Infrared Emission Spectra of Flames [1]

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The infrared emission spectra of a hydrogen flame and of a natural gas flame have been compared in the region from 1.7μ to 24μ. Emission bands have been observed at 1.87μ, 2.78μ, 4.37μ, 6.26μ, and 15μ that are produced by molecules of H_2O and CO_2. Another band at 3.316μ is attributed to methane. From 3.0μ to 3.8μ there are a number of rotational lines, some of which may be produced by OH and others by H_2O molecules. As the temperature of the flame was increased, the rotational lines became more intense. Five lines in the region from 3.4μ to 3.8μ agree closely in position with the predicted rotational lines of the P branch of the $2 \to 1$ vibrational band of OH. These lines correspond to values of K equal to 11, 12, 13, 14, and 15. Wave numbers of some of the observed rotational lines were found to show a good correspondence with predicted values for K equal to 11 to 36, for lines extending from 9μ to 24μ. In addition to this series of lines, there are other lines that are produced by the rotational states of H_2O molecule. A discussion is included of the various methods of observing flame spectra.

I. Introduction

In the February 1948 number of the Journal of Research [2] there is an article on the emission spectra from a Bunsen flame. In that work it was shown that nearly all the emission spectra from the Bunsen flame were produced by H_2O and CO_2 molecules. The CO_2 spectrum has bands in the regions of 4.4μ and 15μ. The CO_2 emission in the $15-\mu$ region is composed of at least three bands with frequencies of 667, 668, and 721 cm^{-1}. These frequencies correspond to the changes in known energy levels. The transitions are (01^10) to (00^00), (02^20) to (01^10), and (10^00) to (01^10). A discussion of the $15-\mu$ emission of CO_2 molecule has been given in a recent report.[3] Nearly all the energy in the region of 2.7μ is radiated by the H_2O molecule. Additional observations included the strong band of water vapor at 6.26μ in the emission spectrum, and many rotational lines extending from 10μ to 24μ.

In the region of 2.8μ to 3.2μ, there are 15 lines that have been attributed to the H_2O molecule. In order to measure the spectrum in the $3-\mu$ region

under different conditions of burning, a commercial gas-oxygen torch was used. The gas and oxygen were completely mixed before burning to produce a smooth, narrow, quiet flame 5 in. high on a port about 1 mm in diameter. The emission spectra of a gas-oxygen flame and a hydrogen-oxygen flame have been measured and the results compared.

II. Experimental Work

A Perkin-Elmer infrared spectrometer, with interchangeable prisms of LiF, NaCl, and KBr, was used as the resolving instrument. Natural gas containing about 88 percent of methane was burned in a gas-oxygen torch, and the flame was changed by varying the amount of oxygen. This caused the flame temperature to be different, with a corresponding effect on the relative intensities of the bands. Some of the bands would increase in intensity and others would decrease in intensity, as the temperature was increased.

Figure 1 shows the emission bands from the flame of a gas-oxygen torch. Natural gas was burned with O_2 in considerable amounts, giving rise to a hot flame. The zero branch of the H_2O combination band is found to be at 1.87μ, and the P and R branches at 1.95μ and 1.78μ, respec-

[1] The results of this paper were reported, in part, at the meeting of the Optical Society of America in October 1947.

