CHEMILUMINESCENT OH* AND CH* FLAME STRUCTURE AND
AERODYNAMIC SCALING OF WEAKLY BUOYANT, NEARLY
SPHERICAL DIFFUSION FLAMES

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Normal-gravity experiments were conducted with inverse diffusion flames of small density difference with their surrounding ambient to study low Grashof number (Gr) flames that were several centimeters in diameter. The intensity of buoyancy was minimized by ejecting diluted air from a porous, spherical burner into a lower-density fuel atmosphere of hydrogen or hydrogen and methane at reduced pressures (<0.25 atm). The resulting weakly buoyant, almost spherical flames were imaged by a UV camera, with narrow-band-limited filters corresponding to electronically excited OH (OH*) and CH (CH*), and then deconvoluted to obtain intensity profiles corresponding to the chemiluminescent species. The experimental results were then compared with computations allowing for detailed chemistry and transport. For the hydrogen flames, the comparison was very satisfactory, hence substantiating the adequacy of the chemistry and the experimental approach. For hydrogen/methane flames, OH* chemiluminescence exhibited two peaks, demonstrating the importance of the H + O + M → OH* + M reaction in addition to the CH + O2 → OH* + CO reaction. The hydrogen/methane flames also experienced a mild degree of buoyancy, which shifted the peak OH* and CH* locations from the calculated values. Through a separate experimental investigation, it was subsequently determined that the effects of weak buoyancy, based on the flame dimension, scale with $Gr^{1/2}$ and are therefore in accord with the low-Gr scaling for heat transfer phenomena. The associated correction satisfactorily explains the shifts in the locations of the experimental OH* and CH* peaks.

Introduction

Recently, there have been increasing interest and confidence in the use of laminar flames as a tool in the interrogation, validation, and compilation of chemical kinetic mechanisms of interest to combustion. For such an approach to be as meaningful and accurate as possible, the flames adopted should be aerodynamically clean and simple so as to minimize the influences and thereby uncertainty in the flame structure caused by the flow field. For diffusion flames, a suitable configuration is that of the burner-generated, steady, spherically symmetric flame. It has been shown [1] that such a flame, with minimal buoyant distortion, can be established in the Earth's gravity by issuing air from the spherical burner into a low-pressure, low-molecular-weight, fuel environment. Furthermore, since the flame is strongly diffusion controlled, its structure also has an extended dimension and thereby improved spatial resolution.

In the present investigation, we shall therefore use such a flame to experimentally determine OH* and CH* chemiluminescent structures of hydrogen and hydrogen/methane flames. By subsequently comparing the experimental structures with those obtained from computational simulation, we aim to assess the adequacy of the reaction mechanisms used, especially those regarding the kinetics of formation of OH* and CH*. In this regard we note that most of the chemiluminescent studies on methane flames [2–6] assume that OH* is mainly produced by

$$\text{CH} + \text{O}_2 \rightarrow \text{OH}^* + \text{CO} \quad (R1)$$

without significant contributions from

$$\text{H} + \text{O} + \text{M} \rightarrow \text{OH}^* + \text{M} \quad (R2)$$

even though O and H are inherently present in methane flames, albeit in trace quantities. Furthermore, the reaction zones of reactions R1 and R2 have been found to be very close to each other for methane flames. The question that naturally arises is the role of reaction R2 in flames of methane and hydrogen mixtures, recognizing that reaction R2 is the primary route of OH* formation in hydrogen flames [7]. It is therefore of interest to assess the
The potential dominance of reaction R1 over reaction R2 even when methane is present only in small amount, and the influence of reaction R2 on the perceived thickness and location of the flame that are frequently interpreted on the basis of the flame luminosity. Specifically, a thickened flame is sometime associated with weakened chemistry, based on one-step, large activation energy considerations, while a knowledge of the contour and movement of the flame surface yields the burning rate of, and the aerodynamic stretch experienced by, a flame. As such, it is important to be able to correlate the flame luminosity with the structure of the flame. For example, Marchese et al. [8] suggested that the knowledge of the OH* distribution should yield a rational indication of the flame position, since the location of the maximum OH* emission was found to be near that of the maximum flame temperature. Alternately, Smooke et al. [9] recommended the maximum CH* as a marker of the flame location, noticing that the CH* profile existed in a thin, high-temperature region. Furthermore, an analysis [5] of the premixed methane/air flame revealed that the ratio OH*/CH* can be a good marker for the local flame stoichiometry for a wide range of equivalence ratios, while Docquier et al. [10] showed that active control of high-pressure flames can be achieved by directly monitoring the chemiluminescence of OH*, CH*, and/or C2*.

