

LASER-INDUCED FLUORESCENCE DIAGNOSTICS AND MODELING OF 10 TORR METHANE/OXYGEN FLAMES

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ABSTRACT

Spatial concentration profiles for CH have been obtained using laser-induced fluorescence in several 10 torr CH₄/O₂ flames at equivalence ratios (Φ) between 0.8 and 1.3. The experimental flow rates, temperature profiles, and a published chemical mechanism have been used in Sandia's flame code to predict CH spatial positions. A comparison of experimental results and computer calculations are presented.

I. INTRODUCTION

The flame environment is one of the most interesting and complex chemical systems. Experimental efforts have been directed to identifying and quantifying molecular and atomic species in flames using a variety of techniques. An increasing experimental kinetics data base and computer modeling advances have made it possible to correlate experimental measurements with computer predictions. It is clear that experimentally monitoring all of the chemical species in any hydrocarbon combustion problem is impractical if not impossible. The ability to predict the behavior of most flame species based on a few experimental parameters is attractive and sometimes necessary for practical applications.

The flame zone is several millimeters wide at 10 torr which allows for the examination of CH with sufficient spatial resolution to resolve its growth and decay. This paper presents modeling and experimental comparisons for CH which extends our previous work.¹ The current work details the behavior of CH (experimental and predicted) for several 10 torr methane/oxygen flames of differing fuel equivalence ratios. We were particularly interested in the results for fuel-rich flames. We monitor OH radical distributions (for temperature measurements) and CH radical concentrations with laser-induced fluorescence, LIF.

II. EXPERIMENTAL

Measurements characterizing a steady-state 10 torr methane/oxygen flame have been outlined previously.¹ Experiments were carried out in a water-cooled, stainless steel 6-way cross containing a water-cooled flat-flame burner.² Pressure measurements were made at the top of the cross using MKS baratron heads. Pressures were maintained at 10 torr to within $\pm 0.5\%$. The flames are supported on a sintered bronze 6-cm diameter mantel. A shroud gas flow of Argon was used whose flow rate was adjusted to match the total mass flow through the burner for each flame studied. CH₄/O₂ flames were studied with equivalence ratios and flows listed in Table 1. The flow rates were measured with calibrated mass flow meters (Tylan). The methane and oxygen were premixed upstream from the burner. Total mass flow was maintained constant for all of the flames studied at 1.140 ± 0.005 mg/s-cm². The previously studied flame had a mass flow of 1.040 ± 0.005 mg/s-cm². Vertical translation of the burner via a bellows assembly with micrometer adjustment allowed a 10 cm range above the burner to be probed with a position reproducibility of ± 0.03 cm.

The CH and OH radicals were detected by LIF with the output of an excimer-pumped dye laser (Lambda Physik 101MSC/FL2002). The diameter of the probe beam was 0.8 mm. We measured CH intensity profiles as a function of position along the burner centerline by tuning the probe laser wavelength to the $P_1(6)$ transition in the $A^2\Delta - X^2\Pi(0,0)$ band at 431 nm (Coumarin 440 dye, Exciton). A Corion 4500 interference filter (433 nm center, 60 nm FWHM) allowed the collection of CH fluorescence in the (0,0) band. The probe laser energies were kept $\leq 4 \mu\text{J/pulse}$. There was essentially no scattered light in the CH experiments. Zeroes were obtained by tuning off of the peak. A second PMT monitored the probe laser intensity using scatter from a roughened aluminum plate. Gated integrators (SRS) monitored signals from the PMT's. The fluorescence signals were weighted by the temperature-dependent Boltzmann population of the probed level determined from the experimental temperature profile. The detected fluorescence signals were also corrected for obscuring of the LIF signal by the burner itself. We assumed a uniform CH electronic quenching rate throughout the flame which has been demonstrated to be reasonable in similar flames.^{3,4}

