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Infrared Emission Spectra of Flames Under High Resolution[1]

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The spectrum of a hydrogen-oxygen flame and an oxyacetylene flame has been measured in the near infrared region with a high-resolution grating spectrometer. In the region from 3.7 to 4.1 μ many lines are observed which have not been classified. They may arise from transitions belonging to the ν_2 or ν_3 bands of water vapor. The intensity of the first overtone band of CO was increased when a high-frequency discharge was passed through the flame and the infrared CN band was increased in intensity when N_2O was mixed with the acetylene. The results are shown in five figures of the observed spectra.

1. Introduction

There have been a large number of researches on the infrared emission of flames in the last 10 years, but investigations in this field extend back to the early period of infrared spectroscopy. In 1890 Julius [1] [2] measured the radiation from flames in which various fuels were used. When CS_2 was used as a fuel, he observed that the strongest bands in emission occurred at the same wavelengths as the bands which were present in the CS_2 absorption spectrum. The emission specturm of H_2O and CO_2 was extensively studied by Paschen [2] and by Rubens and Aschkinass [3]. They observed the shift of the maximum of emission in CO_2 from 4.27 to 4.40 μ with increasing temperature of the flame.

With the improved present-day optics and detectors in grating spectrometers many of the infrared emission bands can be resolved sufficiently to show the rotational lines in the bands, and weak bands can be observed which were not discerned by prism spectrometers. Previous reports [4] have given the measurements on the spectra of C_2, CN, OH, H_2O, CO, and CO_2.

The present investigation was undertaken to observe the effects of adding other fuels to the oxyacetylene flame and to observe the changes in intensity of the emission bands when the flame is irradiated with high-frequency discharges. Also the region from 3.7 to 4.1 μ was measured under high resolution to ascertain if any bands of low intensity could be observed between the OH and H_2O lines.

2. Experimental Method

A grating with 10,000 lines/in. was used in the spectrometer which resolved lines separated by 0.07 cm^{-1} in the 3- to 4-μ region. A description of the instrument, the methods of measuring the wavelengths, and other details are given in a previous publication [5].

The spectrum was observed of an oxyacetylene flame from a mixture enriched in fuel to enhance the bands selected for study. The radiation from the flame was intensified on the spectrometer slit by using a system of mirrors [6].

3. Experimental Results

The use of the 10,000 lines/in. grating in the second order produced almost twice the resolution that was obtained in the first order. An example of the high resolution obtained is shown in figure 1. A part of the emission spectrum of carbon monoxide is shown for the region from 4,250 to 4,310 cm^{-1}. The band head of the 3–1 band occurs at 4,306 cm^{-1} and the figure includes the lines of the *R* branch from *R* 13 to *R* 67. The lines from *R* 53 to *R* 67 are folded back over the region of the *R* lines extending from 33 to 48, but the two sets of lines are sufficiently resolved to be readily observed. When this band was measured with low resolution the lines from *R* 53 to *R* 67 were not observed [4]. Under the burning conditions when this spectrum was observed, the *R* 26 line of this band was the most intense. The lines from *P* 2 to *R* 12 of the 2–0 band also fall in this region. On account of the elevated temperature of the oxyacetylene flame the intensity of the rotational lines near the center of the 2–0 band is low. The first line of this band which stands out above the noise level is *R* 3.

Some bands observed in the infrared spectra of flames are weak in intensity, primarily on account of the low concentration of the molecules. By adding substances which increase the concentration of the molecule or radical under observation, the spectra can be made more intense. An example of such a change in intensity is the CN spectrum which was observed in the flame with and without added gases. It was found that the CN spectrum was greatly increased in intensity when N_2O was introduced into the fuel line. Two traces of the spectrum of CN are shown in figure 2. Because this band occurs in the near infrared region, higher resolution was obtained by using a 15,000 lines/in. grating in the second order. The upper curve was observed with a flame which was rich in fuel. The inner cone extended about 2 in. above the tip of the burner. A region near the top of the inner cone was focused on the entrance slit of the spectrometer. The lower trace was obtained under the same conditions of measurement, but a small amount of N_2O was added to the acetylene before burning. The N_2O produced an increase in intensity of about 50 percent in the lines of this band. By adding larger amounts of N_2O the intensity of the band was increased by a factor of

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[2] Figures in brackets indicate the literature references at the end of this paper.

