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Flame Spectrum of Acetylene from 1 to 5 Microns[1]

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The spectrum of an oxyacetylene flame obtained with a welding torch has been observed and measured by using a Perkin-Elmer spectrometer, with a LiF prism. Bands were observed at 1.2, 1.3, 1.52, 1.85, 2.0, 2.3, 2.48, and 2.8 μ, which agree in position and general appearance with bands originating in the methane flame, except for newly observed bands at 1.5 and 2.3 μ. The 1.5-μ band probably represents the $\nu_1+\nu_3$ combination in the C_2H_2 molecule, and the 2.3-μ band is probably the *R*-branch of the 2 ν_1 band of CO, the *P*-branch being overlapped by the *R*-branch of the 2.7-μ H_2O band.

The band at 2.8 μ shows fine structure on the long wavelength side consisting of 29 lines between 2.8 and 3.6 μ, when a flame of reduced oxygen content is used. With a hot flame obtained with the maximum amount of oxygen, this number is reduced to 10 in the region from 3.1 to 3.7 μ, some of which show good agreement with calculated values for the 2→1 band of OH. On the long wavelength side of the intense CO_2 emission band at 4.45 μ, 27 rotational lines have been observed, some of which agree closely with the rotational absorption lines of the CO fundamental. This structure was also observed in the methane-oxygen flame.

Evidence for the validity of the interpretations of certain features of these bands as originating in OH and CO is critically examined, and it is concluded that further observations with the higher resolution provided by a grating spectrometer, will be required to establish the certain identification of the spectra of OH and CO in the flame.

I. Introduction

Recent spectrometric studies [1, 2][2] of the Bunsen flame and torch flames of natural gas and oxygen mixtures have revealed a considerable amount of structure, not previously observed, in the infrared emission bands. The water vapor and carbon dioxide bands account for nearly all of the emitted energy. There are however a number of other possible features of such flame spectra, interest in which has to a great extent prompted the present series of investigations. These features include bands originating in other combustion products, and in the thermally excited gas molecules previous to combustion. Vibrational-rotational bands of OH appear with increasing intensity as the flame temperature is raised. In the region from 2.8 to 3.7 μ there is observed a series of rotational lines that are produced by OH and H_2O. The relative intensities of these two groups are a function of flame temperature and the chemical composition of the burning substances.

In addition to the bands originating in CO_2, H_2O, and OH, there are bands of low intensity that are attributed to methane, the principal constituent of the natural gas used in the earlier experiments, which is that supplied in the local area for household and commercial use. These bands are detected only when observations are made on the cone of the flame, the under surface of which is the only region where appreciable numbers of thermally excited molecules of unburned gas might be expected to be found.

The study covered by this report was undertaken with a threefold purpose: to determine if the OH rotational components are more intense for C_2H_2 than for CH_4 in combustion; to ascertain in the case of acetylene whether a sufficient

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[1] Part of the subject matter of this paper was presented at the Detroit meeting of the Optical Society of America, Oct. 21 to 23, 1948.

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

amount of CO was in the flame as an intermediate combustion product to permit observation of the characteristic infrared bands, under the most favorable conditions of combustion; and, if possible, to observe the infrared emission bands of the C_2H_2 molecule.

The emission flame spectra of any of the simple hydrocarbons, either saturated or unsaturated, when mixed with air or oxygen, are closely similar in the general features of the energy distribution pattern. It is possible, however, to produce marked changes in the structure of such spectra by varying these conditions, as for instance by increasing the proportion of oxygen in the mixture, which has the effect of elevating the flame temperature as long as the fuel mixture remains on the rich side. The energy pattern is also highly dependent on the region of the flame from which the energy is directed into the spectrometer. The hottest part of the flame, in general, is that just above the tip of the cone, whereas the cone itself is cooler and may emit considerable amounts of radiant energy from unburned molecules of gas.

