Experimental Determination of Rotational Temperatures and Concentrations of OH in Flames from Emission Spectra*

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In order to illustate the use of two-path experiments for correcting for self-absorption, experimental studies to determine the rotational "temperatures" and concentrations of OH in flames burning at atmospheric pressure have been carried out. For mixtures of H_2, C_2H_2, and O_2, as well as for C_2H_2-O_2 flames diluted with A, "anomalous" rotational "temperatures" were observed under conditions in which strong self-absorption was clearly indicated by the intensity ratios for the double-path to the single-path experiments. Unequivocal quantitative estimates of rotational temperatures and of OH concentrations cannot be carried out, even on the assumption that the emitting system is isothermal and in equilibrium. However, by using the results of theoretical studies on two-path experiments carried out by one of us, it is possible to obtain reasonable upper limits for the temperatures and lower limits for the OH-concentrations, based on an assumed Doppler contour for the line-shape and utilizing Oldenberg's estimates for the f values of representative spectral lines. Our experimental studies lead to reasonable rotational temperatures at the tip of luminous cones for mixtures of H_2, C_2H_2, and O_2 and for C_2H_2-O_2 flames diluted with up to 60 percent argon. These observations do not disprove the reality of rotational temperature anomalies in the inner cones of flames. Significant improvement of experimental procedure, and quantitative interpretation of results along the lines used by us, requires additional basic studies with emphasis on the measurement of spectral line-shape and absolute intensities.

I. INTRODUCTION

IN recently published articles on rotational temperature measurements of OH in flames, the problem of the proper interpretation of apparent anomalous temperatures has been discussed. Two recent survey papers, in which extensive references to the published literature may be found, have been prepared by Gaydon[1] and Penner.[2] In order to illustrate the use of two-path experiments in correcting for self-absorption, we have carried out a series of single-path and two-path measurements on flames burning at atmospheric pressure. We have selected for study the H_2—C_2H_2—O_2 and C_2H_2—O_2—A flames and restricted our attention to the tips of the luminous cones. Results obtained on the inner cones have been considered to yield true rotational temperature anomalies.[3] Our experimental data were extensively influenced by self-absorption distortions, with close correlation between apparent temperature and a parameter which measures directly the number density of OH molecules in the light path. To what extent this conclusion can be applied to the inner cones of flames can be settled only by further experimental studies. The appearance of "anomalous" temperatures in self-absorbed systems is well known and has been studied both experimentally and theoretically.

The results of our theoretical studies on two-path experiments have been used to obtain rotational temperature estimates and lower limits for the OH concentrations on the assumption that the radiating system is in equilibrium, that the spectral lines have a Doppler contour, and that Oldenberg's f values are applicable.

In Sec. II we present the results of representative theoretical calculations on two-path to single-path intensity ratios for isothermal emitters. The experimental technique used to perform two-path and single-path emission experiments is described briefly in Sec. III. The results of studies on the H_2—C_2H_2—O_2 system are presented in Sec. IV. Spectroscopic studies on acetylene-oxygen flames diluted with argon are described in Sec. V. A critical evaluation of results and concluding remarks are presented in Sec. VI.

II. PRELIMINARY THEORETICAL CALCULATIONS ON TWO-PATH TO SINGLE-PATH INTENSITY RATIOS

By utilizing the analytical techniques described in previous publications,[4] and the relative intensity tables of Dieke and Crosswhite,[5] it is a simple matter to calculate the ratio of the total intensity of a line observed in a double-path experiment (I_D) to the corresponding intensity for a single-path experiment (I_S). Smoothed curves drawn through the calculated intensity ratios as a function of rotational quantum number K are summarized in Figs. 1 to 3 for an isothermal, equilibrium, emitting system at 3000°K, for the P_1-branch, $^2\Sigma\rightarrow^2\Pi$ transitions of OH, 0,0-band. In Figs. 1 to 3 the quantity $\epsilon' = 1 - \exp(-P_{max}X)$ for the line with $K=1$ represents the usual self-absorption parameter, P_{max} equals the maximum spectral absorption coefficient for the

* Supported by the Office of Naval Research under Contract Nonr-220(03), NR 015–401.

[1] A. G. Gaydon, "Use of Spectroscopy in Elucidating Reaction Mechanism," in *Selected Combustion Problems—Fundamentals and Aeronautical Applications* (Butterworths Ltd., London, May 1954), pp. 132–143.

[2] S. S. Penner, "Spectroscopic Studies of Premixed Laminar Flames," reference 1, pp. 144–166.

[3] See, for example, H. G. Wolfhard's discussion in *Fourth (International) Symposium on Combustion* (Williams and Wilkins Company, Baltimore, 1953), pp. 230–231.

[4] S. S. Penner, J. Chem. Phys. 21, 31 (1953); 22, 101 (1954).

[5] G. H. Dieke and H. M. Crosswhite, "The Ultraviolet Bands of OH," Bumblebee Series Report No. 87 (The Johns Hopkins University, Baltimore, Maryland, November 1948).
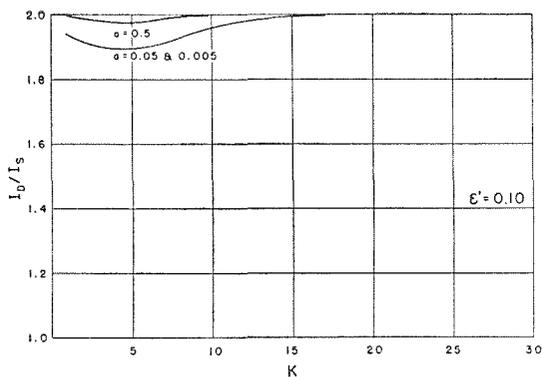
FIG. 1. The theoretical double-path to single-path intensity ratio (I_D/I_S) for the P_1 branch of OH ($^2\Sigma \rightarrow {}^2\Pi$ transitions, 0,0-band) at 3000°K as a function of rotational quantum number of the lower state. Smoothed curves have been drawn through the discrete points corresponding to integral values of K. The self-absorption parameter $\epsilon' = 0.10$ for the first line of the P_1 branch; a represents the line-shape parameter.

line $K = 1$ if the line had a Doppler contour, and X is the product of partial pressure of OH and optical path-length.[4] The parameter

$$a = (b_N + b_C)(\ln 2)^{\frac{1}{2}}/b_D$$

determines the spectral line-shape and measures the relative importance of natural broadening (corresponding to a half-width b_N), collision broadening (corresponding to a half-width b_C), and Doppler broadening (corresponding to the half-width b_D).