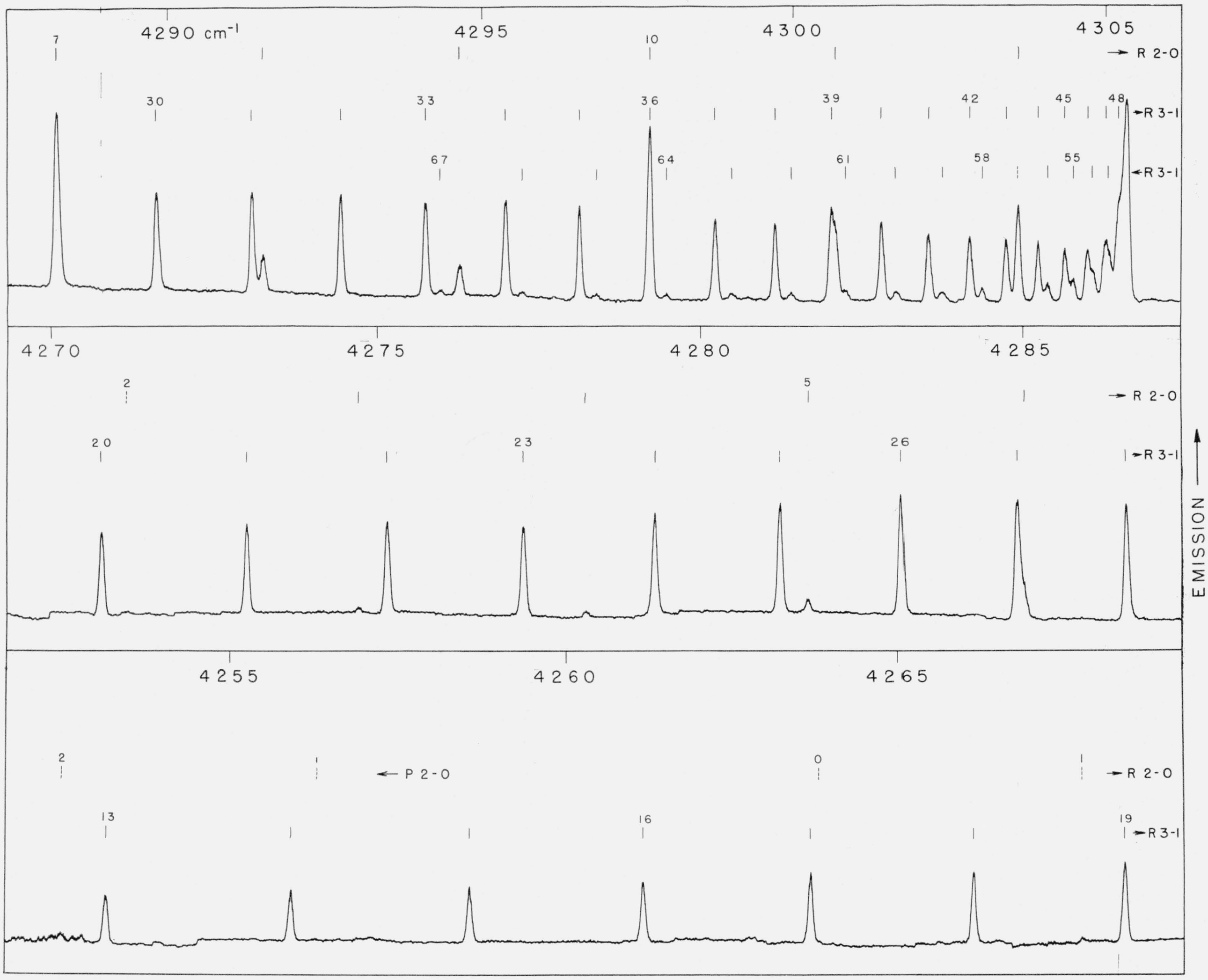

FIGURE 1. *The emission spectrum of* CO *for the 3–1 transition in the region from 4,250 to 4,310* cm^{-1}.

Some of the lines of the 2–0 transition also occur in this region.

four. However, the flame was not stable and the entire band could not be observed under the same conditions.