II. Experimental Procedure

This investigation of the acetylene-oxygen flame was confined to the spectral region from 1 to 5 μ. A Perkin-Elmer infrared spectrometer, fitted with a LiF prism, was used as the dispersing instrument. The only modification of the spectrometer was the removal of the cover of the source box and rotation of the plane mirror to permit location of the flame source at a convenient point without removing or disturbing the globar source unit. A continuous record of the spectrum was obtained by employing the amplifying and recording equipment described in an earlier publication [3]. An industrial oxyacetylene welding outfit, kindly placed at our disposal by this Bureau's welding shop, was used to provide the flame source. The assembly consisted of the usual gas cylinders, pressure regulators, and an assortment of welding torches with port openings of different sizes.

Records of the emission spectrum of acetylene-oxygen mixtures under various conditions of combustion and for selected regions in the flame are reproduced in the figures that follow. In figure 1

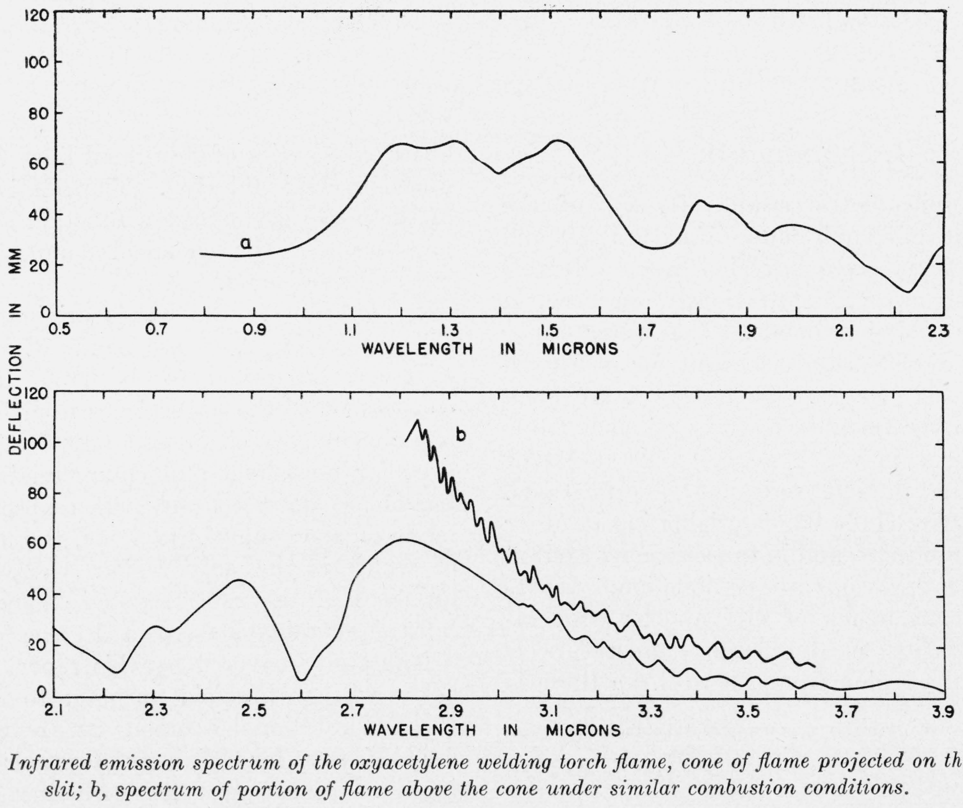

Figure 1. *a, Infrared emission spectrum of the oxyacetylene welding torch flame, cone of flame projected on the spectrometer slit; b, spectrum of portion of flame above the cone under similar combustion conditions.*

(curve *a*) is shown the emission spectrum of the cone of the flame. The amount of oxygen in the mixture was relatively small, so that a cone about 2 cm high was maintained above the tip of the torch. The emitted energy includes the spectrum originating in the cone, together with that from the portion of the surrounding flame at the same elevation. The figure shows emission bands at 1.2, 1.3, 1.5, 1.8, 2.0, 2.3, 2.5, and 2.8 μ. All these bands, except those at 1.52 and 2.30 μ, are produced by carbon dioxide and water vapor. There is considerable overlapping of portions of the P, Q, and R branches of some of the bands occurring in this spectral region. When the cone is focused on the slit, the carbon dioxide and water vapor spectra are reduced in intensity in comparison with higher portions of the flame. These spectra are much more intense above the cone, and previous studies on methane [2] have shown these bands in good detail. The purpose of the study of the emission from the cone was to ascertain if the spectrum originating in the heated acetylene molecules could be detected.

