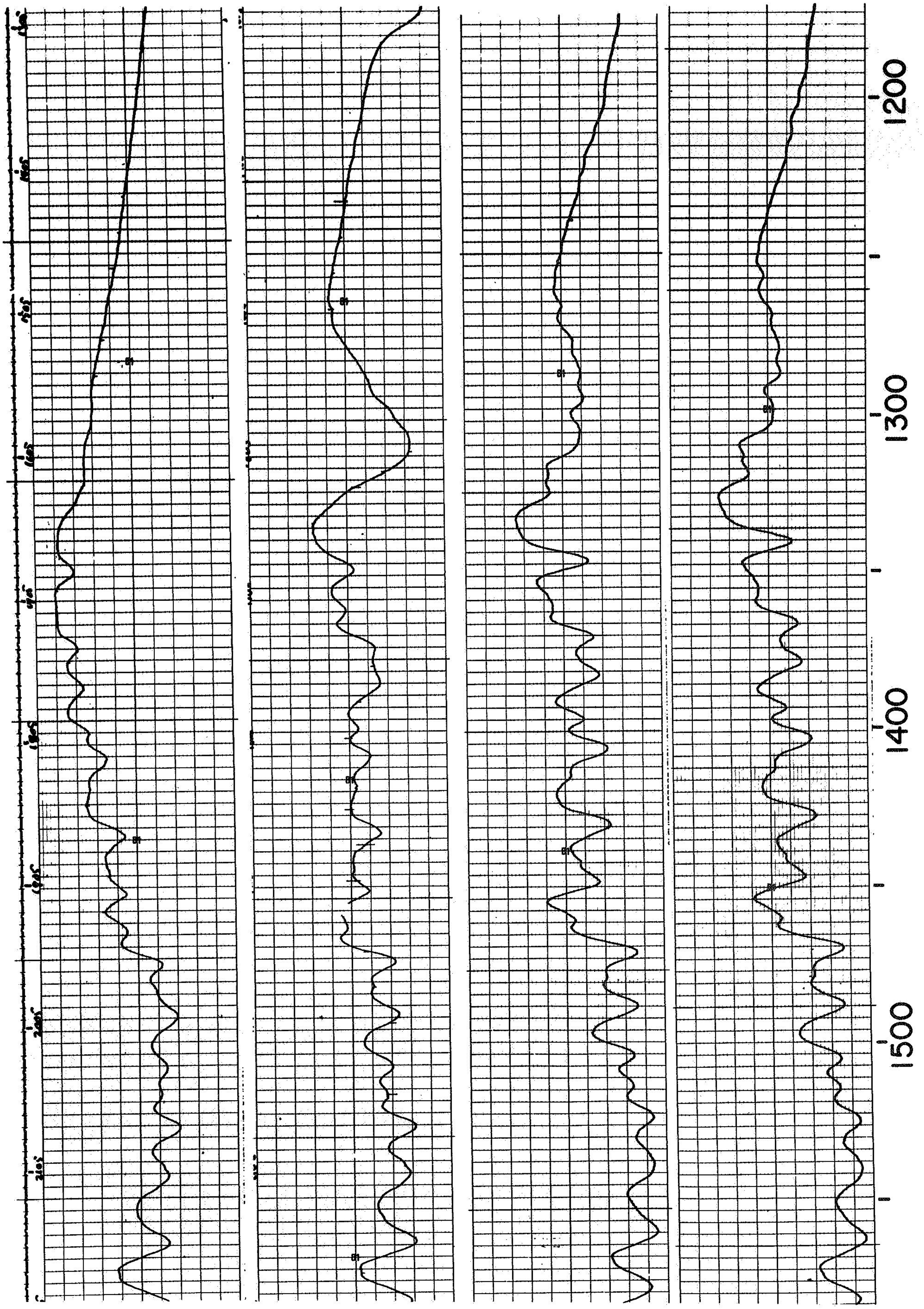


Fig. 4: Spectral region 8.4 to 10.1μ.