The infrared emission of gases excited by a radiofrequency discharge has been reported by Wilkinson, Ford, and Price [7]. They found that the spectrum contained many bands which arose from transitions of the high energy levels of the molecules, and for CO the transitions from 2–0 and 12–10 were observed. On the other hand, in the oxyacetylene flame only the transitions from 2–0 to 8–6 are present with appreciable intensity. The emission spectra from the oxyacetylene flame should be increased in intensity when excited by a radiofrequency discharge. The results obtained with such a discharge through the flame are shown in figure 3. The upper curve is the 2–0, 3–1, and 4–2 transitions of the CO spectrum observed with a rapid scanning rate. The lower curve is the spectrum of the same region with the radiofrequency discharge passing through the flame. Although the high-frequency machine was of low output (100 w) a considerable change in the intensity of the rotational lines can be observed. All the lines of the spectrum observed with the high-frequency discharge have been increased in intensity, and the intensity ratio of the higher transitions to lower transitions has been increased. The intensities of the lines of oxyacetylene flame in the 3–1 and 2–0 bands are about equal, but with the discharge through the flame the 3–1 band is about 50 percent more intense. These preliminary results indicate that the use of the high-frequency discharge in the flame should be of importance in the observation of flame spectra.

The emission spectra of oxyacetylene flames in the region from 3.0 to 3.5 μ are rich in lines which belong to the bands of water vapor. When the spectrum is extended to longer wavelengths the *P* branch of the OH band is the most characteristic feature observed. Between the OH lines there are weak lines which cannot be resolved with medium resolution. The region from 3.5 to 4.0 μ has now been remeasured

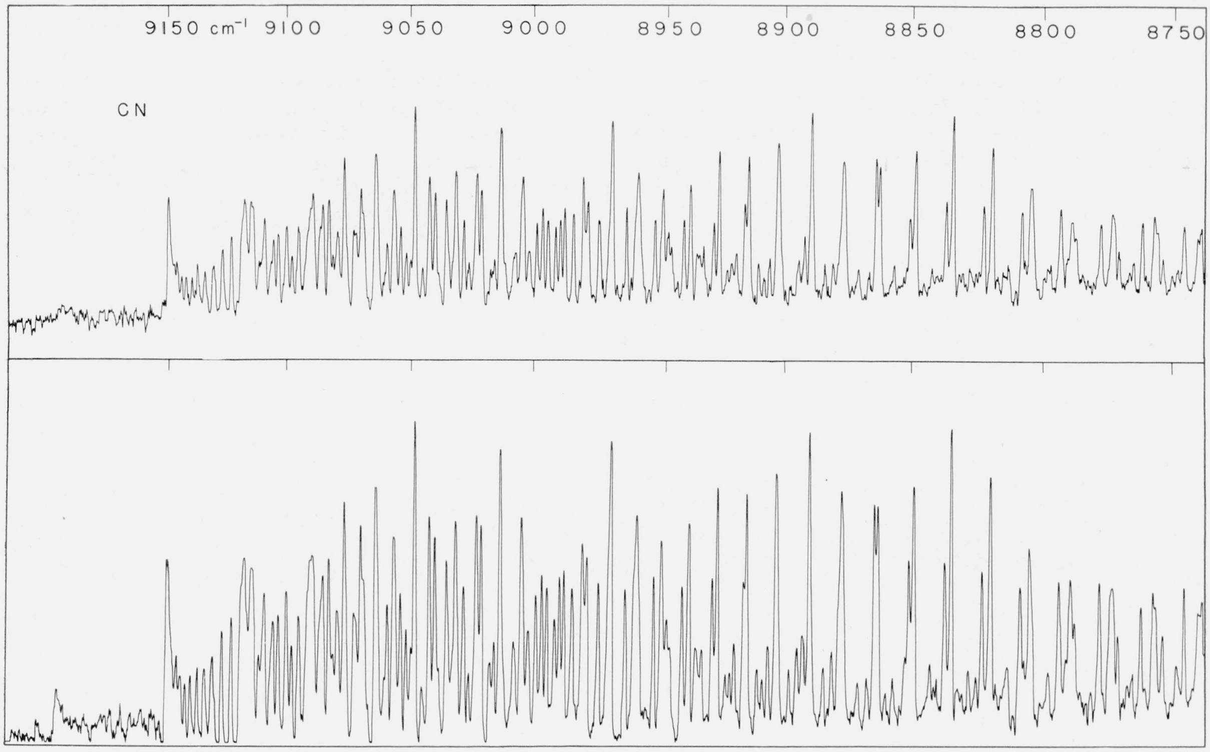

FIGURE 2. *The spectrum of* CN *from 8,750 to 9,150 cm*$^{-1}$.