In view of the above considerations, we shall first measure and compare the experimental structure of the spherical hydrogen flame with that determined through one-dimensional simulation and consequently demonstrate through their agreement the viability of the experimentation and simulation. By subsequently extending the study to hydrogen/methane flames, we shall show that reaction R2 can play an important role in the formation of OH*.

Our results on the methane/hydrogen flames also showed a consistent shift between the measured and simulated OH* and CH* profiles. Expecting that it was caused by the relatively strong buoyant flow associated with these flames compared to the hydrogen flames, we were led to the undertaking of the second project of the present study, namely, the determination of the aerodynamic scaling law for low Grashof number (Gr) flows. This project is of fundamental and practical relevance in its own right. We shall show in due course that the scaling law is in accord with those from studies of heat transfer and droplet combustion.

**Experimental Apparatus**

**Low-Pressure Chamber**

The experiments were conducted in a low-pressure chamber under normal gravity, as shown in Fig. 1. Here nitrogen-diluted oxidizer mixture was issued from a porous, bronze burner (20 μm pore diameter, 1.27 and 0.635 cm sphere diameter) into the low-density fuel environment at chamber pressures ranging from 0.08 to 0.3 atm. A stainless-steel capillary (1.5 mm o.d.) supported the burner and was situated horizontally; frontal images therefore do not show the tube support nor its possible distorting effects. The chamber was continuously supplied with fuel at very low velocity and ventilated to maintain its constant environment. Ignition was achieved by a high-voltage spark discharge near the burner surface. A K-type thermocouple (0.2 mm diameter) continuously measured the burner surface temperature, while a translating K-type thermocouple measured the flame temperature profile in the radial direction. Auxiliary thermocouples measured the upper, middle, and lower regions of the ambient gas.

**Imaging System**

The OH* chemiluminescence images of both hydrogen and hydrogen/methane flames were recorded by a Xybion IMC-201 intensified multispectral video camera with a 105 mm, UV-transmissive lens and narrowband interference filter centered at 310 nm with a full width at half-maximum of 20 nm. For hydrogen/methane flames, CH* emissions were also measured utilizing a narrowband filter centered at 431 nm with a full width at half-maximum of 20 nm. The flame luminosity was always contained within the focal depth of the camera system, so that all images corresponded to a line-of-sight projection. After digital image filtering and processing, the two-dimensional projections were spatially deconvoluted (separately for half of the symmetric projections) to
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Experimental

The hydrogen flame was formed by issuing a 9% O₂/91% N₂ mixture of mass flow rate of 0.078 g/s from a 1.27 cm diameter bronze burner into a pure hydrogen environment at a chamber pressure of 0.079 atm. Fig. 2a shows the OH* flame projection image, and Fig. 2b the corresponding deconvoluted image. The deconvoluted left (−) and right (+) images were kept separated to illustrate that the image was divided in half and those divided images were deconvoluted individually. The sphericity of the flame (defined as the ratio of the horizontal to the vertical diameters of the flame) exceeded 0.98 while its concentricity (defined as the distance between center of the burner and bottom of the flame divided by half of the vertical diameter of the flame) was about 0.92. The measured burner surface and the chamber wall temperatures were used to specify the boundary conditions for the simulation.