The band recorded at 1.52 μ was not present in the methane spectrum [1] and is attributed to the acetylene molecule. It checks well in position with the $\nu_1+\nu_3$ vibration of acetylene. The intensity is low, but the band appears in a region that is free of bands of water vapor and carbon dioxide and can be easily observed.

The band at 2.3 μ is interpreted as being part of the harmonic band of CO, observed in absorption with high resolution by Lagemann, Nielsen, and Dickey [4]. It should consist of P and R branches, but the P branch of this CO band is overlapped by the R branch of the ν_3 vibrational band of H_2O at 2.5 μ, which makes it impossible to observe its real profile. Further evidence of CO emission in the torch flame will be considered in a discussion of structural features observed in the 4.7-μ region.

The fundamental band, ν_3, of acetylene is located at 3 μ. In this series of observations its presence could not be clearly established. The *P* branch of the ν_3 vibrational band of H_2O is in the same region, and because of its great intensity could have completely obscured the emission from C_2H_2. It may be noted that the curve reproduced shows a broad emission band extending from 2.6 to beyond 3.1 μ, with almost no structure, in marked contrast to the traces obtained with methane. It is probable that the acetylene trace through this region represents a superposition of the spectra of H_2O, C_2H_2, and other molecules formed by combustion.

When the region of the flame above the cone was focused upon the slit, an energy trace illustrated by curve *b*, figure 1, was obtained. The conditions of combustion were maintained the same as for curve *a*. It is to be noted that much more fine structure is observed for the region from 2.8 to 3.6 μ, and the intensity of emission is greater than for the corresponding observations on the cone of the flame.

Figure 2, curve *a*, illustrates the emission pattern from 1.6 to 3.7 μ, when a moderate amount of oxygen, more than that used in the observations illustrated by figure 1, is introduced into the burning mixture. The region of the flame above the cone was selected for observation.

The zero branch of the 1.85-μ band originating in the H_2O molecule appears rather sharp, but the *P* branch at 2 μ is quite broad. This modification of its profile is caused by three CO_2 emission bands in this region. The 2.3-μ band, attributed to CO, is greatly reduced in intensity, whereas there is a marked increase in emitted energy throughout the 2.7- to 3.0-μ region. It was difficult to resolve the fine structure in the latter region. The rotational structure is clearly marked from 3 to 3.7 μ. These rotational lines have been studied previously in connection with the investigation of the methane flame. Although similar in appearance, some differences in clearness of the observed fine structures, attributed to different proportions of oxygen, are apparent.

In figure 2, curve *b*, is shown the region from 3.1 to 3.7 μ when still larger amounts of oxygen are supplied to the burning mixture. The flame is very hot, and the observed rotational lines, having a different spacing from that appearing when low oxygen is introduced, are very prominent. Altogether 10 emission maxima of nearly uniform spacing are clearly discernible in this wavelength interval. Of these, the five lines from 3.35 to 3.7 μ agree in position, within the limits of experimental error of these observations, with the rotational lines of OH as calculated by Dieke [5] for the $2\rightarrow1$ rotational-vibrational band, corresponding to the transitions, P(11) to P(15). The five emission maxima from 3.1 to 3.35 μ do not correspond in wave number to the $1\rightarrow0$ or $2\rightarrow1$ band. It is possible that these lines are blends