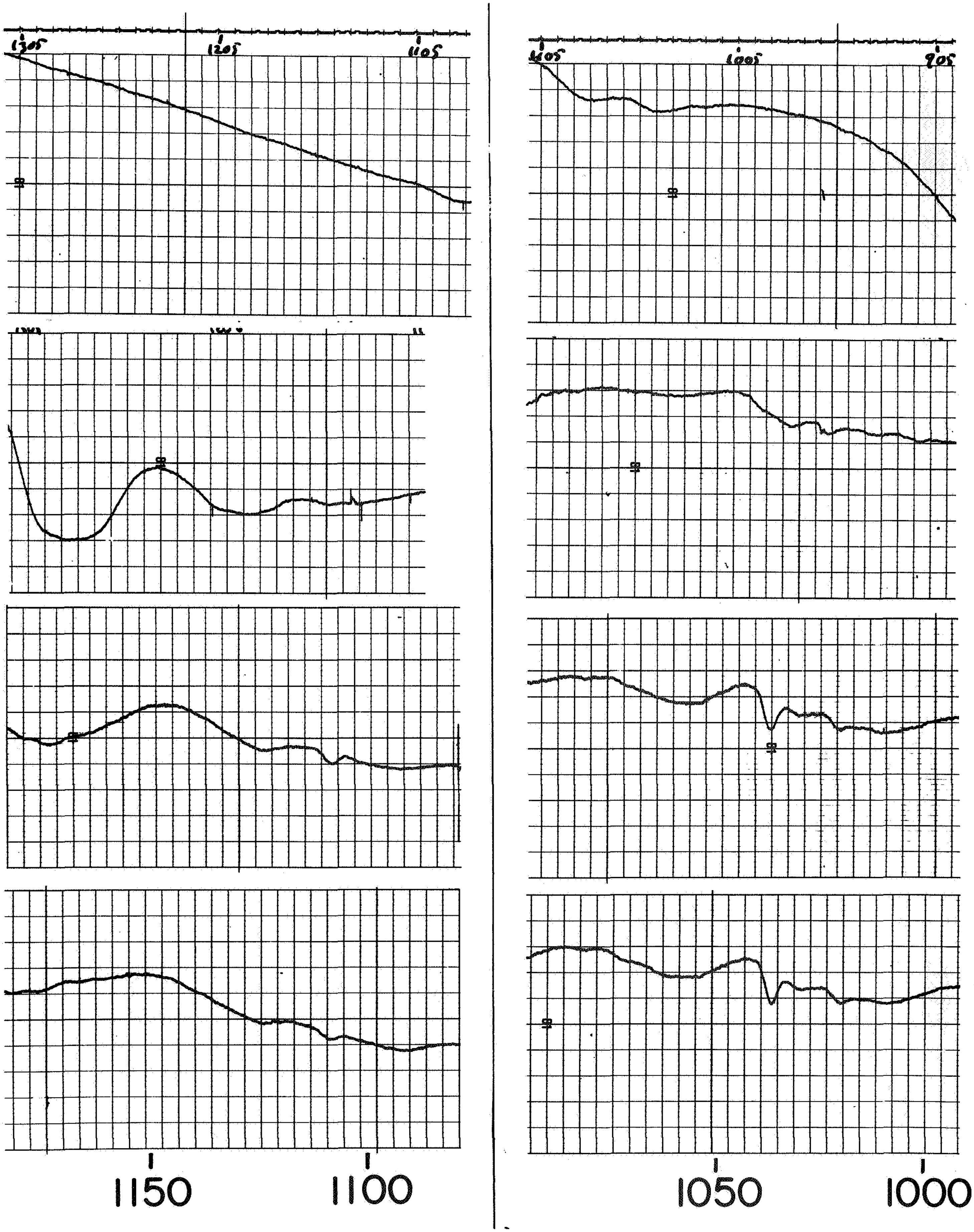


Fig. 5: Spectral region 12.3 to 15.4μ.