The flame temperature profiles were obtained using a Pt/ 13% Pt-Rh thermocouple (Omega - Type R, 0.01 inch diameter wire). The thermocouple leads were housed in a ceramic tube. The bare thermocouple was acid washed and then coated with a high temperature adhesive cement⁵ (Ceramabond 569) which was cured using the manufacture's recommended procedure. The coated junction was positioned above the center of the burner with the leads parallel to the burner surface. For OH temperature measurements, OH excitation spectra were obtained using the frequency doubled output of the dye laser (coumarin 540A, Exciton). The OH probe laser had a diameter ≤ 0.8 mm and the energy was kept below $0.5 \mu\text{J/pulse}$. OH radicals were excited in the $A^2\Sigma - X^2\Pi(1,0)$ band from 281 to 285 nm. A Corning 7-54 filter (320 nm center, 120 nm FWHM) transmitted fluorescence in the (1,0) and (0,0) band. Radiation corrections⁶ for the thermocouple readings were calibrated using the OH LIF rotational temperature measurements in the $\Phi = 0.9$ flame previously studied. The radiative effect of the burner surface to the thermocouple was accounted for by a view factor for a sphere to a disk.⁷

III. MODELING

We have previously shown that OH and CH relative concentration profiles could be reasonably modeled in a $\Phi = 0.9$ flame using the chemical mechanism of Miller and Bowman,⁸ excluding the nitrogen containing species. The same mechanism is used in this study and consists of 33 chemical species and 150 reversible reactions. Chemical thermodynamic data and rate coefficients were evaluated using CHEMKIN-II which can account for the pressure dependence of the appropriate reactions.

To model the CH profiles we used PREMIX,⁹ a one-dimensional flame code developed at Sandia for modeling premixed, laminar flames. PREMIX calculates the steady-state species spatial profiles and requires the following as input: a chemical mechanism, transport properties, total pressure, flow rate, burner diameter, and the vertical temperature profile.

IV. RESULTS AND DISCUSSION

A. Temperature measurements

Thermocouple measurements were made throughout each flame as a function of height above the burner. The thermocouple temperature readings were corrected as outlined above. Listed in Table 1 are the maximum corrected temperature reading for each flame. The corrected temperature profiles are shown in Figure 1. Typical corrections for the 0.15 cm diameter coated junction varied from 100 to 550 K over the measurement range of 1000 to 1700 K. These corrections are large but consistent with the large junction diameter used in these experiments. Such large diameters were necessary to insure the integrity of the coating. Uncoated thermocouple temperature measurements have been shown to be completely unusable in a similar flame due to the very large catalytic effect.¹ Flame

deposited SiO_2 coatings were found to be very fragile and could be used in only for a few measurements before the coating deteriorated. The Ceramabond coating was very sturdy, lasting for numerous flames, and is easy to apply.

Also presented in Figure 1 are the LIF OH rotational temperature measurements for the $\Phi = 0.8$ flame. The agreement is very good for this flame which has a 10% higher gas flows than the calibration flame. Temperatures at 1.5 cm above the burner for all of the flames were measured using OH excitation spectra as a check on the correction method used. Very good agreement was found for all of the flames at this position, the corrected reading always within the $\pm 2 \sigma$ experimental uncertainty.

B. Concentration measurements

Experimental relative concentration profiles for CH are shown in Figure 2 for flames $\Phi = 0.8, 0.9,$ and 1.0 . Results for flames $\Phi = 1.15$ and 1.3 are presented in Figure 3. Symbols in both of these figures are connected with a dashed line and the symbol legend is presented in Figure 1. All experimental concentrations are on the same relative scale (left axis). Also shown in Figures 2 and 3 with solid lines are the PREMIX calculated steady-state CH profiles (right axis) for the respective equivalence ratios. The two vertical axes (relative and absolute) have been chosen such that the maximum experimental concentration for $\Phi = 1.0$ flame equals the PREMIX calculated maximum for that flame.