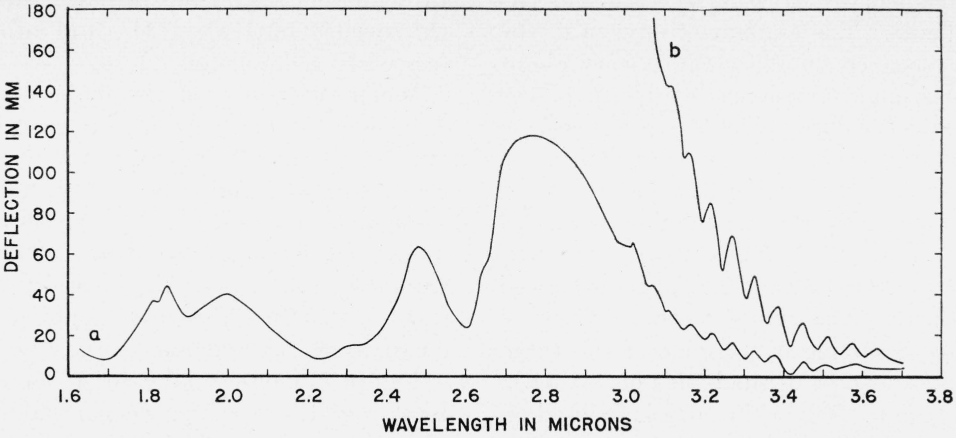

FIGURE 2. *a, Emission spectrum of the oxyacetylene flame, region above the cone, oxygen content greater than under conditions illustrated by figure 1; b, spectrum of oxyacetylene flame between 3.1 and 3.7μ, maximum oxygen content.*

of parts of each of these bands that are overlapped, and that the resolution of the instrument is not sufficient to separate the components of each band. Furthermore, some of the rotational components in the P-branch of the ν_3 band of H_2O may well extend into this region, particularly those associated with high-level transitions, which may be excited, at these elevated temperatures, and which would be located at longer wavelengths than transitions terminating in the normal state. In this connection it is particularly emphasized that the distribution and relative intensities of the fine structure components are extremely sensitive to proportions of the fuel mixtures, permitting considerable shifting of observed maxima where the resolution is insufficient to reveal all the details. The calculated and observed wave numbers as well as the line numbers, which are the K-values for the initial levels in absorption, are given in table 1. The calculated values for each band series are taken from Dieke's table. It is to be noted that the calculated wave numbers used for comparison with observed values are in each instance the average of four numbers, required by the existence of two electronic band systems, characterized by analogous vibrational levels, each of which is split by a spin doubling. The four possible transitions being of equal statistical probability, an arithmetical mean is taken. The experimentally observed rotational structure of the high-temperature acetylene flame corresponds almost identically with the spectrum observed in this region with the high temperature hydrogen-oxygen flame, which was recently measured with the same instrument.

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

K	P (calculated [5])	P (observed)	P (observed)
	cm^{-1}	*cm*$^{-1}$	μ
11	2945.8	2952	3.388
12	2897.8	2899	3.449
13	2848.9	2848	3.511
14	2799.3	2801	3.570
15	2748.8	2749.5	3.637

The CO_2 emission band at 4.4 μ, originating in the hot acetylene flame, is of high intensity. The corresponding absorption band, located at 4.25 μ, is also very intense, being nearly opaque at 4.23 and 4.27 μ, where the respective minima of the two branches of the band are located. Part of this absorption may be produced by reversal in the flame. The concentration of CO_2 in the air in the room is also increased, with the result that there is increased absorption by CO_2 in the air path between source and spectrometer. The energy distribution pattern in this region is reproduced in figure 3. Comparison with the corresponding trace for a Bunsen burner flame [1] shows both absorption and emission to be more pronounced in the instance of acetylene, in line with a relatively much more rapid and abundant evolution of CO_2 in the burning of C_2H_2.