[2] E. K. Plyler, J. Research NBS 40, 113 (1948) RP1860.
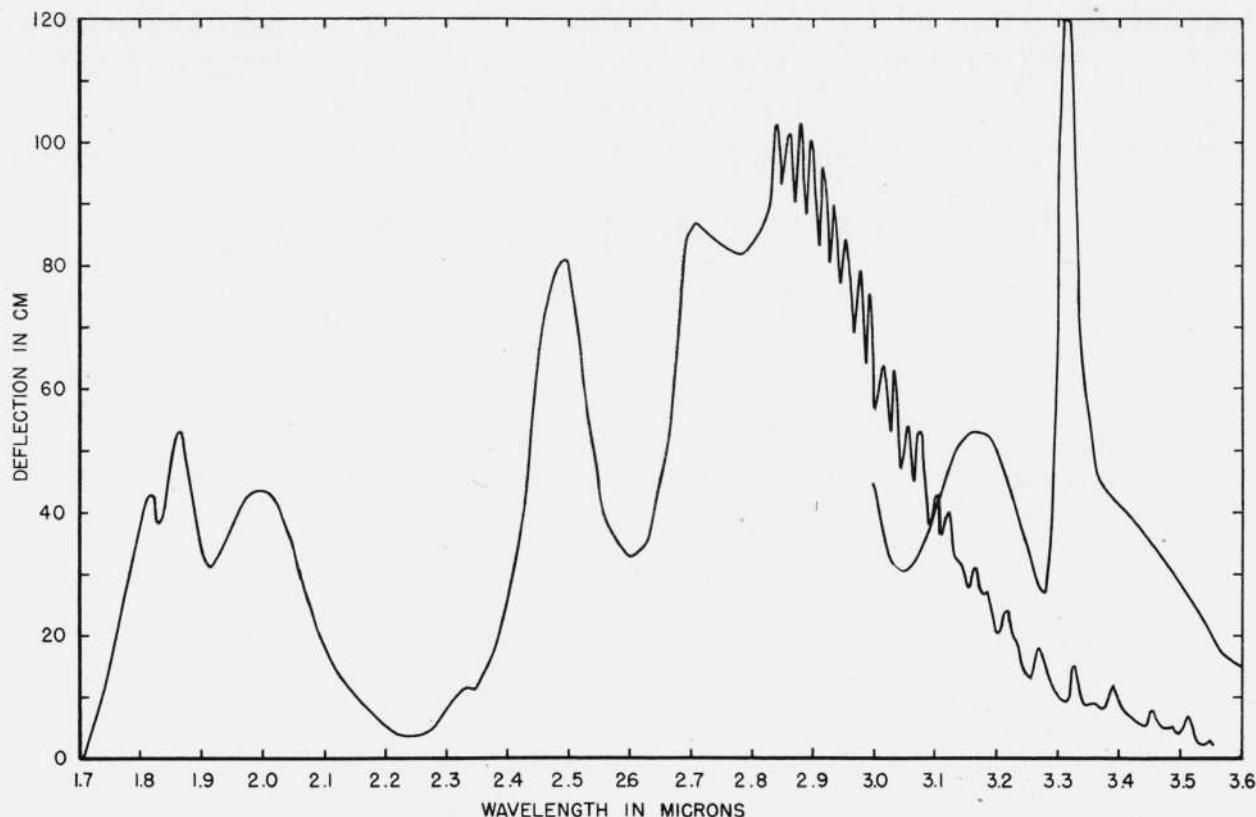
[3] E. K. Plyler, Science 107, 48 (1948).

FIGURE 1. *Infrared emission spectrum of a natural gas-oxygen flame.*

The spectrometer slits were 0.18 mm in width, and an LiF prism was used. The methane band at 3.3 μ was measured from a gas-air flame with cone of flame focused on spectrometer slit, and the slits were 0.25 mm in width.

tively are also resolved from the Q branch. However, the resolution of the LiF prism was not sufficient for resolving any of the rotational structure. In the region from 2.84μ to 3.55μ there are many rotational lines. When less oxygen is used in the flame the lines from 2.84μ to 3.1μ stand out more prominently, and the faint lines in the region from 3.1μ to 3.55μ disappear. The intense band with a sharp maximum at 3.315μ was observed when small amounts of oxygen were introduced in the burner and a large cone was present in the flame. The region of the cone was focused on the entrance slit of the spectrometer. The zero branch is sharp and of good intensity. The R branch is observed and is of maximum intensity at 3.16μ, and is well separated from the zero branch.

In figure 2 the emission spectra of the hydrogen flame are shown for the spectral region of 1.7 to 3.9 μ. The $1.87-\mu$ maximum, which is the zero branch of a combination band of the H_2O molecule, is quite intense. The P branch is relatively less intense in the hydrogen flame than in the gas flame. The greater intensity of the gas flame may be caused by the radiation of the CO_2 molecule in the region of 2μ.

The zero branch at 2.71μ is somewhat reduced by the absorption of the CO_2 and H_2O molecules in the air. However, in figures 1 and 2 there has not been any correction applied for the atmospheric absorption. A comparison of the two figures indicates that there is considerable emission from CO_2 in this region. The R branch of the H_2O band has the greatest intensity at 2.5μ and the P branch at about 2.9μ. As shown in figure 2, the rotational lines in the P branch of the 2.7μ-H_2O emission band are well marked, and 19 lines are observed in the region from 2.80μ to 3.25μ. The slits of the spectrometer were 0.185 mm wide, and the flame had considerable oxygen.