Reference to Figs. 1 to 3 shows that small values of I_D/I_S can be produced only for large values of ϵ'; in agreement with the line-shape effect noted previously,[4] strongest self-absorption, i.e., smallest values of I_D/I_S, are observed for the narrowest spectral lines ($a \sim 0$). In accord with expectations, the ratio I_D/I_S approaches two for weak spectral lines corresponding to large values of K.
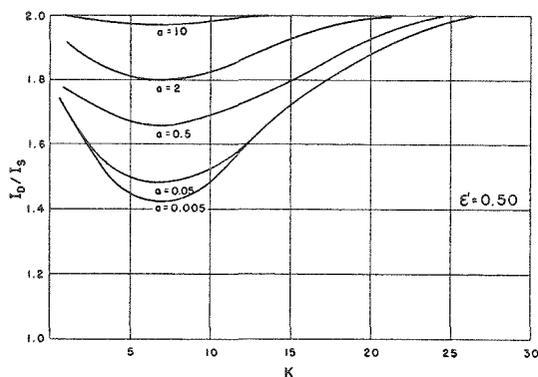

FIG. 2. The theoretical double-path to single-path intensity ratio (I_D/I_S) for the P_1 branch of OH ($^2\Sigma \rightarrow {}^2\Pi$ transitions, 0,0-band) at 3000°K as a function of rotational quantum number K of the lower state. Smoothed curves have been drawn through the discrete points corresponding to integral values of K. The self-absorption parameter $\epsilon' = 0.50$ for the first line of the P_1 branch; a represents the line-shape parameter.

The theoretical results shown in Figs. 1 to 3 suggest the direct experimental determination of I_D/I_S as a sensitive method for detecting the influence of self-absorption distortions. For isothermal systems, this ratio will approach two, independently of the value of the line-shape parameter a, if ϵ' goes to zero; for all reasonable values of a (i.e., $a \leq 0.5$), I_D/I_S is small for the strongest lines for $\epsilon' \geqslant 0.90$, which is a rough estimate for ϵ' on the basis of equilibrium calculations[6] for representative flames utilizing the best published absolute intensity measurements for OH.[7] As long as interpretation of experimental data must be based on the assumption that the emitting system is isothermal, we propose to use the variation of the ratio I_D/I_S with K at least as a qualitative measure of the number density of OH in the light path. In more conventional terminology, an increase in the apparent rotational
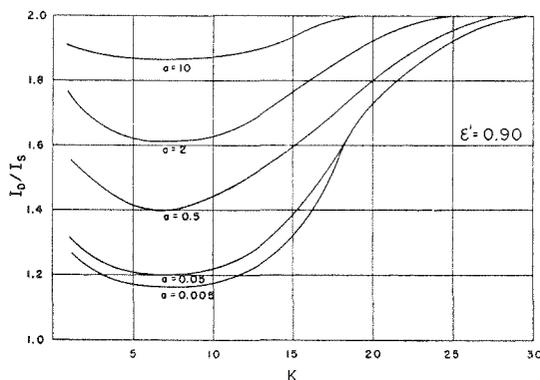

FIG. 3. The theoretical double-path to single-path intensity ratio (I_D/I_S) for the P_1 branch of OH ($^2\Sigma \rightarrow {}^2\Pi$ transitions, 0,0-band) at 3000°K as a function of rotational quantum number K of the lower state. Smoothed curves have been drawn through the discrete points corresponding to integral values of K. The self-absorption parameter $\epsilon' = 0.90$ for the first line of the P_1 branch; a represents the line-shape parameter.

temperature for single-path experiments, when coupled with a decrease in the smallest observed value for I_D/I_S, is to be expected on the basis of the known distortion produced by self-absorption.[4] For minimum values of I_D/I_S below about 1.4, it has been demonstrated that rotational temperatures of 4000°K or higher are to be expected, the exact temperature depending on both the values of ϵ' and of a.

III. EXPERIMENTAL TECHNIQUE

A 1.5-m grating spectrograph with a theoretical resolving power of 48 800 was used for all of the experimental studies. The spectra were recorded photographically and densitometered according to conventional procedures. Two types of burners were employed: (a) a high quality copper oxygen-acetylene welding tip with an inside diameter of 0.071 cm; (b) a converging con-

[6] S. S. Penner, J. Chem. Phys. 20, 507 (1952).
[7] O. Oldenberg and F. F. Rieke, J. Chem. Phys. 6, 439 (1938); R. J. Dwyer and O. Oldenberg, ibid. 12, 351 (1944).

toured nozzle with a main tube inside diameter of 0.625 cm and an exit section diameter of 0.156 cm. For some flames the converging nozzle gave a stable flame with a strongly luminous inner cone almost free of outer cone gases.

Emission spectra of the inner cone were obtained by focusing at the tip of the inner cone in such a manner that a sharp image was produced at the plane corresponding to the 20-micron wide entrance slit of the spectrograph. For each flame two sets of data were obtained: (1) an emission spectrum with a 9-in. focal length spherical mirror placed in back of the flame at a radial distance from the center of the inner cone equal to the radius of curvature of the mirror (double-path experiment)[8]; (2) an emission spectrum of the flame without the use of the spherical mirror (single-path experiment). A schematic diagram of the flame image formed at the entrance slit for single- and double-path emission spectra is shown in Fig. 4, together with a representative photograph of the two superimposed images produced in the double-path experiment. A mask was placed over the slit which admitted light from a portion of the flame 2 mm in height.