In the region between 4.8 and 4.9 μ, as shown in figure 3, a structural pattern was observed, which,

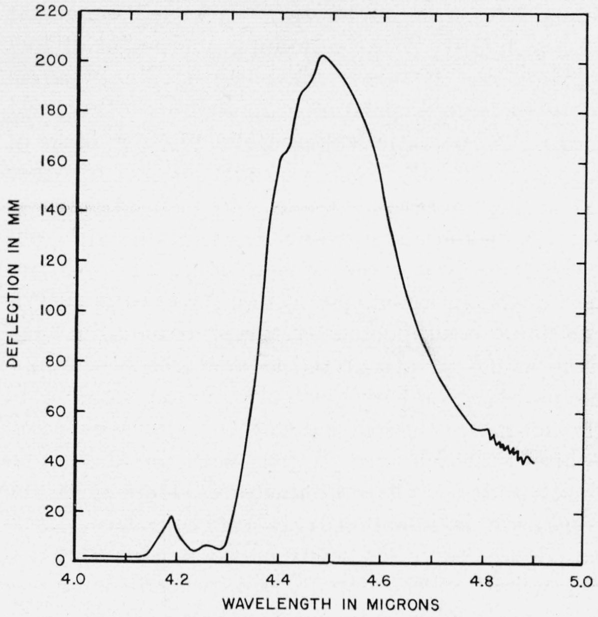

FIGURE 3. *Emission spectrum of the oxyacetylene flame in the region between 4.1 and 4.9μ, showing absorption and emission of* CO_2, *also fine structure attributed to* CO.

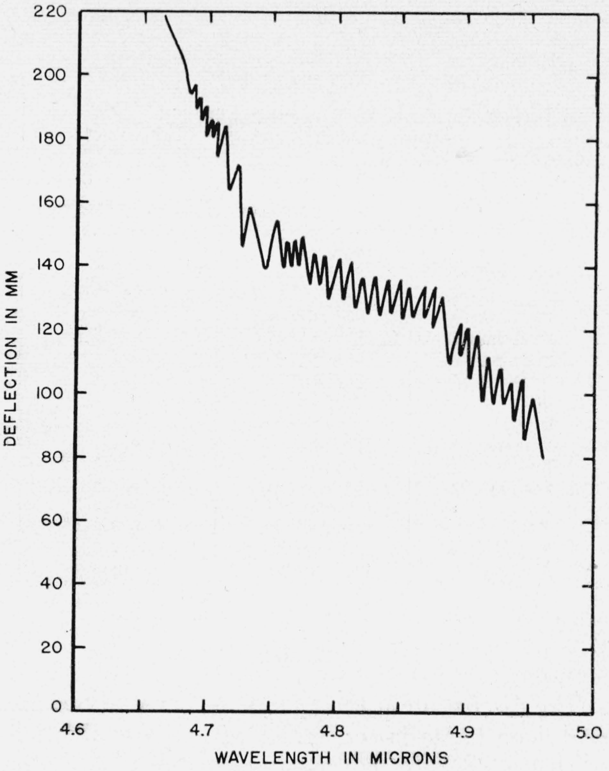

FIGURE 4. *Small-scale reproduction of fine structure pattern, attributed to* CO, *under optimum conditions for observation.*

although not of high contrast with respect to the background energy, exceeded the noise level of the amplifier. On the basis of preliminary observations, it was apparent that this structure might have been produced by variations in the flame intensity, or by the rotational structure originating in another molecule superposed on the portion of the CO_2 band extending into this region. By reducing the oxygen in the mixture, it was found possible to operate the flame in such a manner as to increase the contrast and cause the lines to stand out strongly above the background of the CO_2 emission band. This seemed to eliminate flickering as a cause of the effect. A trace of one of the records is reproduced in figure 4. This record was made under the most satisfactory conditions attained in these experiments. A possible interpretation of this structure, on the basis of the magnitude of the separation of the components and the probable presence of intermediate combustion products, is that it originates in CO, specifically the long wavelength portion of the negative branch of the 1→0 band. By comparing the wavelengths of the emission peaks with the absorption data of Lagemann, Nielsen and Dickey [4], it is found that seven, or roughly half of the measured maxima in the interval where reported data permit comparison, agree within experimental error with the absorption lines reported by those authors. This comparison is shown in table 2, which lists the positions of all maxima observed in this work. Possible reasons for disagreement of the other emission maxima are the presence of additional lines from the 2→1 band of CO, also the partially superposed 1→0 isotope band of $C^{13}O^{16}$, and that there may be considerable structure from high-level transitions of CO_2. All of these causes may be expected to produce shifts in the observed maxima where the resolution is incomplete. A reexamination of the recordings made with the methane flame showed the same structure to be present in the spectrum of burning mixtures. The overlapping of the CO_2 and CO spectra, and the fact that CO burns readily after formation, makes it difficult to observe this structural pattern unless the critical conditions are maintained. The use of a LiF prism, which reaches its highest dispersion in this region, has of course been highly advantageous in the current investigations of flame spectra.