When the flame was made hotter by increasing the oxygen by a small amount, these lines were less conspicuous. The flame was adjusted so that

the lines were of greatest contrast to the background, and they were observed with a somewhat narrower slit. Under these conditions it was found that several of the lines had bulges on their sides. It was not possible to completely separate the complex structures with the LiF prism, but it is highly probable that many other lines could be observed in this region if higher resolution were employed.

The curve marked b in figure 2 represents the flame spectrum from 3.0μ to 3.4μ when the oxygen is increased. The greater deflections are produced, in part, by increasing the amplication of the thermocouple output by about 50 percent. Under the different flame conditions the rotational components show a considerable variation in intensity. At wavelengths beyond 3.1μ the lines have greater intensity, and it has been possible to extend the observation of rotational structure to 3.8μ. Curve c in figure 2 was measured by increasing the slits to 0.25 mm and increasing the

amplication by a factor of two compared to the value used in the region from 1.7μ to 3.4μ. The wavelengths of the rotational lines are listed in section III.

The infrared emission in the region from 3.5μ to 5.0μ from the flame was studied, when mixtures of natural gas and oxygen were used. It was found that the emitted energy could be more than doubled by increasing the oxygen. The corrections for the atmospheric absorption and also the self absorption of the flame were calculated from observed data. By passing radiation of one flame through another flame, it was found that the flame absorption amounted to about 20 percent at 4.22μ. This was measured by having one flame focused on the entrance slit and placing another flame in the path between the first flame and the entrance slit. The sum of the energies of the two flames burning separately was compared with the energy of the two flames burning at the same time. The corrected energy curve for the
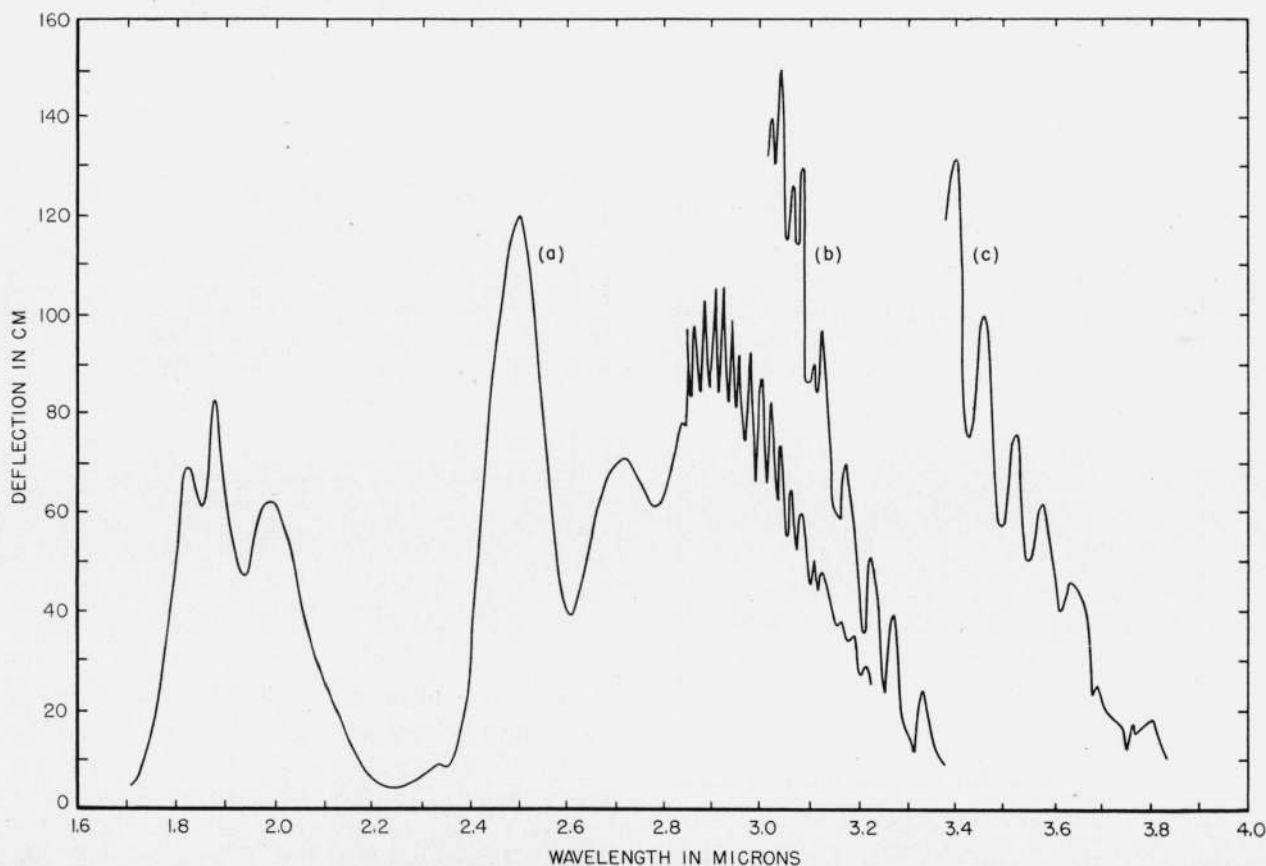