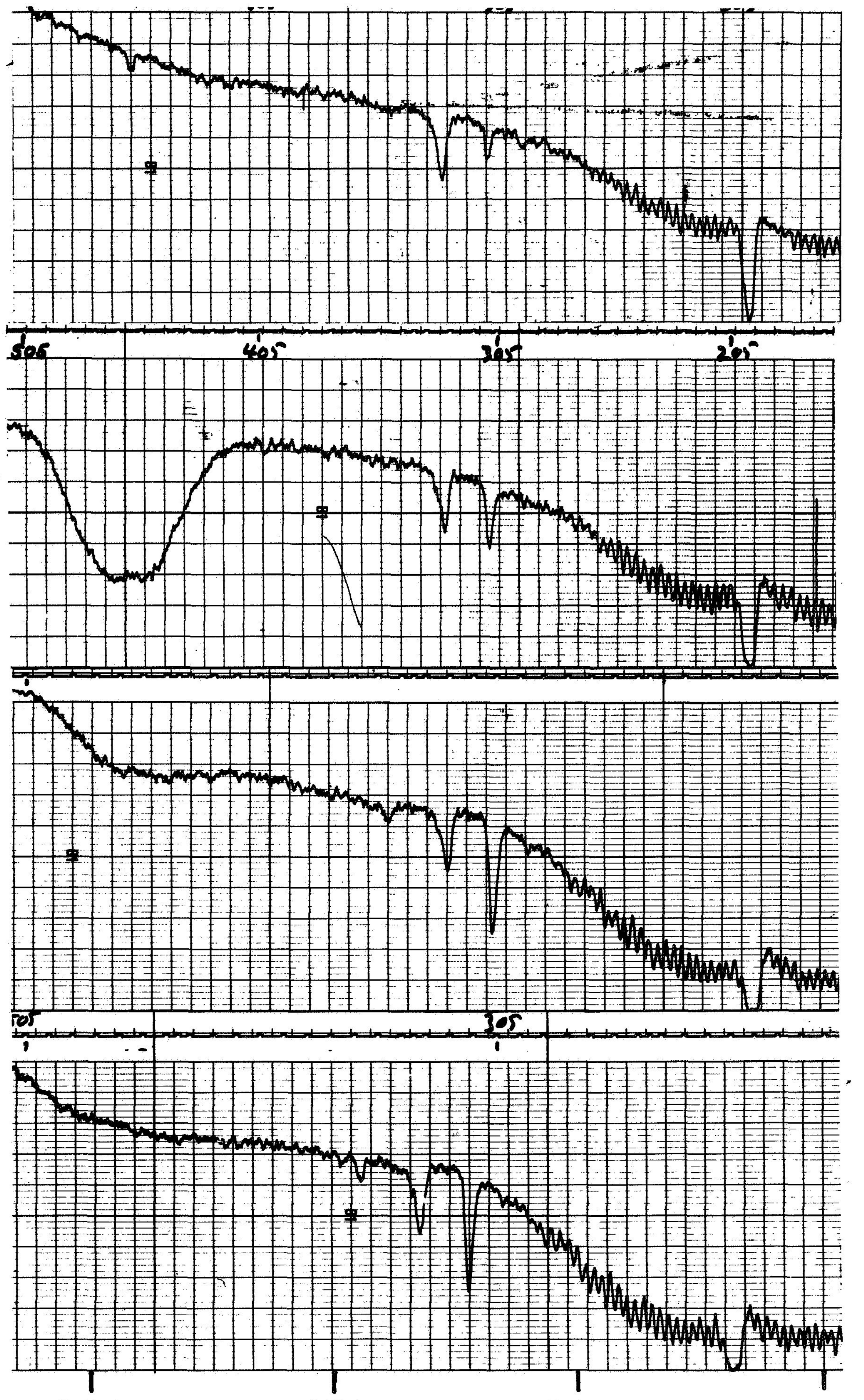


Fig. 6: Spectral region 15.0 to 20.0μ.