A good two-path experiment is one in which the double-path to single-path intensity ratio (I_D/I_S) approaches a value of two for the weaker spectral lines. The fact that we approached this objective satisfactorily is demonstrated by the experimental data described in Sec. IV and V and, more directly, by the plot shown in Fig. 5, where the single-path intensity for the inner cone of a stoichiometric $C_2H_2-O_2$ flame is plotted against the intensity obtained for a double-path measurement, but with a 50 percent transmission quartz filter inserted in the light path. For a perfectly reflecting mirror, the experimental data should approach the dotted curve for the weaker spectral lines, i.e., for small values of I_S. Reference to Fig. 5 shows that representative experimental data do, in fact, exhibit this behavior. The deviations from the limiting curve are the result of self-absorption, in accord with the theoretical studies presented in the previous section.

The data shown in Fig. 5, as well as the experimentally determined values of I_D/I_S discussed in the following sections, show that values of I_D/I_S surprisingly close to two were obtained, although the theoretical upper limit for a mirror with reflectivity 0.92 is $I_D/I_S = 1.92$. We have studied the optical system with some care and conclude from this work that no distortions which vary with wavelength, and could conceivably influence the analysis of experimental data, were present. Among the experiments performed by us are the following:

(a) Systematic studies in which unused portions of the spherical mirror were blocked off successively showed no dependence of the I_D/I_S curves (normalized
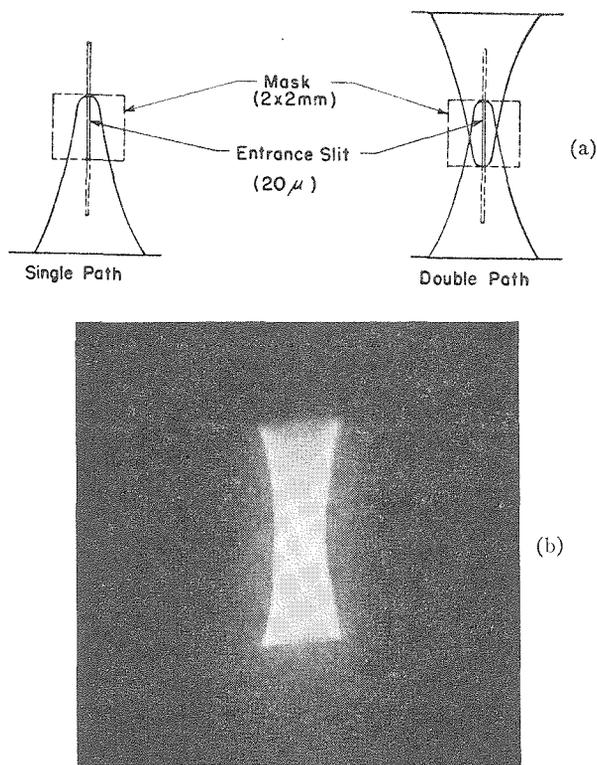

FIG. 4. (a) Schematic diagrams of single- and double-path image of the inner cone of a luminous flame at the plane of the spectrograph entrance slit. (b) Photograph of inner cone images at the plane of the spectrograph entrance slit for a double-path experiment.

to two for large values of K and low intensities) on mirror size, as long as the aperture of the spectrograph entrance slit was filled completely.

(b) Single-path "temperature" measurements with the mirror placed at 90° and 120° with respect to the flame-entrance slit axis gave the same results as flame emission studies without mirror. Fluorescence effects cannot have influenced our observed values for I_D/I_S
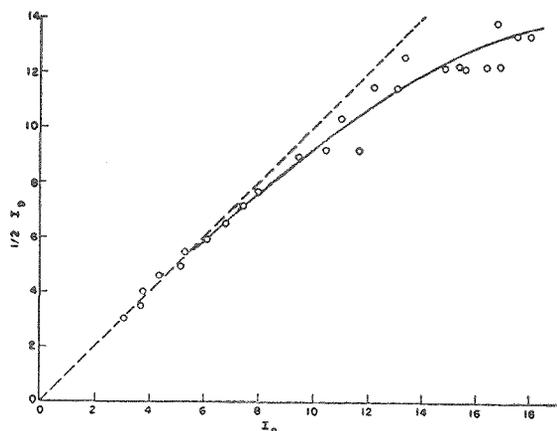

FIG. 5. Double-path intensity, reduced by 50 percent, as a function of single-path intensity for representative lines of an acetylene-oxygen flame.

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[8] Preliminary two-path experiments were carried out in our laboratory by Mr. J. C. Stewart during the summer of 1953.

to an appreciable extent. In concluding the present discussion we wish to emphasize the fact that the measured ratios I_D/I_S are most accurate for spectral lines of moderate strength and least accurate for the weakest spectral lines.

Film calibration was carried out for each film by utilizing flame spectra obtained in the outer cones of the flames studied. A calibrated two-step quartz filter was employed for this purpose. Good film calibration data could usually not be obtained from inner cone spectra because of strong temperature gradients, which affected significantly the distribution of intensities for the long spectral lines needed for calibration.

IV. EMISSION SPECTRA OF $H_2-C_2H_2-O_2$ FLAMES

Experimental measurements of emission spectra have been made for stoichiometric $H_2-C_2H_2-O_2$ mixtures in which the ratio of H_2 to C_2H_2 was varied systematically. Representative results of I_D/I_S as a function of K are summarized in Figs. 6 to 8. The experimental data shown in Figs. 6 and 7 were obtained with the contoured burner with 0.156 cm inside diameter; the data of Fig. 8 were obtained from a flame stabilized on the smaller (0.071 cm inside diameter) burner. By keeping the fuel to oxygen mixture ratio in stoichiometric proportions, the adiabatic flame temperature for the gas mixtures was also maintained at roughly the same value, thereby minimizing the effects of temperature changes on the observed results. Reference to Figs. 6 and 7, and to similar data obtained for other gas compositions, shows that the minimum value of I_D/I_S corresponds to practically the same value of K, namely $K=11$, for all gas compositions, for the P_2 branch as well as for the Q branches. Distortion of experimental data by self-absorption occurred in every experiment since I_D/I_S is always appreciably less than two for the stronger lines. The observed values of I_D/I_S are relatively largest for the H_2-O_2 system containing no acetylene (Figs. 6 and 7, and similar curves for other gas compositions), i.e., the extent of self-absorption is smallest for this gas mixture. A comparison of the data shown for stoichiometric H_2-O_2 mixtures in Figs. 6 and 8