The lower curve is the spectrum obtained when N_2O has been added to the fuel.

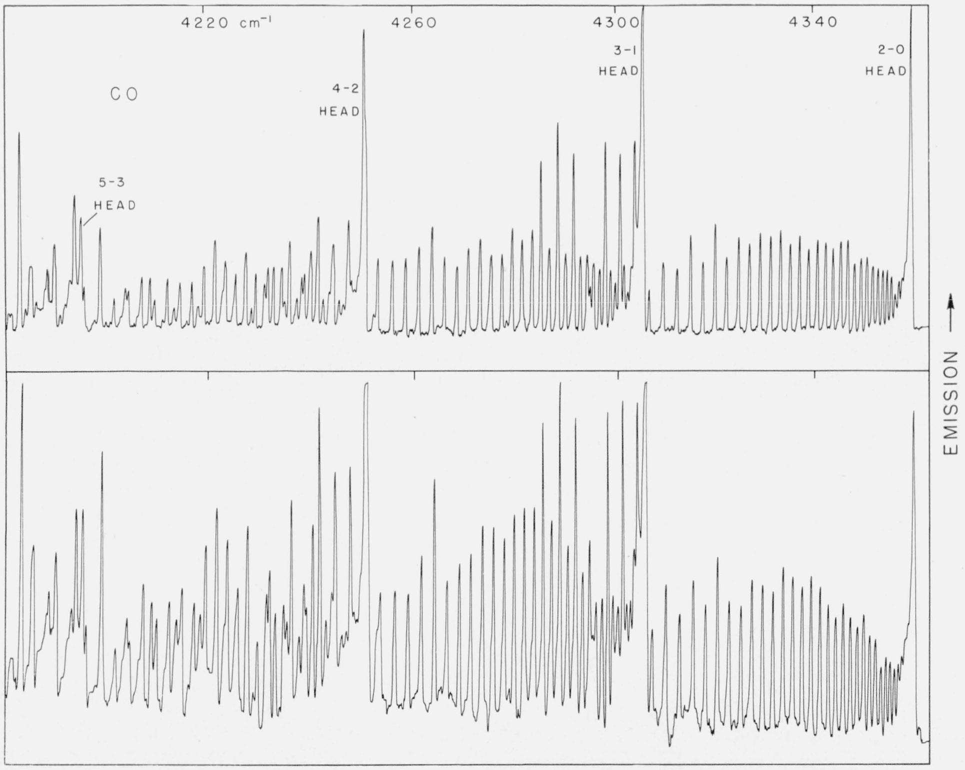

FIGURE 3. *The emission spectrum of* CO *in the first overtone region.*

The lower curve was obtained when the flame was irradiated with a high-frequency discharge.

under high resolution, and a large number of lines have been observed. The spectrum of a flame, figure 4, was observed for a rich mixture of the fuel and the OH lines of the 2–1 and 1–0 bands are fairly intense. The CO_2 band was very intense compared to the other structure and that part of the spectrum was observed with slits one-third as large as those used for the other regions. The lines of the 001–000 band of CO_2 were resolved to R 118. The band head of 01′1–01′0 is double on account of the l-type doubling and some of the l–type doublets of the R-branch lines of this band are resolved, but the atmospheric absorption of CO_2 in the optical path of instrument becomes so large at 2,380 cm^{-1} that the band cannot be observed to its center.

The spectrum of a hydrogen-oxygen flame (fig. 5), has also been observed for the region from 2,370 to 2,660 cm^{-1}. The spectrometer slits were two-thirds