FIGURE 2. (a), Infrared emission spectrum of a hydrogen-oxygen flame. (b), Hotter flame and amplification increased 50 percent; (c), hotter flame and amplification increased 100 percent.

Infrared Emission Spectra of Flames

4μ to 5μ region did not vary by a significant amount from the curve shown in the previous paper (see footnote 2), and it is not shown here.

In figure 3 is shown the 6.26μ H_2O emission band. This was observed in the hydrogen flame with a considerable amount of oxygen. A rock-salt prism was used in the spectrometer, and the slits were 0.280 mm wide. There is very little emission in the center of the band, and the R branch has maximum energy at 5.35μ, and the P branch at 6.75μ. The rotational structure is not well resolved, but three strong lines can be seen between 7.5μ and 8.0μ. The energy radiated by the flame is of low intensity. In figure 4 is shown the record of the energy emitted from 10μ to 15μ where it is a maximum. The position of the maximum of intensity within this region varies with the temperature of the flame. The energy emitted by the flame is very much dependent on the amount of oxygen that is introduced. For example, if the flame is hot, with a relatively high proportion of oxygen, the energy is about constant in the 10μ to 15μ region. For cooler flames with less oxygen, the energy increases continuously from 10μ to 15μ. The marked changes in relative intensity of the rotational lines

of the water vapor molecule that are produced by flame changes may prove to be a method of measuring flame temperatures. However, no quantitative measurements were carried out on the relation between temperature and emitted energy. All observations were made in the portion of the flame above the cone, except when otherwise noted.

The rapid decrease in intensity of the rotational lines of the H_2O molecule in the region from 13 to 15μ is caused largely by the absorption of the NaCl prism and by CO_2 in the atmosphere. The results shown in figure 4 are for a flame exhibiting maximum intensity at about 12μ. This flame was hotter than one showing constant energy, but the considerable drop in the observed energy in the 14μ to 15μ region is caused by absorption of the NaCl prism. This region of the spectrum was also observed with a KBr prism, and the envelope of the emission lines changed form with the temperature. For the hottest flames, the maximum intensity was observed at about 12μ, and with cooler flames, the maximum intensity was at about 15μ.
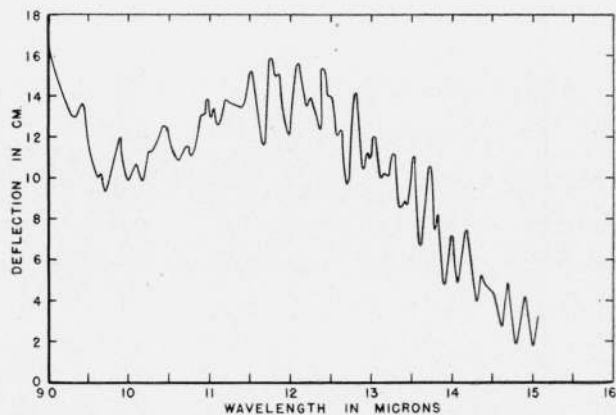
FIGURE 4. *Rotational lines of the hydrogen-oxygen flame from 9 to 15μ.*

The slits were 0.5 mm wide, and an NaCl prism was used.