FIG. 7. Observed values of I_D/I_S as a function of K for a mixture containing 66 percent oxygen, 25 percent acetylene, and 9 percent hydrogen. (Inside diameter of contoured burner: 0.156 cm.)

clearly shows less self-absorption of points on the P_2 branch for the smaller burner. This observation emphasizes the obvious fact that for self-absorbed emitters the apparent rotational temperature obtained from single-path experiments is a function of burner size.[9]

An interesting feature of the experimental results is the apparent splitting between the P_1 and P_2 levels for values of K less than about 9, a splitting which may indicate any one of the following: (a) relatively larger populations in the lower P_1 levels; (b) variation of the line-shape in such a way as to make the lower P_1 lines narrower; (c) an intensity ratio of P_1 to P_2 lines for small values of K which is greater than the calculated intensity ratio.[10] As is to be expected on the basis of intensity considerations based on the data given, for example, by Dieke and Crosswhite,[5] the Q-branch points lie below those of the P_2 branch in all cases.

The emission spectra obtained in single-path and in double-path experiments have been used to obtain rotational temperatures by drawing "best" curves through conventional plots of the logarithm of (observed intensity divided by the product of appropriate transition probability and fourth power of the frequency at the line center) as a function of the rotational energy of the initial (upper) state. The rotational "temperatures" obtained from the double-path experiments were invariably higher by a few hundred degrees than the corresponding "temperatures" obtained in single-path experiments. No particular significance can be attached to the absolute value of the difference between the two-path and single-path "temperatures" since a "temperature" derived by drawing a straight line, even through points following the calculated contours of self-absorbed emission curves,[4] is not defined with great accuracy. On the other hand, the fact that the two-path experiments yield the higher tempera-
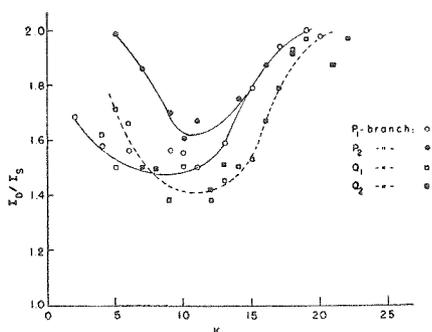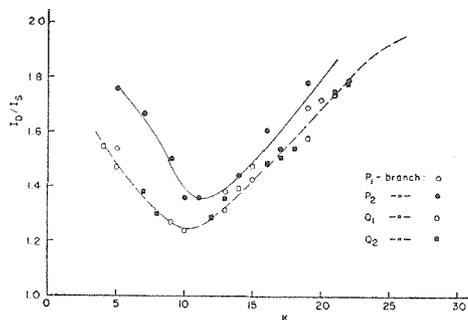
FIG. 6. Observed values of I_D/I_S as a function of K for a stoichiometric hydrogen-oxygen flame. (Inside diameter of contoured burner: 0.156 cm.)

[9] In order to assess the importance of self-absorption on apparent rotational temperature, studies of the type described in reference 4 should be consulted. On the basis of the experimental and theoretical data now available, it appears that reasonable "temperatures" for the inner cone are obtained for hydrogen-oxygen mixtures but not for the systems containing acetylene. See Sec. VI for further details.

[10] For further discussion of this result see Sec. VI.

tures, lends qualitative support to our contention that we are dealing with extensively self-absorbed systems.

In the absence of self-absorption, the parameter $2-(I_D/I_S)_{min}$ would be equal to zero for all possible line profiles. Hence we may take this quantity as a qualitative measure of the extent of self-absorption in the flame. In Fig. 9 we have plotted the apparent single- and double-path emission temperatures obtained with the contoured burner (0.156 cm inside diameter), as well as the parameter $2-(I_D/I_S)_{min}$, all obtained from the experimental data for the P_2 branch, as functions of the percentage of acetylene in the initial fuel mixture. Reference to Fig. 9 shows a remarkable parallelism between the experimentally determined self-absorption parameter $2-(I_D/I_S)_{min}$ and apparent rotational temperatures in emission experiments. Even without further calculations, it is apparent that the "anomalous" temperatures produced by addition of C_2H_2 to H_2-O_2 mixtures simply reflect an increase in the OH concentration and in the extent of self-absorption. The temperature level for all of the inner cone emission experiments is undefined and cannot be computed, on the basis of conventional plots for the determination of rotational temperatures, from the experimental data, even assuming isothermal emitters, without quantitative knowledge of self-absorption and line-shape parameters. More detailed considerations, using our method of analysis for two-path experiments, are deferred to Sec. VI, where we attempt a quantitative interpretation of experimental data on the basis of assumed isothermal emitting systems with a line-shape parameter a which is constant and equal to zero for different values of K.

Our single-path emission experiments have yielded rotational "temperatures" (for both burner tips used by us) which are in satisfactory agreement with experimental results published by other investigators. For example, Kane and Broida[11] show a rotational "temperature" for the inner cone of stoichiometric H_2-O_2 mixtures of about 2900°K, which is seen to be in excellent agreement with our single-path temperature estimate of 3000°K (compare Fig. 9); the adiabatic flame
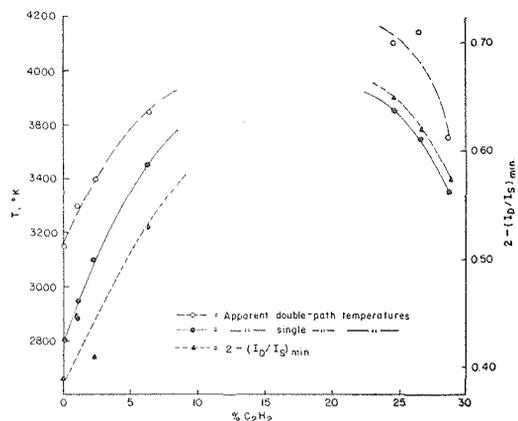
FIG. 9. Apparent rotational temperatures and the self-absorption parameter $2-(I_D/I_S)_{min}$ as functions of percentage of acetylene for stoichiometric hydrogen-acetylene-oxygen mixtures. (Inside diameter of contoured burner: 0.156 cm; P_2 branch, $^2\Sigma\rightarrow{}^2\Pi$ transitions of OH, 0,0-band.)