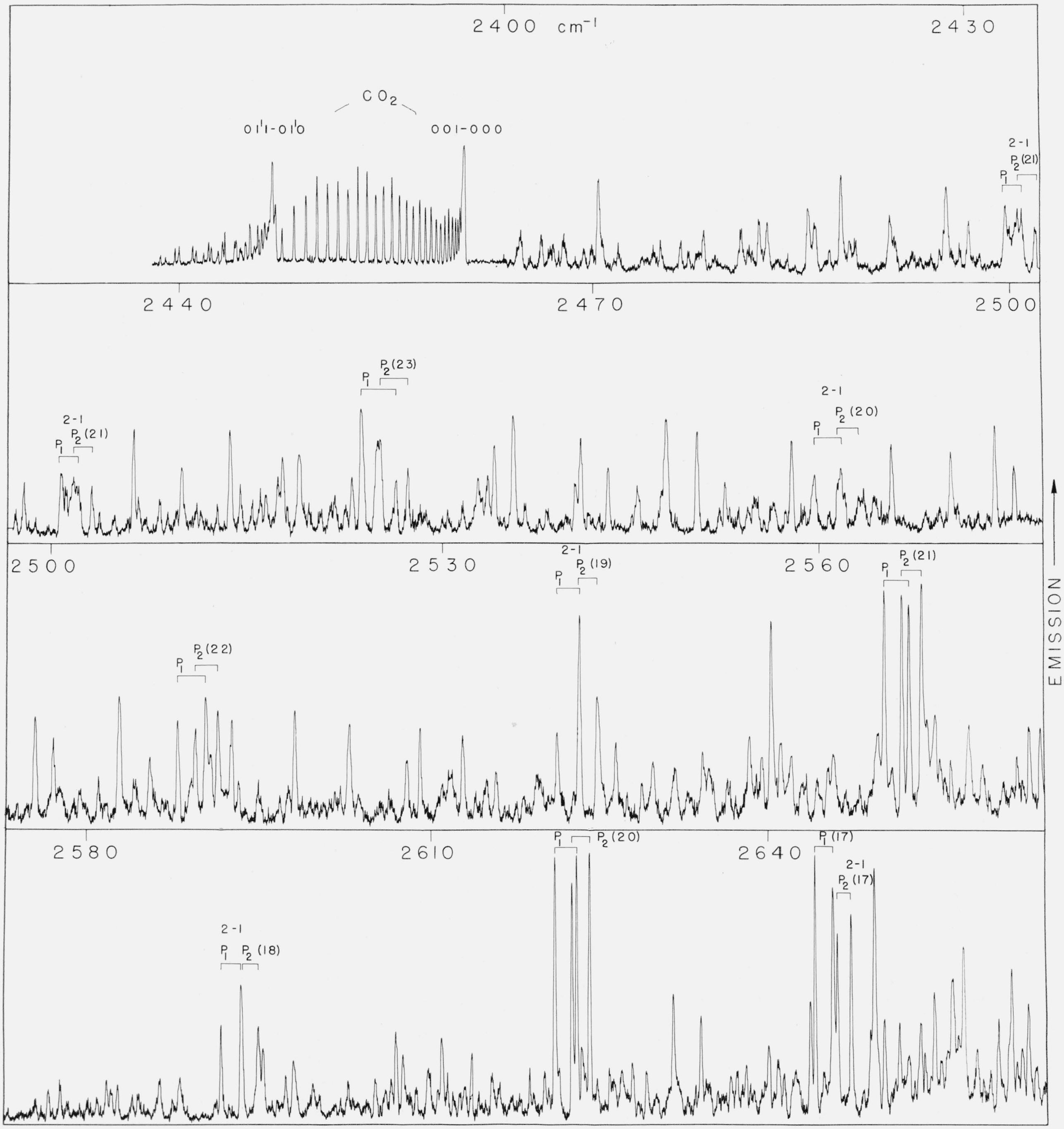

FIGURE 4. *The emission spectrum of an oxyacetylene flame from 3.7 to 4.1 μ.*

Part of the CO_2 spectrum and some of the lines of OH are a prominent part of the spectrum.