The region from 15μ to 24μ has been measured with a KBr prism and is shown in figure 5. As the region of 24μ is approached, the energy becomes very small. The spectrum shown in figure 5 represents the observations on the hydrogen flame. Its emitted energy is greater than observed for the natural-gas flame, except in the region of 15μ.
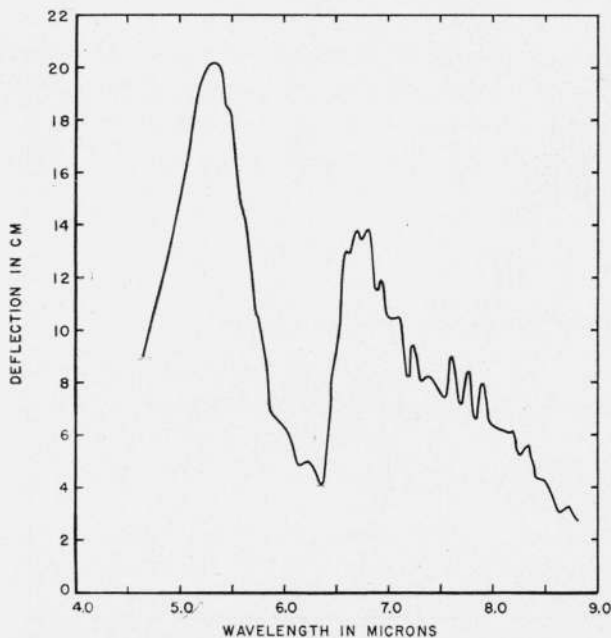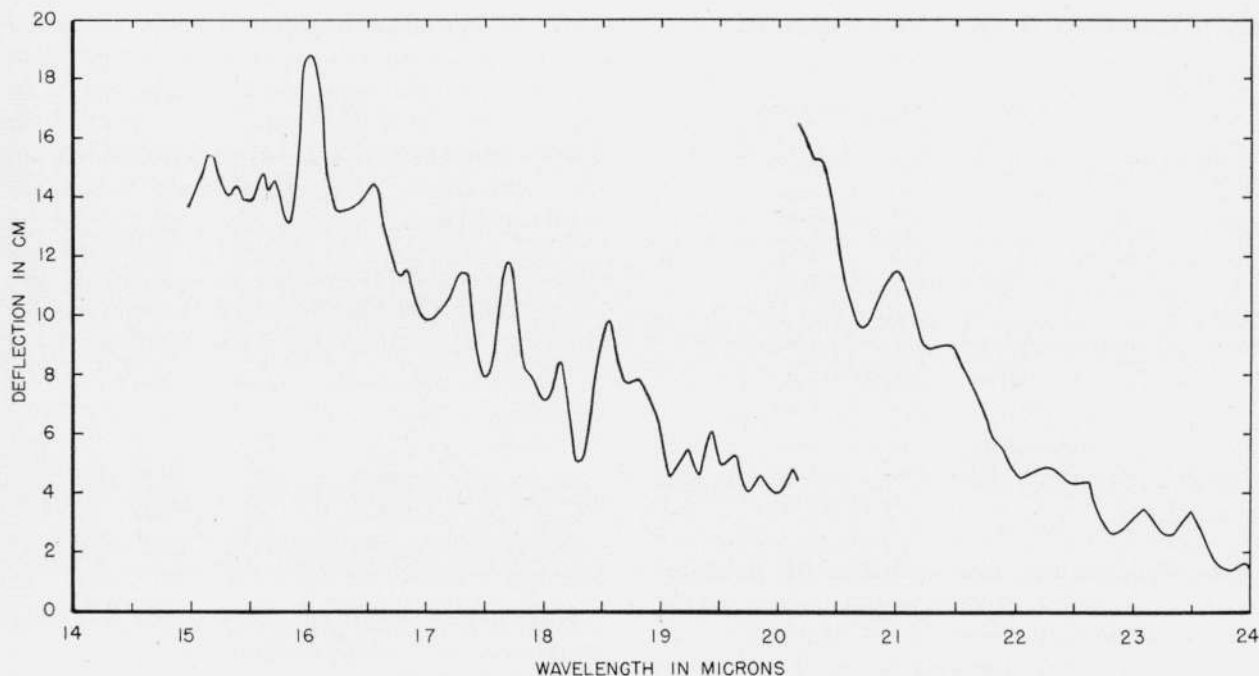

FIGURE 3. *Emission spectrum of the 6.26μ band of the* H_2O *molecule as obtained from a hydrogen-oxygen flame.*

A rock salt prism was used, and the slits were 0.28 mm in width.