temperature for stoichiometric H_2-O_2 mixtures is about 3100°K. For stoichiometric $C_2H_2-O_2$ mixtures, Kane and Broida report a value of about 4200°K,[11] Shuler and Broida[12] report a value of 3500°K, whereas our estimate is about 3600°K (compare Fig. 9);† the adiabatic flame temperature for the stoichiometric $C_2H_2-O_2$ flame is about 3300°K. The fact that substitution of C_2H_2 for some of the H_2 in stoichiometric fuel $-O_2$ mixtures causes an increase in the apparent rotational temperatures of OH is well known.[3]

V. EMISSION SPECTRA OF $C_2H_2-O_2-A$ FLAMES

Extensive single-path emission studies on the inner cones of diluted flames have been carried out by Kane and Broida.[11] We have repeated some of their studies on $C_2H_2-O_2-A$ flames using both the conventional single-path and our double-path techniques, again restricting our observations to the tips of the inner cones.

Representative results for I_D/I_S as a function of K, obtained with the contoured (0.156 cm inside diameter) burner tip, are shown in Fig. 10 for a stoichiometric acetylene-oxygen mixture containing 60 percent argon. Compared with the undiluted $O_2-C_2H_2$ data, the flames containing argon show somewhat stronger self-absorption. The reasons for this behavior are not obvious, although increased OH-number density in the light path may reflect, in part, the fact that the diluted flames show larger and less sharply bounded inner cones, which may be responsible for an increase in the optical path length.

Plots of the single-path or double-path apparent rotational temperatures and of the self-absorption parameter $2-(I_D/I_S)_{min}$ for the P_2 or Q branches, as functions of percentage of argon, again show qualita-
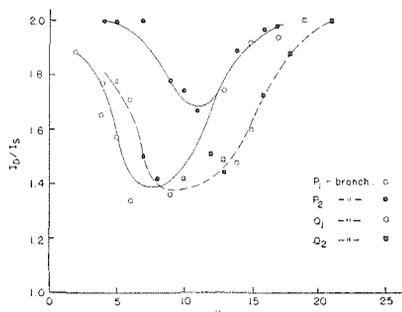

FIG. 8. Observed values of I_D/I_S as a function of K for a stoichiometric hydrogen-oxygen flame. (Inside diameter of straight burner tube: 0.071 cm.)

[11] W. R. Kane and H. P. Broida, J. Chem. Phys. 21, 347 (1953).

[12] K. E. Shuler and H. P. Broida, J. Chem. Phys. 20, 1383 (1952).
† The differences in the reported rotational temperatures can be explained in terms of differences in the methods of observation.
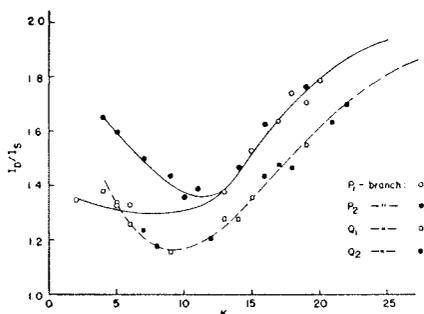
FIG. 10. Observed values of I_D/I_S as a function of K for stoichiometric acetylene-oxygen mixtures containing 60 percent argon. (Inside diameter of contoured burner: 0.156 cm.)

tive correlation, within the limits of experimental reproducibility.

The apparent rotational temperatures determined from our single-path experiments for various argon concentrations do not increase with argon concentration in the same manner as the rotational temperatures of Kane and Broida,[11] who used a straight-tip burner with about the same inside diameter as our contoured burner, and a contoured burner which was roughly eight times as large as ours.

VI. QUANTITATIVE INTERPRETATION OF EXPERIMENTAL RESULTS

Before proceeding with an attempt at quantitative interpretation of the experimental results, a remark concerning the lack of quantitative correlation between the extent of self-absorption and total emitted intensities (for the spectral lines) appears to be in order. The required exposure time to obtain the same blackening on a photographic plate is a rough measure of the total emitted radiant intensity. For cool systems, the possibility of obtaining low relative radiant intensities and, at the same time, large values for $2-(I_D/I_S)_{\min}$, cannot be ruled out.

It is the purpose of the following discussion to show that the experimental data obtained by us can be correlated satisfactorily on the assumption that we are dealing with isothermal equilibrium systems. In particular, it will be demonstrated that overall thermodynamic considerations concerning maximum possible concentrations of OH in the inner cones of flames are compatible with lower limits for OH-concentrations calculated from two-path experiments. Our method of analysis is a concession to our ignorance and represents only a first step at a true understanding of the radiation characteristics of flames. Since we must make the serious (and invalid) approximations that the emitters are isothermal and that all of the spectral lines can be characterized by a single value for the line-shape parameter a, our calculations and conclusions are not definitive. Nevertheless, it is gratifying to note that we can get a rational account for the observed results without introducing such concepts as a nonequilibrium bimodal population distribu-

tion for the excited OH radicals, which would not make proper allowance for the large extent of self-absorption observed in our flames.

The experimental determination of I_S and I_D, from which the ratios I_D/I_S are calculated, answers only the question of whether or not self-absorption distortions are present. If self-absorption does occur, then the conventional methods for the determination of rotational temperatures are inaccurate. There are three essentially undetermined parameters which can be adjusted to fit the experimental data. The unknown quantities are: (1) the spectral line-shape, which may not be uniform for a given branch and may be different from one branch to another; (2) the number density of (excited) OH radicals in the emitting light path; (3) the rotational temperature. Once the line-shape parameter a is known, we can use the analytical procedures described in previous publications[13,14] to calculate $P_{\max}X$, rotational temperature, and number density of OH-radicals in the emitting light path. In the absence of better information concerning line-shape, it will be sufficient to describe the analytical procedure for $a=0$ for several sets of experimental data. The basic theory is reviewed briefly in Sec. VIA and the results of interpretation of the experimental data are described in Sec. VIB.