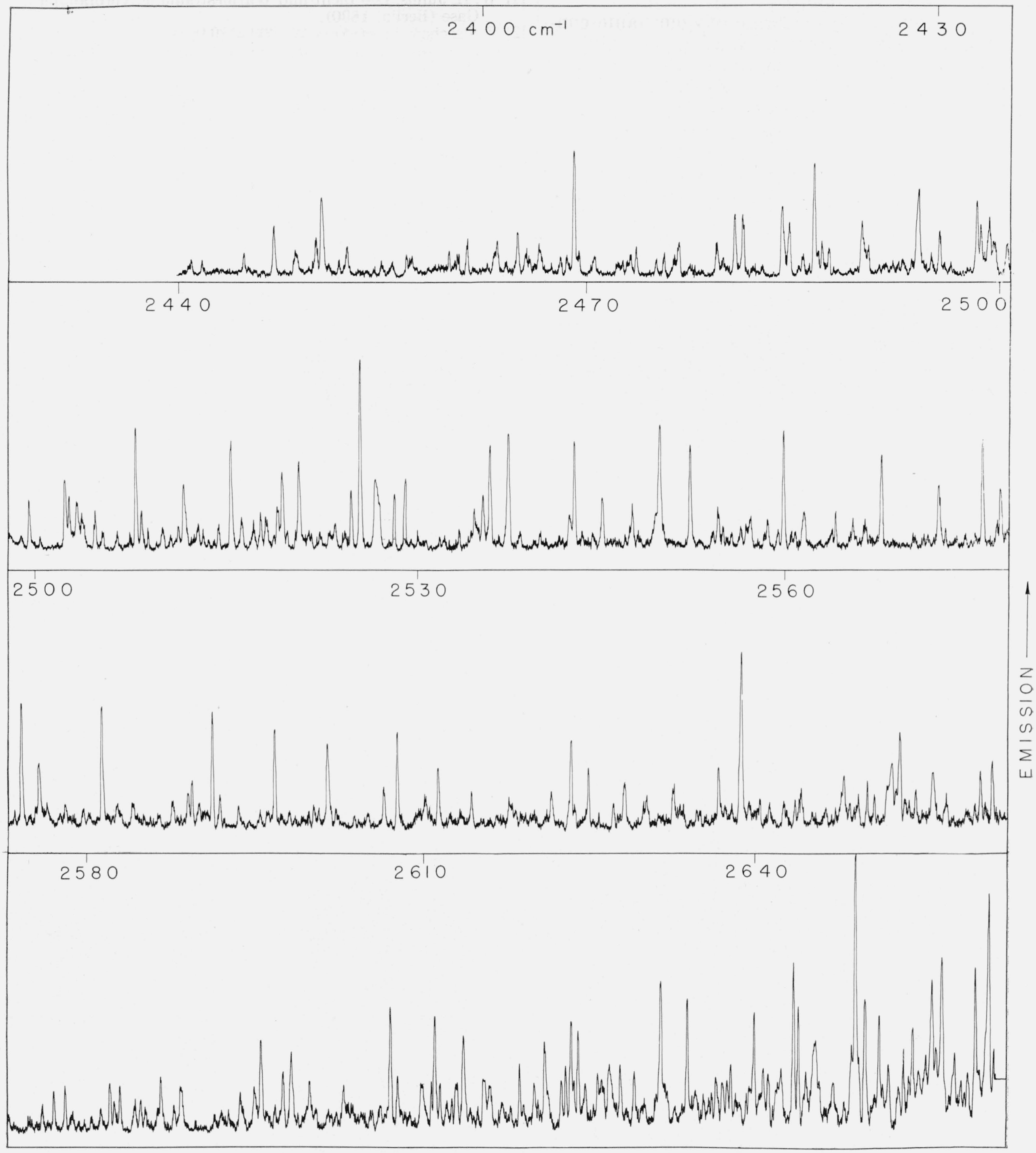

FIGURE 5. *The emission spectrum of a hydrogen-oxygen flame from 3.7 to 4.1 μ.*

Many of the lines in this spectrum correspond with those observed in the oxyacetylene spectrum.

as wide for measurements of figure 5 as for those of figure 4, but all other operating conditions of the instrument were the same.

The spectrum of the hydrogen-oxygen flame contains OH lines which are less intense than those in the oxyacetylene flame. Also, the CO_2 bands are absent in the hydrogen-oxygen flame. Most of the remaining lines of the spectrum are more intense in figure 5 than in figure 4. The region from 3.0 to 3.7 μ was also measured and many lines were observed. Almost all of these lines arise from the bands of OH and the $2\nu_2$ and ν_3 bands of water vapor.

The identifications of most of the lines in the 3.7- to 4.1-μ region, other than those of OH and CO_2, have not been made. A few lines fall in the series which have been identified as a part of ν_3 rotational structure of H_2O. The remaining lines may be a part of the ν_2 or ν_3 band of water vapor, but at present it has not been possible to identify them as arising from the transitions in those bands.

4. References

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