FIGURE 5. *Rotational lines of the hydrogen-oxygen flame from 15 to 24μ measured with a* KBr *prism.*

The slits were 0.53 mm wide from 15 to 20μ and 0.7 mm from 20 to 24μ.

III. Discussion

In the previous paper (see footnote 2), measurements of the Bunsen flame were reported, and the bands produced by the CO_2 and H_2O molecules were noted. Because of some overlapping of the two spectra, certain regions of the spectrum could not be well segregated. For this reason a comparison of the hydrogen-oxygen torch flame with the Bunsen natural-gas—air flame would assist in the study of the emission spectra of the H_2O molecule. This is especially true of the region 1.7μ to 4.9μ. The long wavelength branch of the H_2O band at 2.7μ has been partially resolved, and about 19 lines can be seen in figure 2. By increasing the sensitivity of the instrument and increasing the temperature of the flame, lines are observed to about 3.8μ. The lines from 3.3μ to 3.8μ are probably produced by OH and H_2O molecules, but it has been found possible only in a limited region to make assignments from calculated values for transitions between the energy levels of either H_2O or OH. One exceptional instance will be discussed in another part of this paper. Higher resolution will be necessary in this region in order to permit accurate and complete assignment of lines to series.

It has been found that these lines check very closely with the series of $\Delta j = -1$ and $\Delta K = 0$ for the H_2O molecule and give rise to a spacing of about 20 cm^{-1}. However, there are several other series to be expected corresponding to the higher rotational states of the H_2O molecule, which would also give rise to lines in this region. So this one series may only, in part, explain the presence of these lines. The curves *b* and *c* of figure 2 show the effect of temperature on the lines, and the relative intensities are considerably altered. In table 1 the wavelengths and frequencies of the observed rotational lines are listed. Because of the high temperature of the flame, the rotational-vibrational bands have the energy reduced near the center and increased at larger rotational states. This causes the spread in frequency from the P to R maxima to increase. In the R branch there is considerable crowding of the rotational lines.

The band at 3.316 μ in figure 1 was observed at greatest intensity when the axis of a large cone of the flame was focused on the entrance slit of the spectrometer. The R branch is readily recognized, but the P branch of the band is weak. The zero branch is intense, and the region of maximum intensity is removed from the methane band, observed in absorption, by about 4 cm^{-1}. As

Infrared Emission Spectra of Flames

Wavelength	Wave number	Wavelength	Wave number
μ	cm⁻¹	μ	cm⁻¹
2.827	3,537	3.076	3,250
2.841	3,519	3.100	3,225
2.855	3,502	3.117	3,208
2.874	3,479	3.063	3,161
2.895	3,454	3.216	3,109
2.912	3,434	3.267	3,060
2.929	3,414	3.325	3,007
2.948	3,392	3.388	2,951
2.971	3,365	3.448	2,900
2.992	3,342	3.513	2,846
3,013	3,318	3.568	2,802
3,032	3,298	3.645	2,743
3,056	3,272		

higher temperatures are reached in the methane gas there will be a gradual shift to longer wavelengths for the zero branch of the band.

The authors are indebted to G. H. Dieke of Johns Hopkins Univ., who furnished them with a table of the calculated wave numbers of the vibrational-rotational lines of OH and also the wave numbers for the pure rotational lines.[4] Many lines arise from the 1→0 transition in vibrational levels and also from the 2→1 transition. The wave numbers calculated by Dieke were plotted, and it was found that the overlapping of the different series in the region from about 3,000 to 4,000 cm⁻¹ was so great that the available instruments could not separate the different states. However, in the region from 2,500 to 3,000 cm⁻¹, the overlapping is not so great, and a series of five lines that were observed in the hydrogen flame check will with predicted transition in the 2→1 vibrational band. The observed lines are shown in figure 2, c. With low oxygen concentrations in the mixture, these lines are very weak. The flame mixture was adjusted to give the greatest energy in this region, and it was a hot flame. When observations were made in the region of 3μ, it was found that the lines as shown in figure 2 were not as well resolved with a hot flame as with a moderate flame. But as the longer wavelength region of the band is reached, high flame temperatures are necessary to bring out the rotational lines. The 2→1 band has P, Q, and R branches and there are two series. Each line is double. Thus for each value of K (rotational levels) there exist four lines with