The qualitative shape of these profiles were as expected. Ground state CH radicals peak in each of the flames and the distances of these peaks above the burner surface are found to increase with higher equivalence ratio. Such behavior has also been observed in 40 torr C_2H_2 flames.¹⁰ The general shape of the calculated CH steady-state profiles is in qualitative agreement with the experimental profiles. Higher CH concentrations are observed for higher flame equivalence ratios. Table 2 summarizes the quantitative comparison of the significant results: location of the profile maximum, the profile width, and concentration. The location of the profile maximum above the burner is reasonably well predicted for all of the flames. The model predicts the peak location to be approximately 1 mm closer to the burner than observed experimentally for each of the flames. This difference appears to be constant for all of the flames. For the profile widths, the calculated widths (FWHM) are the same as the experimentally observed widths within experimental uncertainty. For the concentration comparison, the calculated concentrations were divided by the relative experimental concentrations and then multiplied by the experimental profile for the $\Phi = 1.0$ flame. Table 2 shows that the $\Phi = 0.8, 0.9, 1.0,$ and 1.15 flames are in good agreement within experimental uncertainty assuming the above scaling method. The largest difference is the slight over prediction of the $\Phi = 1.3$ flame. This may be due to the presence of higher hydrocarbons in the richer system which are not in the chemical mechanism. Another assumption made is that the quenching rate is a constant as a function of height above the burner. Although this is valid for methane flames, it has been shown to break down in flames using higher hydrocarbon fuels.¹¹

CH concentration profiles are very sensitive to the spatial temperature profile. The very good agreement of the location of the concentration maxima between predicted and calculated and the good agreement for the $\Phi = 0.8$ flame between corrected thermocouple readings and LIF OH measurements, suggest that the thermocouple coating and correction method employed here is valid. The position of 1.5 cm above the burner for comparing the corrected thermocouple measurements with the OH rotational temperatures was chosen because of the fairly small temperature gradient at this position and the fairly good temperature separation of the flames (see Figure 1). A small systematic error in the temperature measurement in the region just above the burner is difficult to determine due to the very large temperature gradient present there and the finite probe size for both a thermocouple or a laser probe beam.

VI. CONCLUSIONS

The agreement between experimental measurements and modeling calculations of CH concentration profiles for 10 torr methane/oxygen flames has extended confidence in the predictive ability of the behavior of this specie in fuel-lean to slightly fuel-rich flames. These results indicate that the chemical mechanism used is consistent with the experimental observations but are not a confirmation of the mechanism or a verification of any individual kinetic rate. These results along with other species measurements, primarily other radical species, will begin to verify the chemical mechanism. Although CH is a minor chemical player in any hydrocarbon flame, the presence of ground-state CH only in the flame front makes the ability to predict its behavior extremely useful.

VII. ACKNOWLEDGEMENTS

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VIII. REFERENCES

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Table 1. Experimental Conditions^{a,b}

Φ	CH ₄ (slpm)	O ₂ (slpm)	Maximum T ^c (K)
0.8	0.44	1.10	2006
0.9	0.67	1.08	2093
1.0	0.53	1.06	2169
1.15	0.59	1.03	2273
1.3	0.65	1.00	2286

^a Total mass flows for each of the flames was 1.140 ± 0.005 mg/s/cm².

^b Argon shroud gas was flowed to match the mass flow rate in the burner.

^c Radiation corrected temperature (see text).

Table 2. Comparison of Experimental and Modeling Results

Flame Φ	Profile Maximum Location (cm)			Profile Width (cm)		Peak Height Ratio Model/Experiment (Scaled to $\Phi = 1.0$) ^c
	Experiment ^a	Model	Difference (Exp - Model)	Experiment ^b	Model	
0.8	0.55	0.49	0.06	0.80	0.64	0.79 ± 0.19
0.9	0.60	0.51	0.09	0.71	0.68	1.07 ± 0.21
1.0	0.65	0.55	0.10	0.75	0.72	1.00
1.15	0.75	0.66	0.09	0.86	0.78	1.27 ± 0.22
1.3	0.95	0.84	0.11	1.03	0.93	1.72 ± 0.29

^a ± 0.08 cm uncertainty includes the measured positional uncertainty and the laser probe radius.