VIA. Theoretical Considerations Relating to the Interpretation of Experimental Data

For isothermal systems the observable total intensity ratio for a single-path to a double-path experiment, I_S/I_D, is a function only of the parameters $P_{\max}X$, and a for the specified line, i.e.,

$$I_S/I_D = f(P_{\max}X, a). \tag{1}$$

Theoretical curves for $f(P_{\max}X, a)$ as a function of $P_{\max}X$ and a have been published previously.[13,14] Hence the experimentally determined values of I_S/I_D for the spectral lines can be used for the determination of $P_{\max}X$ (for example, with the aid of Fig. 3 of reference 14) if a is known.

The quantity $(P_{\max})_K$ is related to the integrated absorption S_K for the line identified by the rotational quantum number K through the expression

$$(P_{\max})_K = (S_K/\omega_K)(mc^2/2\pi kT)^{\frac{1}{2}}, \tag{2}$$

where ω_K is the wave number at the line center, m is the mass of the radiator, c equals the velocity of light, k is the Boltzmann constant, and T represents the absolute temperature. Suitable units for use in Eq. (2) are $P_{\max}$ in cm^{-1} atmos^{-1}, S_K in cm^{-2} atmos^{-1}, ω_K in cm^{-1}, and $mc^2/2\pi kT$ dimensionless. The quantity X is to be set equal to the product of the partial pressure (in atmos) of OH (irrespective of the energy state in which the OH occurs since X is not a function of K), and the optical path length L (in cm). The integrated intensity

[13] S. S. Penner, J. Chem. Phys. **20**, 1341 (1952).
[14] S. S. Penner, J. Chem. Phys. **21**, 686 (1953).

S_K is related to the dimensionless oscillator strength f_K associated with the Kth line through the expression[15]

$$S_K = 2.3789 \times 10^7 (273.1/T) f_K (N_l/N_T) \times [1 - \exp(-hc\omega_K/kT)] \quad (3)$$

where N_l/N_T represents the fraction of the total number of OH radicals present in the lower state for the transition or transitions giving rise to the line with quantum number K.

From Eqs. (2) and (3) it follows that

$$(P_{\max})_K = \frac{2.3789 \times 10^7}{\omega_K} \frac{273.1}{T} \frac{N_l}{N_T} f_K \left(\frac{mc^2}{2\pi kT}\right)^{\frac{1}{2}} \quad (4)$$

since the term $\exp(-hc\omega_K/kT)$ is negligibly small in our studies. Hence the quantity $(P_{\max})_K$ can be calculated if f_K and T are known.

In order to determine T, an explicit relation is needed for S_K. The basic relation[6] for S_K is

$$S_K = \frac{64\pi^4}{3} N_u (\omega_K)^4 q_K^2 / c\rho_K^0, \quad (5)$$

where N_u is the number of molecules per unit volume per unit pressure in the upper energy level for the transition giving rise to the line with index K, q_K^2 is the square of the matrix element for the indicated transition, and $c\rho_K^0/4$ is the intensity of radiation emitted from a blackbody at the wave number ω_K. The dimensions of S_K are cm^{-2} atmos^{-1} if N_u is in cm^{-3}-atmos^{-1}, ω_K in cm^{-1}, q_K^2 in erg-cm^3, and $c\rho_K^0$ in ergs-cm^{-2}. At equilibrium the number of molecules in the upper energy state is given by the relation

$$N_u = N_T \frac{g_u \exp(-E_u/kT)}{Q},$$

where g_u is the statistical weight of the upper level E_u, involved in the given transition, and Q is the total partition function. Furthermore,

$$c\rho_K^0 = 8\pi hc\omega_K^3 \frac{1}{[\exp(hc\omega_K/kT)] - 1}.$$

Hence Eq. (5) becomes

$$S_K = \frac{8\pi^3 N_T}{3hcQ} \omega_K g_u (q_K)^2 [\exp(-E_l/kT)] \times [1 - \exp(-hc\omega_K/kT)]$$

[15] In previous publications (see references 4, 6, and 14) we have deleted the factor N_l/N_T so that the dimensions of S_K are cm^{-2} atmos^{-1} evaluated for molecules in the lower state involved in the given transition. In this case it is necessary to make proper allowance for the Boltzmann factor in evaluating X, which then represents the product of the partial pressure of OH in the lower state for the given transition and the optical path length L. The factor $\exp(-hc\omega_K/kT)$ is negligibly small in most cases, and is usually omitted from Eq. (3).

and the following explicit relation for $(P_{\max})_K$ is obtained from Eq. (2):

$$(P_{\max})_K \simeq \frac{8\pi^3 N_T}{3hcQ} \left(\frac{mc^2}{2\pi kT}\right)^{\frac{1}{2}} g_u (q_K)^2 \exp(-E_l/kT). \quad (6)$$

On the right-hand side of Eq. (6) only the quantities $g_u(q_K)^2$ and $\exp(-E_l/kT)$ are functions of K for a given radiating system. Furthermore, X is independent of K in the present formulation. Therefore, the temperature T can be obtained from the measured values of

$$(P_{\max}X)_K = (P_{\max})_K X$$

from the following basic expression, which has been published previously[13]:

$$\frac{\partial ln\{(P_{\max})_K X/[g_u(q_K)^2]\}}{\partial E_l} = -\frac{1}{kT}. \quad (7)$$

The form of Eq. (7) is such that it is particularly suited for the interpretation of strongly self-absorbed spectra corresponding to large values of $P_{\max}X$. For values of $P_{\max}X$ close to zero, for which conventional single-path techniques give useful results, the inevitable experimental scatter involved in the determination of $P_{\max}X$ is often so large that the utility of Eq. (7) is greatly reduced.

The steps involved in the quantitative interpretation of flame spectra are thus seen to be the following:

(1) For an assumed, measured, or calculated line-shape parameter a, determine $(P_{\max})_K X$ from the measured values of I_S/I_D from Fig. 3 of ref. 14.

(2) Determine the rotational temperature T for equilibrium according to Eq. (7).

(3) For the measured values of T calculate $(P_{\max})_K$ according to Eq. (4) using the known values of f_K and ratios N_l/N_T determined from equilibrium calculations.

