Infrared Emission Spectra of Cyanide and Dicarbon Radicals [1]

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The infrared region from 1 to 1.3 microns has been studied for low-intensity radiation in an oxyacetylene flame with a rich fuel mixture. When the inner cone was focused on the slit of the spectrometer, two regions of the spectrum showed rotational structure that has been identified as arising from C_2 and CN. The lines have been classified, and from their intensities the flame temperature has been found to be $2,600° \pm 200°$ K.

1. Introduction

Several studies have recently been reported [1, 2, 3] [3] in which flame spectra were observed in the near infrared region under high resolution. The rotational structure in the vibration-rotation bands of CO, OH, and H_2O was resolved to an extent, permitting the determination of the rotational energy distribution, which corresponded to equilibrium temperatures in the neighborhood of $2,600°$ K. This is somewhat lower than the temperature of $3,000°$ that has been reported for the OH distribution on similar flames, when studied by the near-ultraviolet spectra [4,5]. In the latter case the spectra arise from electronic transitions of high-transition probability, with lifetimes of the excited state from 10^{-6} to 10^{-8} sec, whereas for the infrared vibration-rotation transitions the transition probability is much less, and the excited-state lifetimes are from 10^{-2} to 10^{-3} sec.

It was therefore a matter of interest that, in the course of exploratory studies, it was possible to identify electronic transitions, from the CN and C_2 radicals, falling in the infrared region. A determination of the rotational temperatures and concentration of excited molecules from these spectra might shed further light upon the nature of the combustion process and the region of flame radiation, since here, we are observing transition of relatively high probability arising from states of low excitation potential (1 to 2 electron volts). The present paper reports some details of these observations, which, although not of high quantitative accuracy, appear to establish that the infrared radiation, from whatever source, yields somewhat lower temperatures than the shorter wave radiation.

2. Experimental Method

The measurement of the spectrum of flames in the near infrared region has been carried out by the use of a grating spectrometer. The grating has 15,000 lines per inch and has a ruled surface of 5 by 7½ in. A lead sulfide cell is used as the detector, and a chopper placed in front of the slit modulates the radiation with a frequency of 1,080 c/s. With intense spectral lines a partial resolution of 90,000 is obtained. The optical arrangement of the spectrometer has been described [6] and will not be repeated here.

The emission spectrum of a fuel-rich oxyacetylene flame was measured in the region from 1.0 to 1.3 μ. In the region above the inner cone of the flame the spectrum showed the emission bands of H_2O, and OH with a strong continuous background. When the flame was adjusted so that the inner cone extended about 2 in. above the tip of the torch burner, an entirely different spectrum was observed from the inner cone of the flame. Figure 1 shows the observed spectra of CN, and figure 2 shows the observed spectra of C_2.

3. Discussion of CN Bands

CN has two intense electronic band systems, each with an f-value in the neighborhood of 0.02. The violet system ($^2\Sigma^+ - ^2\Sigma^+$) is a characteristic feature of carbon-rich flames burning in air; the red system ($^2\Pi_i - ^2\Sigma^+$) has also been observed in such sources, but less prominently, in the red and near infrared. The origin of this system has recently been found [7, 8] to lie farther in the infrared than was earlier believed. The (0,0) band, which extends from 9195.6 cm^{-1} to beyond 8500 cm^{-1}, has its origin at 9117.3 ± 0.1 cm^{-1}. This band was photographed with high resolution by Kiess [8], who used a carbon arc in air as the source, and it was observed with a low-resolution infrared spectrometer by Herzberg and Phillips [7] from a discharge through benzene vapor.

This band has been observed as a very prominent feature of the radiation from the inner cone of a fuel-rich oxyacetylene flame. In the radiation from the outer cone it may be present very weakly but is masked by water-vapor emission in the same region. The slit width was about 1.5 cm^{-1}. Under these conditions the complex rotational structure, consisting of 6 strong branches and 2 weak satellite branches, is not fully resolved, but a number of the lines, especially in the strong Q branches, stand out clearly.