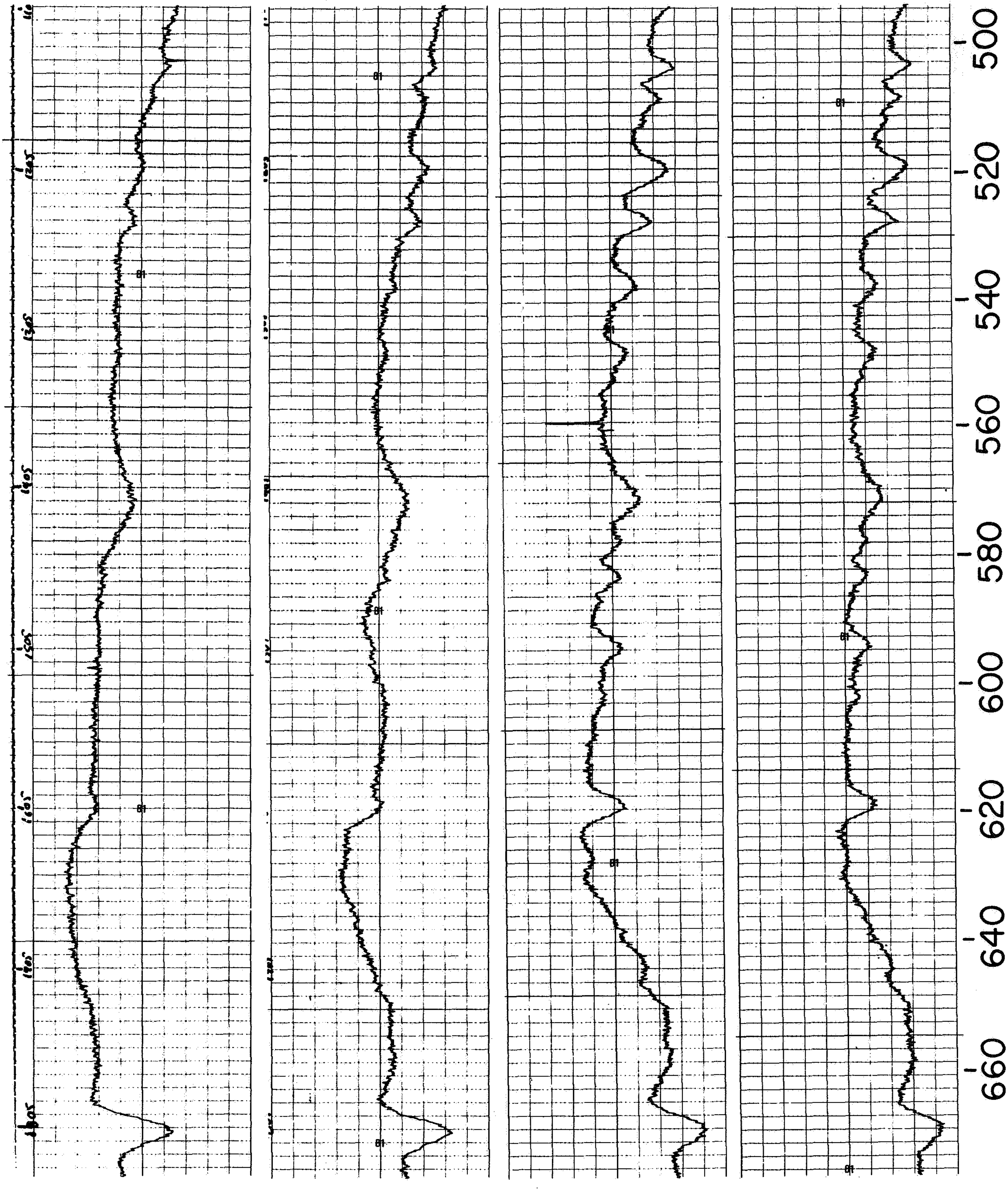


Fig. 7: Spectral region 20.0 to 26.0μ.