^b ± 0.16 cm uncertainty.

^c $\pm 2 \sigma$.

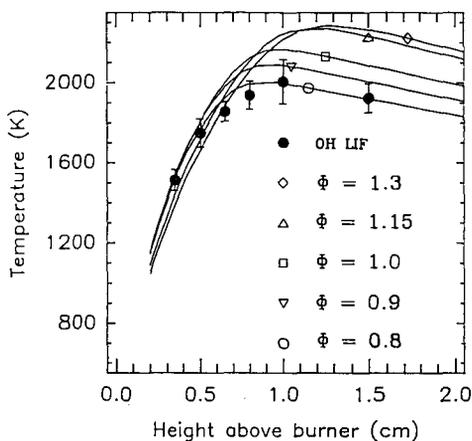


Figure 1. Temperature measurements as a function of height above the burner for the flame listed in Table 1: Corrected readings for a coated Pt/Pt-13% Rh thermocouple (solid lines); OH LIF temperatures derived from excitation spectra (filled circles) for the $\phi = 0.8$ flame.

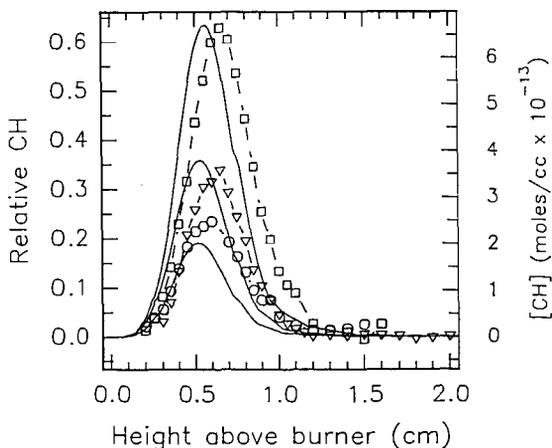


Figure 2. Concentration profiles for CH versus height above the burner for the flames $\phi = 0.8, 0.9, 1.0$, listed in Table 1 (symbol legend defined in Figure 1): Experimental concentration profile (symbols connected with a dashed line, left axis); PREMIX calculated CH radical profile using chemical mechanism listed in Reference 8 (solid line, right axis). Relative experimental concentrations have been scaled to the PREMIX calculated maximum value for the $\phi = 1.0$ flame.

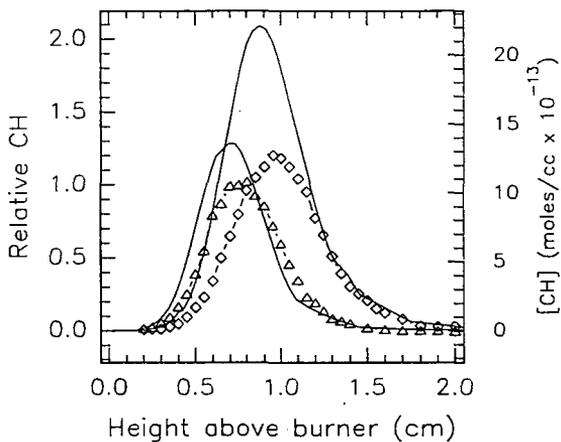


Figure 3. Concentration profiles for CH versus height above the burner for flames $\Phi = 1.15$ and 1.3 , listed in Table 1 (symbol legend defined in Figure 1): Experimental concentration profile (symbols connected with a dashed line, left axis); PREMIX calculated CH radical profile using chemical mechanism listed in Reference 8 (solid line, right axis). Relative experimental concentrations have been scaled to the PREMIX calculated maximum value for the $\Phi = 1.0$ flame.