[3] Figures in brackets indicate the literature references at the end of this paper.
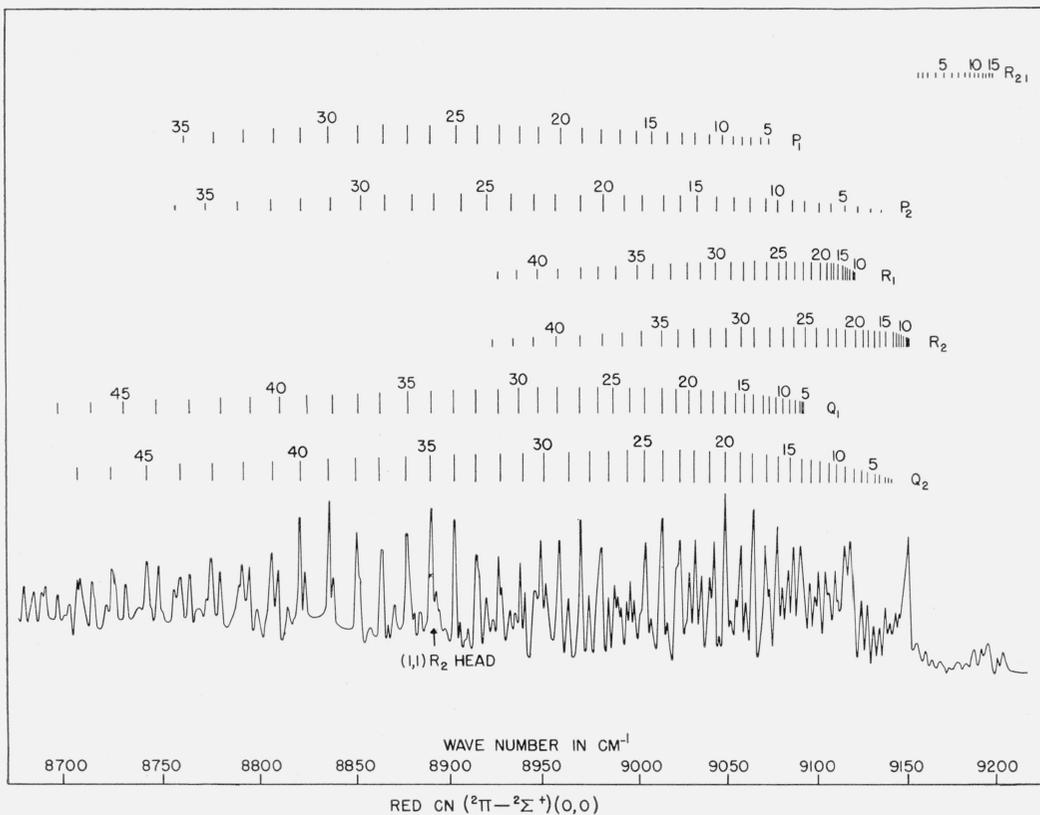
FIGURE 1. *Infrared emission of* CN *in the region 1 to 1.2 μ as observed from an oxyacetylene flame.*

The lines in the upper part of the figure show the calculated position and intensity for this band.
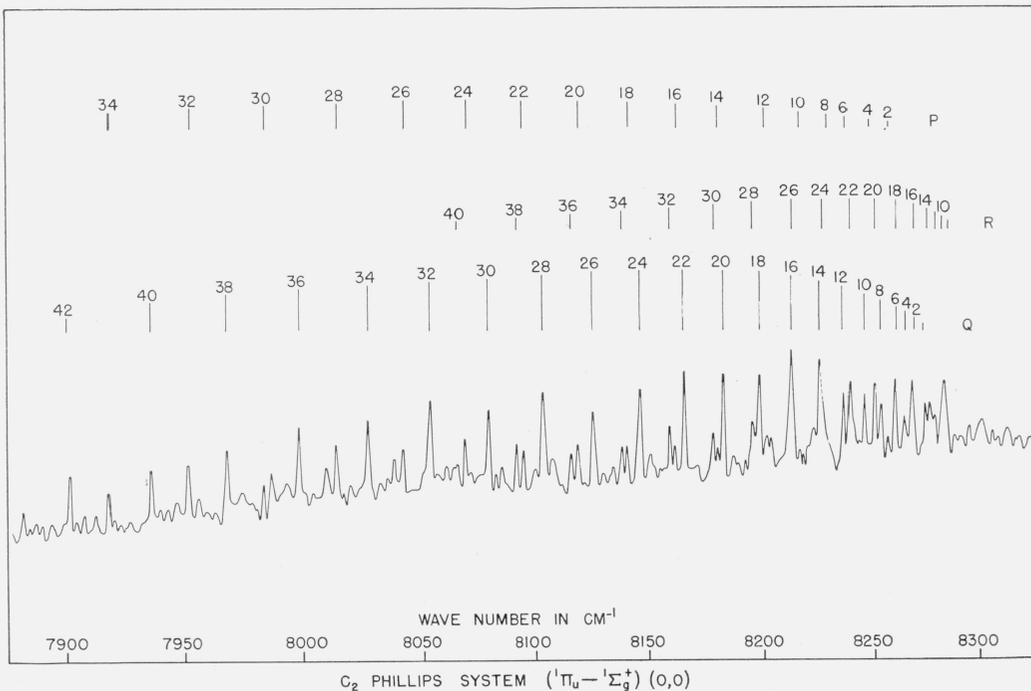

FIGURE 2. *Infrared emission spectrum of* C_2 *from an oxyacetylene flame.*

The positions of the rotational lines of the P, Q, and R branches are shown above the spectrum.