TABLE 2. *Comparison of data from the spectrum of* CO *with observed structural features in the flame spectrum of* C_2H_2

Observed rotational structure in the absorption spectrum of CO [4]		Observed emission maxima in the C_2H_2 flame
$C^{12}O^{16}$	$C^{13}O^{16}$	
Wave number cm^{-1}	*Wave number cm*$^{-1}$	*Wave number cm*$^{-1}$
P(10) 2103.12	----------	2103.0
P(11) 2099.01	----------	2100.3
----------	----------	2098.1
P(12) 2094.69	P^1(1) 2092.35	2094.6
P(13) 2090.56	P^1(2) 2088.57	2091.1
P(14) 2086.27	P^1(3) 2084.85	2087.2
P(15) 2081.95	P^1(4) 2081.12	2082.4
P(16) 2077.57	P^1(5) 2077.33	2078.1
P(17) 2073.19	P^1(6) 2073.49	2075.1
P(18) 2068.69	P^1(7) 2069.52	2070.4
P(19) 2064.31	P^1(8) 2065.73	2066.5
P(20) 2059.79	P^1(9) 2061.81	2061.8
P(21) 2055.31	P^1(10) 2057.81	2058.9
----------	P^1(11) 2053.79	2054.6
P(22) 2050.72	P^1(12) 2049.75	2051.3
P(23) 2046.14	P^1(13) 2045.61	2048.3

III. Conclusions

The discussion of the results of this study of the acetylene flame is concerned with the evaluation of the evidence of emission spectra originating in C_2H_2 itself, and in CO, and OH. The presence of C_2H_2 is indicated by a relatively faint band at 1.52 μ, attributed to the $\nu_1+\nu_3$ vibration, which was not observed in the other flame spectra studied, also by a somewhat more pronounced background of emission in the 3-μ region where the fundamental band is expected to appear. No fine structure was observed in either of these features.

It is concluded that flames of all fuels mixed with high proportions of oxygen, hydrogen, methane, and acetylene emit the spectrum of the free radical OH, because of the appearance of an apparently identical set of five successive emission maxima that agree within experimental error with the positions of a succession of minima in the 2→1 absorption band as computed by Dieke. Support for this conclusion is weakened somewhat by the failure of the adjoining succession of five maxima on the short wavelength side to agree with computed positions in this or other OH series. A possible explanation of this lack of agreement on the basis of superposition of other structural features, mainly those originating in H_2O, will require further observation with improved resolution for confirmation. The excitation of the emission spectrum of CO in the acetylene flame is supported by the presence of a weak band at 2.3 μ, interpreted as a branch of the harmonic band, and by a set of emission maxima on the long wavelength side of the emission band, ν_3 of CO_2, which agree in part with the absorption minima for the CO fundamental. Here again the resolution is insufficient to separate any superposed structures that may cause an apparent displacement of the bands and prevent complete agreement with calculated values. It is to be emphasized that, although the evidence leading to the interpretations given is considered fairly strong, it is not altogether conclusive, so that the interpretations are to be regarded as tentative until the observations can be repeated with higher resolution. Such observations are expected to be undertaken in the near future with a grating spectrometer now rapidly approaching completion.

IV. References

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WASHINGTON, February 8, 1949.