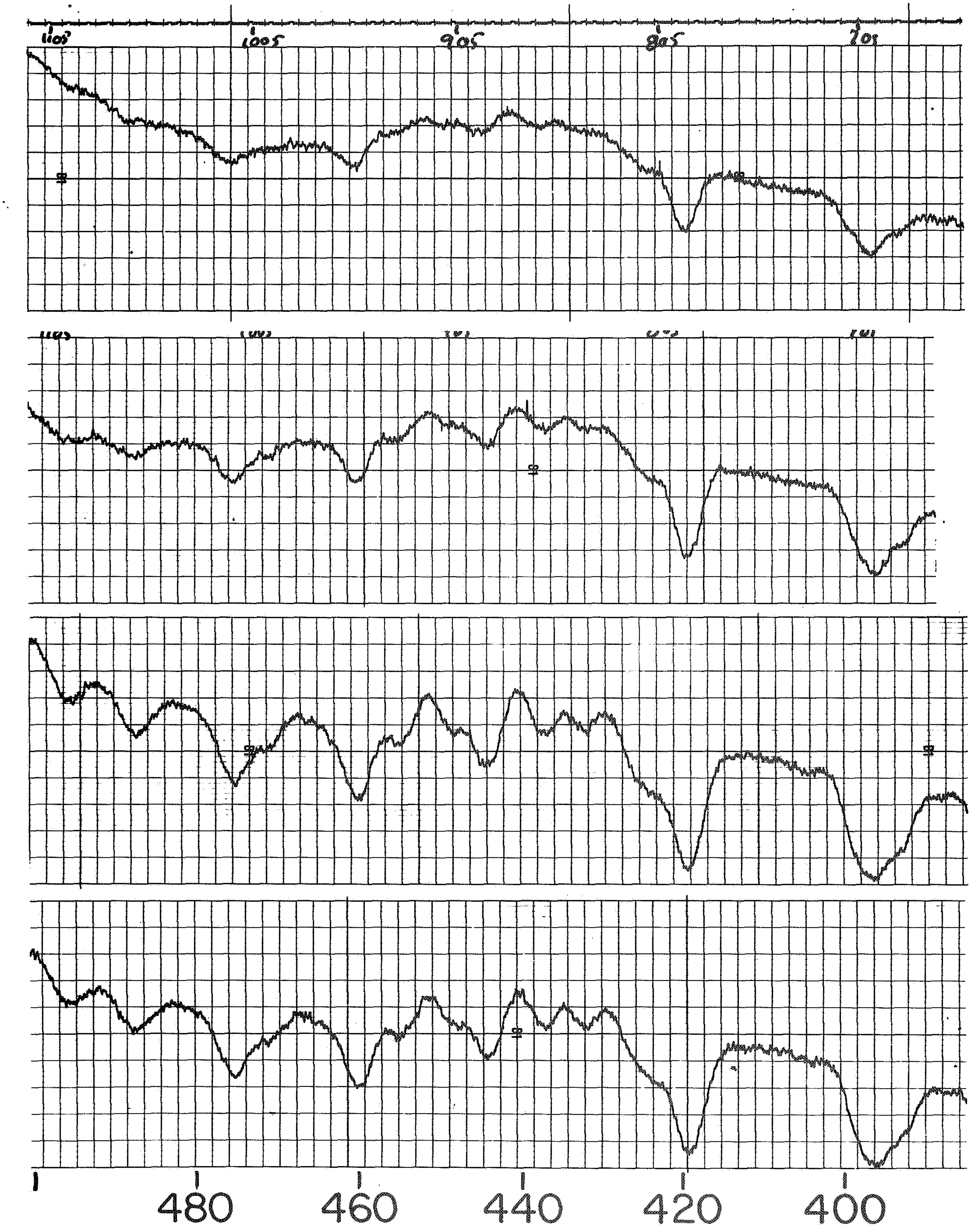


Fig. 8: Changes in relative strength of the 8.6μ absorption band of PAN.