In view of the imperfect resolution, it does not seem feasible to use this band for a determination of the rotational temperature. It was, however, verified that the observed intensities are in rough agreement with the calculated intensity by assuming $T = 2,500°$ K. Hence one may conclude that there is no large deviation from thermal equilibrium involved in the excitation of the various rotational levels within this band.

The order of magnitude of the $CN^2\Pi$ concentration may be very roughly estimated. If we accept the estimate of Herzberg and Phillips [7], the integrated intensity of the entire red system corresponds to an f-value of 0.02. By assuming a temperature in the range $T = 2,800°$ K, the vibrational distribution is such that about 59 percent of the molecules are in the zero level. Since the (0,2) band at 5,059 cm^{-1} could not be observed, the (0,1) band at 7,075 cm^{-1} could barely be recognized. These facts indicate that at least 50 percent of the total radiation from the $v = 0$ level is in the (0,0) state. Hence $\int k_\nu d\mu$ for (0,0) $\sim 5 \times 10^5 \times 0.5 \times 0.6 \sim 1.5 \times 10^5$ cm^{-2} atm^{-1}. From a rough estimate based on the intensity of other thermally excited spectra, the average emissivity over the band width of 300 cm^{-1} is ~ 0.01. Accordingly, $N_{CN^*} = 0.01 \times 300/1.5 \times 10^5 = 2 \times 10^{-5}$ cm atm. For the inner-cone thickness of 0.10 cm, this gives a concentration of CN^* of 2×10^{-6} atm; if in thermal equilibrium with the ground state, the total concentration of $CN = 2 \times 10^{-4}$ atm. This is 10^5 times greater than the estimated concentration at therman equilibrium. If these very rough results are confirmed by more quantitative measurements of the emissivity, it means that the CN^* is formed in some of the chemical reactions in the inner cone, and that the radiation is chemiluminescent in origin. Temperature measurements derived from observations of these bands would then have little meaning, except to demonstrate whether the radical survives through enough collisions to attain thermal equilibrium within its rotational modes. This appears to be the case.

4. Discussion of C_2 Bands

Several electronic band systems have been observed for C_2 in flames. The ground state is $^3\Pi_u$; the Swan bands in the visible spectrum are due to a transition from the $^3\Pi_g$ to the ground state. Two low-lying singlet states are also known; the transition between them, $^1\Pi_u - {}^1\Sigma_g^+$, was discovered by Phillips [9], who located the (2,0), (3,1), (3,0), (4,1), and (5,2) bands in a discharge. The same bands, lying between 7700 to 9000 A, were found by Hornbeck and Herman [10] in the photographic infrared in the oxyacetylene flame. As the constants of both electronic states are accurately known ($^1\Sigma_g^+$ is the lower level of the Mulliken bands, and $^1\Pi_u$ the lower level of the Deslandres-D'Azumbuja bands), it is possible to calculate with precision the positions of the lines of the (1,0), (0,0), and (0,1) bands, which should be the strongest bands of the system under conditions of thermal excitation. The f-value of the system has not been measured or calculated, but it should be of the same order as the Swan bands, and the other band systems involving similar electron-transfer spectra [11], namely, ~ 0.02.

We have now observed the (1,0) and (0,0) bands, which are the most intense features of the emission from the inner cone of the fuel-rich oxyacetylene flame in the region of the spectrum where they occur. The (1,0) band has its head at 9865.7 cm^{-1}, (10107 A), and may be followed to beyond the 40th line of the Q branch, at 9491.5 cm^{-1}. The rotational structure is relatively open, there being only the three branches characteristic of a $^1\Pi_u - {}^1\Sigma_g^+$ transition; a strong Q branch, and P and R branches that are weaker by a factor of 2. Moreover, because of the zero spin of the C^{12} nucleus, only even values of J, for the lower state, appear. The spacing of the Q-branch lines at the maximum, near $J = 24$, is 22 cm^{-1}, which permits clear resolution of all three branches, even with the relatively wide slits of ~ 1.5 cm^{-1} required. The (1,0) band is overlapped by a strong violet-shaded band head at 10330 A. As the second-order visible radiation was not completely removed by filters, this is clearly the (0,0) Swan band in the second order, the strongest band in that system. It is of interest that the ratio of intensity of the Swan-Phillips systems showed no significant variations with conditions of excitation.