(4) From the measured values of $(P_{\max})_K X$ and the calculated values of $(P_{\max})_K$ it is now possible to estimate X, the product of partial pressure of OH, p_{OH}, and optical path length, L. If L is also known from the observed flame shape, then p_{OH} itself is determined and, since the total pressure is known, the absolute concentration of OH may be deduced.

VIB. Quantitative Interpretation of Experimental Data

We proceed with the quantitative interpretation of experimental data by making both temperature and concentration estimates.

(1) Temperature Estimates

Plots of $\log\{(P_{\max})_K X/[g_u(q_K)^2]\}$ as a function of E_l, obtained by following the steps (1) and (2) for the interpretation of experimental data, are shown in Figs. 11 to 14.
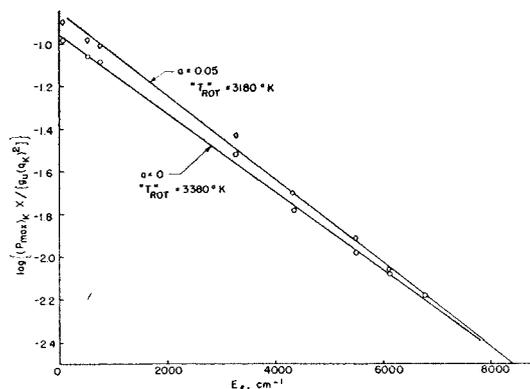
FIG. 11. The quantity $\log\{(P_{max})_K X/[g_u(q_K)^2]\}$ for the P_1 branch as a function of E_l for $a=0$ and $a=0.05$ for a stoichiometric mixture of acetylene and oxygen.

FIG. 13. The quantity $\log\{(P_{max})_K X/[g_u(q_K)^2]\}$ as a function of E_l for $a=0$ for a stoichiometric mixture of hydrogen, acetylene, and oxygen containing 24.3 percent acetylene.

The experimental data obtained for the P_1 branch for stoichiometric acetylene-oxygen mixtures have been used to construct Fig. 11 for two values of a, namely $a=0$ (pure Doppler broadening) and $a=0.05$. Reference to Fig. 11 shows equally good fits for the experimental data for both values of a, and surprisingly good correlation of experimental data for the P_1 branch. The curves look as though the value of a is uniform for all of the P_1 lines. The apparent single-path temperature is seen to be reduced from 3600°K to about the adiabatic flame temperature (3380°K) for $a=0$ and below the adiabatic flame temperature (3180°K) for $a=0.05$. We are unable to say which temperature estimate is closer to the truth. It is easily seen that $a=0$ leads generally to upper limits for the temperature. For this reason, and for the sake of consistency, we shall use $a=0$ throughout the following discussion keeping in mind, however, that the "true" temperatures are apt to be appreciably lower than our estimates.

All the experimental data obtained for stoichiometric acetylene-oxygen flames have been used to construct Fig. 12. The lower P_2-branch points and most of the Q-branch points are seen to lie below the best curve for the P_1 branch. The data shown in Fig. 12 behave as
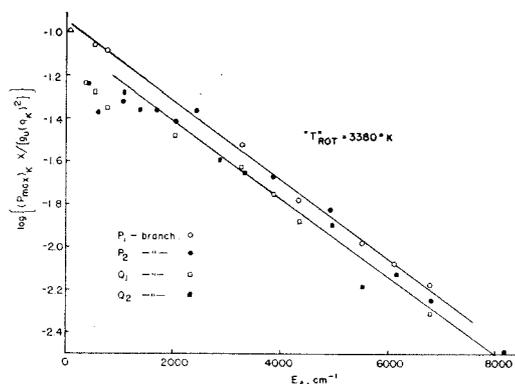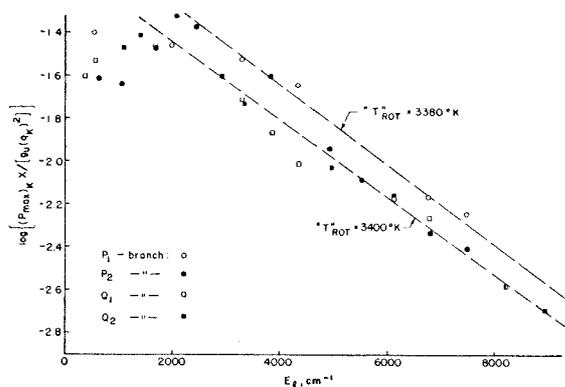
though the lower P_2- and Q-branch lines are relatively too weak or else have half-widths considerably larger than the P_1 lines; for K larger than 7 or 8, the Q-branch points fall on a curve which is roughly parallel to, but displaced from, the best curve drawn through the P_1 points. For some value of a not much larger than 0.05 the P_2-branch and Q-branch points can be made to coincide nearly with the P_1-branch points. In the absence of estimates of the effect of vibration-rotation interactions on intensities, and without quantitative line-shape data, we are therefore unable to attach any significance to the apparent discrepancies noted in Fig. 12.[16]

A plot of $\log\{(P_{max})_K X/[g_u(q_K)^2]\}$ as a function of E_l is shown in Fig. 13 for the stoichiometric $H_2 - C_2H_2 - O_2$ mixture containing 24.3 percent of C_2H_2. The "temperature" is seen to be reduced from 3850°K to below 3400°K. Splitting between the Q-branch points and the P_1-branch points is seen to occur in the same manner as for the stoichiometric $C_2H_2 - O_2$ mixture.

FIG. 12. The quantity $\log\{(P_{max})_K X/[g_u(q_K)^2]\}$ as a function of E_l for $a=0$ for a stoichiometric mixture of acetylene and oxygen.
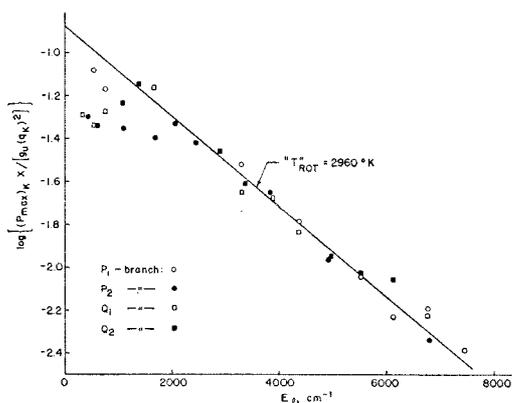

FIG. 14. The quantity $\log\{(P_{max})_K X/[g_u(q_K)^2]\}$ as a function of E_l for a stoichiometric mixture of acetylene and oxygen containing 60 percent argon.