nearly the same wave number. It was not possible with the prism instrument to separate the lines, and only one maximum could be observed. In table 2 the calculated values are taken from Dieke's table, and they are averaged values of all four components. The experimental values are correct to 4 cm⁻¹.

TABLE 2. *Calculated and observed wave numbers for rotational lines in the P branch of the 2→1 band of* OH

K	P (calculated)	P (observed)	P (observed)
	cm⁻¹	cm⁻¹	μ
11	2946.3	2,950	3.388
12	2897.9	2,896	3.448
13	2848.9	2,848	3.513
14	2799.2	2,803	3.568
15	2748.8	2,744	3.645

These five lines that appear relatively free from interference or overlapping show such close agreement with predicted positions, that it appears practically certain that they constitute the part of the rotational structure of the P branch of the 2→1 band of OH, for K values, 11 to 15 inclusive. This structure is observed only because the emission of the H_2O molecules has become relatively weak in this limited interval. For the region of shorter wavelengths, the H_2O emission is so strong as to completely mask the OH spectral structure so that it is not possible to observe lines showing the characteristic intervals for the 2→1 band and the 1→0 band.

In table 3 the wavelengths and wave numbers of the rotational lines from the hydrogen flame are listed. The observations to 15μ were made with an NaCl prism and from 15μ to 24μ with a KBr prism.

This table comprises all of the measured values of the emission maxima that appeared in the recordings of the spectrum of the hydrogen flame, shown in figures 4 and 5. This observed spectrum appears to consist of the superposed systems of pure rotational lines of OH and H_2O.

In order to examine the evidence that the rotational OH emission spectrum has been produced, table 4, giving a comparison of the calculated and observed line positions, has been constructed. The calculated wave numbers, corresponding to K values 11 to 22, are obtained from Dieke's table.

[4] *G. H. Dieke*, Table of OH bands, private communication.

TABLE 3. *Observed rotational lines in the spectrum of the hydrogen flame in the region from 9 to 24 μ*

λ (μ) (observed)	cm⁻¹ (observed)	λ (μ) (observed)	cm⁻¹ (observed)	λ (μ) (observed)	cm⁻¹ (observed)
9.43	1,060	13.43	745	20.11	497
9.63	1,038	13.53	739	20.41	490
9.89	1,011	13.70	730	20.98	477
10.07	993	13.83	723	21.47	466
10.03	970	13.99	714	21.91	456
10.44	958	14.17	706	22.26	449
10.73	931	14.35	697	22.63	442
10.90	917	14.49	690	23.08	433
10.98	911	14.68	681	23.50	426
11.04	905	14.91	671	23.96	417
11.19	894	15.16	659	-------	-------
11.54	867	15.35	652	-------	-------
11.75	851	15.61	641	-------	-------
11.85	844	15.70	637	-------	-------
12.09	827	16.01	625	-------	-------
12.25	816	16.58	603	-------	-------
12.41	806	16.82	595	-------	-------
12.48	801	17.31	578	-------	-------
12.63	791	17.70	565	-------	-------
12.79	781	18.13	552	-------	-------
12.94	772	18.54	539	-------	-------
13.03	767	18.79	532	-------	-------
13.14	761	19.22	520	-------	-------
13.28	753	19.43	515	-------	-------

TABLE 4. *Observed and calculated wave numbers of the pure rotational lines of OH*