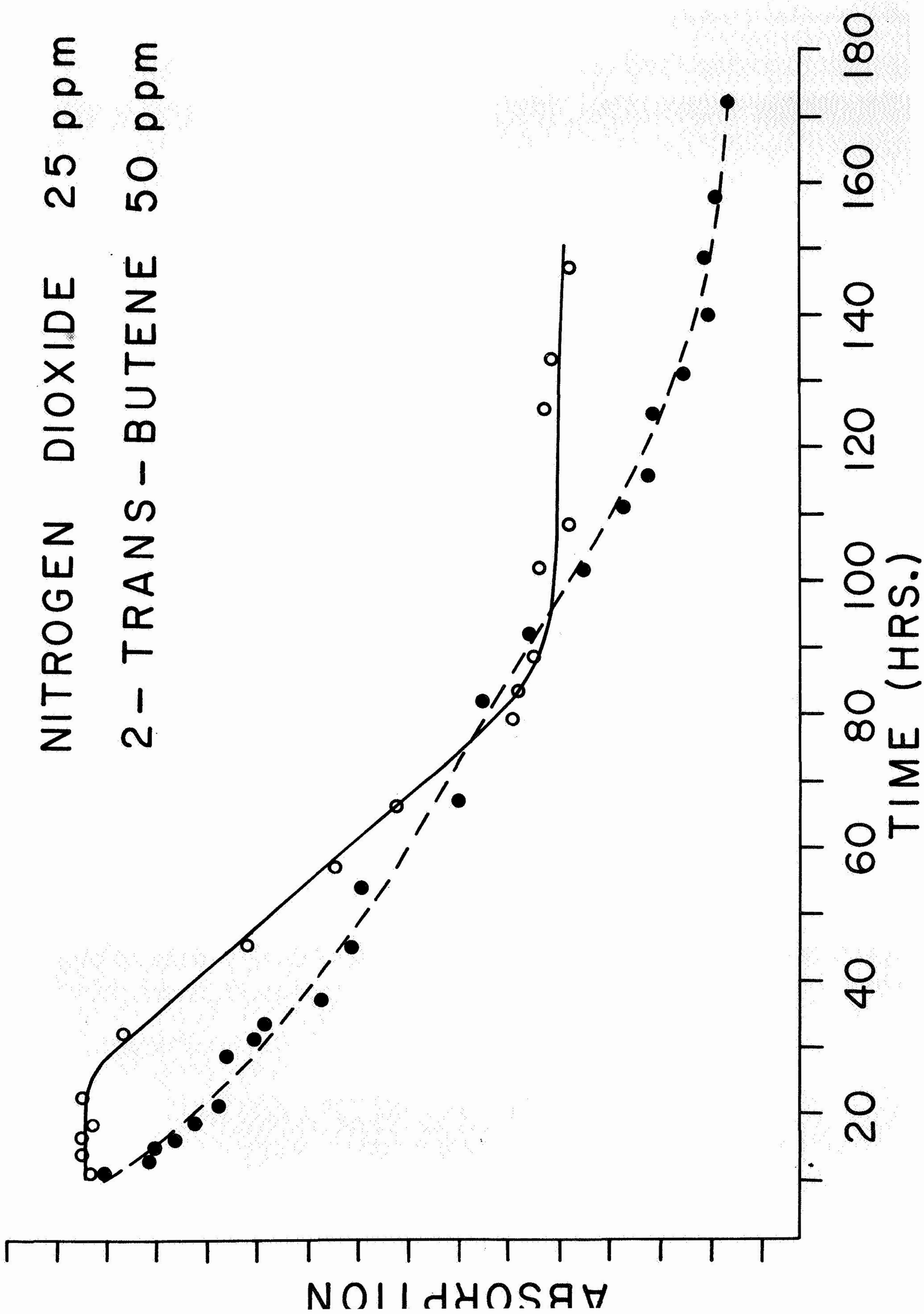


Fig. 9: Changes in relative strength of the 12.6μ absorption band of PAN.