The (0,1) band falls in the region of strong emission due to OH and moderately strong emission due to H_2O. A number of the stronger lines of the Q branch, from $J'' = 10$ to 30, may be identified by comparing tracings of the inner- and outer-cone radiation in this region; the inner cone favors C_2, the outer, H_2O. Considerable overlapping occurs, however, and, under the most favorable conditions, the intensity of C_2 does not exceed 30 percent of that of the OH lines in the region.

The (0,0) band is quite free from overlapping under the conditions where it appears strongly. Hence the relative intensities of the resolved Q, P, and R lines may be used to determine a C_2 rotational "temperature". The rotational transition probabilities for $^1\Pi - {}^1\Sigma$ are well known [12]. By plotting log $I/S_{j}\nu^4$ against E' a fairly good straight line is obtained, whose slope corresponds to a temperature of $2,600 \pm 200°$ K.

This "temperature" determination from the observation of a band of C_2 is relatively rough, due to the necessity of using wide slits and the presence of a considerable background and noise level. It is certain, however, that the rotational distribution yields a temperature of the same order as that given by CO and OH, for the outer cones, and indicated by CN, as well as what is calculated for over-all thermal equilibrium in the reaction products. This is in marked contrast to findings in similar flames when the Swan bands of C_2 are observed [13] where "temperatures" in excess of $4,000°$ K are indicated. This would appear to mean that the triplet states, involved in the Swan transition, are formed in the chemical reaction with excess rotational energy and that they are not able to attain equilibrium through

collisions in their radiative lifetime of $\sim 10^{-7}$ sec. The singlet states, on the other hand, involved in the Phillips transition are formed either by chemical reaction with no excess rotational energy or by collisions efficient enough to bring their rotational mode in equilibrium with the rest of the flame in their lifetime of $\sim 10^{-6}$ sec.

The emissivity of the strongest lines of the (0,0) and (1,0) bands is of the same order as that of $CN(0,0)$; i. e., perhaps 0.03. Since most of the radiation from the 0 level is in the state (0,0) the (0,1) state is less intense by a factor of 5 or thereabouts, and we can, as with CN, estimate the concentration of excited $C_2({}^1\Pi)$, if an f-value of 0.02 is assumed for the system. Because of the more-open rotational structure, the result is about one order less than CN, i. e., about 10^{-7} cm atm for the excited state. The position of the singlet system relative to the ground state is not precisely known; Herzberg estimates $5,300$ cm^{-1} for the ${}^1\Sigma_g^+$ level. This would place the total C_2 concentration at about 10^{-4} atm, again very much in excess of the calculated equilibrium values, indicating a chemiluminescent rather than a thermal origin for this species.

Some of this work has been reported before the American Physical Society [14].

5. References

[1] E. K. Plyler, W. S. Benedict, and S. Silverman, J. Chem. Phys. **20,** 175 (1952).
[2] W. S. Benedict, E. K. Plyler, and C. J. Humphreys, J. Chem. Phys. **21,** 398 (1953).
[3] W. S. Benedict, Arnold M. Bass, and E. K. Plyler, NBS J. Research **52,** 161 (1954) RP2485.
[4] A. G. Gaydon, Spectroscopy and combustion theory (Chapman & Hall, Ltd., London, 1948).
[5] H. P. Broida, J. Chem. Phys. **19,** 1383 (1951); H. P. Broida and K. E. Shuler, J. Chem. Phys. **20,** 168 (1952); H. P. Broida and G. T. Lalos, J. Chem. Phys. **20,** 1466 (1952).
[6] Earle K. Plyler and Norman Gailar, J. Research NBS **47,** 248 (1951) RP2249.
[7] G. Herzberg and J. G. Phillips, Astrophys. J. **108,** 163 (1948).
[8] C. C. Kiess, Astrophys. J. **109,** 551 (1949).
[9] J. G. Phillips, Astrophys. J. **107,** 389 (1948).
[10] G. A. Hornbeck and R. C. Herman, J. Chem. Phys. **19,** 512 (1951).
[11] G. Stephenson, Proc. Phys. Soc. [A] **64,** 99 (1951).
[12] G. Herzberg, Molecular spectra and molecular structure I. Diatomic Molecules, p. 208 (D. Van Nostrand, New York, N. Y., 1950).
[13] A. G. Gaydon and H. C. Wolfhard, Proc. Roy. Soc. [A] **201,** 570 (1950).
[14] W. S. Benedict and Earle K. Plyler, Phys. Rev. **83,** 245 (1951).

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