K	R (calculated)	R (observed)	R (observed)
	cm^{-1}	cm^{-1}	μ
11	431.8	433	23.08
12	465.3	466	21.47
13	498.4	497	20.11
14	530.9	532	18.79
15	562.7	565	17.70
16	593.8	595	16.82
17	624.2	625	16.01
18	653.9	652	15.35
19	682.9	681	14.68
20	711.0	714	13.99
21	738.3	739	13.53
22	764.8	767	13.03
23	790.6	791	12.63
24	815.6	816	12.25
25	839.9	844	11.85
26	863.4	867	11.53
27	886.2	886	11.28
28	908.2	911	10.98
29	929.5	931	10.73
30	950.0	---	-----
31	969.8	970	10.31
32	988.8	993	10.07
33	1007.0	1,011	9.89
34	1024.5	---	-----
35	1041.2	1,038	9.63
36	1057.2	1,060	9.43

Actually there are four possible lines for each K, but inasmuch as the resolution available in these experiments did not permit observation of these separate components, the four values are averaged in each instance to give the computed line position. Dieke's calculations were carried out only as far as K-value, 22. We have extended them to K, 36, by extrapolation. It is estimated that the error in this extrapolation cannot exceed 1 cm⁻¹, which is well within the estimated experimental error of the observations for this region of the spectrum, namely 4 cm⁻¹.

Of the 26 entries in table 4, all but 2 show agreement between the observed and calculated positions within the limits of experimental error. In almost all instances of failure to find experimental evidence for an emission line of OH, there is an intense maximum probably originating in H_2O overlapping the calculated position. Some of the listed lines appear only as bulges on the sides of the profiles of other intense maxima, but agreement with the predicted position seems to confirm their reality. The evidence for the reality of this system of rotational lines of OH rests mainly on its completeness rather than on the precision of the observations. The appearance of a small number of scattered combinations dispersed through another complex spectrum might well be regarded as fortuitous, but when the observed system is practically complete, the probability that it is real seems to be overwhelming.

The numerous remaining lines shown in figures 4 and 5 and listed in table 3, are produced by higher rotational states of the H_2O molecule. As mentioned above, some of these overlap or coincide with OH, making it practically impossible to estimate the relative intensities of the lines in the OH system. A noteworthy instance is the very intense maximum at 16.0μ, which undoubtedly receives by far the greater contribution from H_2O, masking an OH line in the same location.

IV. Conclusion

The emission spectra of a gas-oxygen and hydrogen-oxygen flame have been compared in the region from 1.7μ to 3.8μ. Nearly all of the energy in the 1.9μ region is produced by the H_2O molecule. A small increase in the energy of the gas flame in

the 2-μ region may be caused by emission of CO_2. The rotational lines that are observed at about 3μ are present in both flames, but they extend to longer wavelengths in hydrogen-oxygen flames. The intensity of the observed bands can be increased at least twofold by increasing the oxygen. The emission in the region of 10μ can be greatly increased with high-temperature flames. The energy remains about constant from 9μ to 16μ and then decreases gradually to 24μ. With a moderate flame temperature the energy increases from 9μ to 15μ and then decreases as the wavelength is increased.

In this study of the emission of flames, it has been shown that the amount of oxygen that is introduced into the flame has marked influence on the intensity of the band. In the 3-μ region, the relative intensities of the rotational lines may be varied considerably by changing the temperature of the flame. For a quantitative study of emission spectra originating in a flame, it would be necessary to measure the quantity of fuel gas and oxygen that are mixed for burning. A gas-oxygen torch or a regulated burner, giving rise to a steady flame, makes it much easier to obtain smooth traces on the recorder for the energy emitted. The results can be repeated closely. For quantitative determinations, the steady flame is very desirable. However, in many industrial applications, the turbulent flame is the more common type, and the Bunsen burner flame approaches nearer to industrial burner flames. This study has been chiefly concerned with the study of the emission spectra of CO_2 and H_2O in flames. The flames resulting from burning various hydrocarbons and alcohols will also have considerable energy emitted by CO_2 and H_2O molecules. There may be other bands in the observed flame spectra of various fuels that are characteristic of the molecular or atomic groups. The bands are usually of low intensity.

In addition to a controlled burner, a spectrometer of high aperture ratio is needed. This makes it possible to observe low-intensity bands. Because of the decrease in the observed intensity produced by the absorption of H_2O and CO_2 molecules in the air, an instrument that is free from atmospheric absorption is better suited for quantitative measurements. For the study of many problems, an instrument of moderate resolution is satisfactory. In the measurement of the rotational lines within a band, a grating spectrometer is better suited.