[16] If one so chooses, one may refer to the discrepancies noted in Figs. 12 to 14 as population and, therefore, temperature "anomalies."

Plots of $\log\{(P_{\max})_K X/[g_u(q_K)^2]\}$ as a function of E_l for stoichiometric hydrogen-oxygen mixtures show large scatter of data, presumably because the values of $P_{\max}X$ are relatively small, and, therefore, the demands on experimental accuracy are more stringent. Furthermore, the single-path temperature estimates remain practically unchanged.

A plot for estimating the temperature for the stoichiometric acetylene-oxygen mixture containing 60 percent argon is shown in Fig. 14. The single-path temperature estimate of over 4000°K is seen to be reduced below 3000°K by making proper allowance for self-absorption distortions; the adiabatic flame temperature for this sytem is about 3000°K. For K greater than about 7, all of the points belonging to the P and Q branches behave as though they have about the same line-shape. Correlation of experimental data is seen to be excellent.

Remarks similar to those made for the mixture containing 60 percent argon apply to the systems with 20 percent argon and 40 percent argon. In each case the lines behave as though the addition of argon tends to make all of the lines, for K greater than about 7, of the same width, the scatter being somewhat larger for the mixture containing 20 percent argon than for the mixtures containing 40 percent and 60 percent argon.

We may summarize the attempts at making quantitative temperature estimates as follows:

(1) Proper allowance for self-absorption reduces the single-path temperature estimates roughly to the adiabatic flame temperature for $a=0$ and below the adiabatic flame temperature for larger values of a.

(2) Apparent discrepancies in our plots can be "explained" by making postulates concerning either (a) the effect of vibration-rotation interactions on relative intensities of lines, or (b) the variation of equivalent line-shape parameter a from one branch to another, and from one value of K to another for a given branch.

(3) Significant improvement in the method of analysis is not possible without quantitative information concerning spectral line-shapes.

(2) Concentration Estimates

The product of partial pressure of OH (p_{OH}) and optical path length (L) is X, which can be determined from the available experimental data by following steps (1) to (4) for the interpretation of experimental data.

The results of representative calculations utilizing the line $K=2$ of the P_1 branch are given in Table I for the stoichiometric acetylene-oxygen flame and for the same combustible composition diluted by the addition of 60 percent argon. Reference to Table I shows that the value of X is about 13 percent larger for the diluted flame than for the undiluted flame. The optical path

length L cannot be estimated with any degree of accuracy in either case. We are therefore unable to say whether or not the larger value of X for the diluted flame indicates a larger partial pressure of OH in the inner cone.[17] As was noted in Sec. V, the inner cones of diluted flames become progressively less well defined as the amount of diluent is increased. It is therefore possible that the effective value of L for the diluted flame is so much larger than for the undiluted flame that p_{OH} is actually smaller in the diluted flame. Additional quantitative work along these lines appears to be indicated. In the meantime it is of interest to note that, for reasonable estimates of L (i.e., L of the order of a few millimeters), the calculated values of p_{OH} turn out to be of the same order of magnitude as theoretical equilibrium values of p_{OH}.

In conclusion some remarks concerning the apparent absence of "anomalous" rotational temperatures above the inner cone of flames appear to be in order. It is reasonable to assume that this result indicates both the

TABLE I. Concentration estimates of OH for two representative flames, based on measurements for the second line of the P_1 branch.

Flame	T(°K) for $a=0$	$P_{\max}X$ for $a=0$[a]	$P_{\max}$, (cm-atmos)$^{-1}$[b]	X (cm-atmos)
Stoichiometric acetylene-oxygen flame	3380	1.32	66	2.00×10^{-2}
Stoichiometric acetylene-oxygen flame containing 60 percent argon	3000	1.91	85	2.25×10^{-2}

[a] Determined from measured values of I_D/I_S.
[b] Calculated according to Eq. (4) from the f values reported by Oldenberg and Rieke (see reference 7). The use of absolute intensity estimates made by P. J. Dyne (Technical Report No. 12, Contract Nonr-220(03), NR 015 210, California Institute of Technology, November, 1953) would reduce $P_{\max}$ roughly by a factor of two and double the extimates for X.

absence of "anomalous" rotational temperatures and of extensive self-absorption, or else a fortuitous compensation of errors produced by unknown temperature and concentration gradients. In view of theoretical studies showing the build-up of oxygen atom concentrations greatly exceeding the equilibrium value in ozone decomposition flames,[18] it is perhaps not unreasonable to interpret the observed extensive self-absorption at the tip of the inner cones of many flames by assuming some build-up of OH above the equilibrium concentration. An alternate "explanation" could be based on the hypothesis that the effective value of L for inner-cone

[17] It is easy also to invent a change in line-shape with addition of argon which will produce lower apparent pressures of OH in the diluted flame than in the undiluted flame.
[18] Hirschfelder, Curtiss, and Bird, Molecular Theory of Gases and Liquids (John Wiley and Sons, Inc., New York, 1954); Theodore von Kármán and S. S. Penner, "Fundamental Approach to Laminar Flame Propagation," in Selected Combustion Problems—Fundamentals and Aeronautical Applications (Butterworths Ltd., London 1954).

emission studies is larger than for outer-cone experiments. It has been stressed repeatedly[4] that a relatively small increase in the value of X can be reflected by a surprisingly large apparent temperature rise in a conventional single-path emission experiment. For this reason we do not regard the absence of "anomalous" rotational temperatures for the burnt gases as a problem.

The present investigations have been confined to the tips of inner cones of flames, and suggest that rotational temperature anomalies either do not exist at this position or else are masked by self-absorption distortions. In published papers by Broida and others, emphasis is placed on the fact that the largest rotational temperature anomalies are normally observed within the inner cones of flames. The interpretation of experimental data obtained from inner cones is perhaps more complicated because of the more severe thermal gradients in the line of sight.