The hydrogen/methane experiments used the 0.635 cm diameter burner and involved issuing a 17% O₂/83% N₂ oxidizer mixture at a mass flow rate of 0.024 g/s into a 19% H₂/5% CH₄/76% He environment at a chamber pressure of 0.1 atm. Ambient mixture concentration was determined through systematic experimental trials to maximize CH* emissions while minimizing the addition of CH₄ to preserve spherical symmetry. The OH* and CH* images are shown in Figs. 2c and 2d, respectively. The sphericity of the flame exceeded 0.98 and the concentricity was about 0.88. Note that the pixel intensities for the two images were calibrated by the maximum and minimum intensities of the OH* image. Deconvoluted images are not presented due to space limitation. Temperatures were measured in the same manner as that for the pure hydrogen case to specify the boundary conditions for the simulation.

Computational

The hydrogen and hydrogen/methane flames were computationally simulated using the Sandia burner-stabilized premixed flame code [12], with boundary conditions modified for non-premixed burning. Radiative transport including both emission from and absorption by H₂O, CO₂, and CO was calculated using the statistical narrow-band model with exponential-tailed inverse line strength distribution [13], with the radiation parameters taken from Ref. [14]. The mass flow rate m, burner surface temperature Tₜ, and ambient temperature Tₐ were specified by the experiment, along with the boundary mixture composition. The computational domain was set as the effective radial distance (24.8 cm) from the burner surface to the chamber wall, calculated using the physical volume of the chamber interior. The chamber wall temperature, which remained spatially uniform throughout the experiment, is therefore Tₐ.

The program allows for detailed chemical kinetics, multicomponent diffusion, and variable thermal properties.

Map local luminosity as a function of radial position. Three-dimensional images of flame chemiluminescence were then constructed from vertical stacks of Abel [11] deconvoluted two-dimensional slices.

Chemiluminescent Flame Structure

Fig. 2. (a) Digitized line-of-sight integral projection. (b) Deconvoluted image OH* for the hydrogen flame. Pure hydrogen on the outside with oxidizer (9% O₂/91% N₂) issued at 0.078 g/s to the 0.635 cm radius burner at pressure 0.079 atm. (c) OH*. (d) CH*, digitized line-of-sight integral projections. 17% O₂/83% N₂ issued from the 0.3175 cm radius burner at mass flow rate of 0.024 g/s into 19% H₂/5% CH₄/76% He environment at pressure 0.079 atm. Brightness of images was calibrated to maximum and minimum intensity values of OH* image. (e) Digitized line-of-sight integral projection. (f) Deconvoluted image of OH* emission from a low-Gr scaling experiment. Pure methane on the outside with air (21% O₂/79% N₂) issued to the 0.635 cm radius burner at low pressures. Note that the gravity direction is down the page and the arrows indicate the direction of deconvolution.
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Fig. 3. Computed temperature and species profiles for the case of 9% O₂/91% N₂ injected into a chamber filled with pure hydrogen, at \( T_s = 483 \) K, \( T_0 = 305 \) K, \( m = 0.078 \) g/s, and \( p = 0.079 \) atm. The measured location of the maximum temperature is indicated by the arrow.

Fig. 4. Computed heat release and molar fraction of OH* (normalized with maximum value of the series) and experimentally observed OH* normalized intensity profiles for the case of pure hydrogen versus 9% O₂/91% N₂, \( m = 0.078 \) g/s, and \( p = 0.079 \) atm. The measured location of the maximum temperature is indicated by the arrow.

The \( \text{H}_2/\text{O}_2 \) reaction mechanism used for pure hydrogen flames was that of Mueller [15], which consists of 9 species and 19 elementary reaction steps, excluding argon. The OH* chemiluminescence reactions were added to the above mechanism. The OH* is produced primarily from reaction R2 and quenched through OH* + M \( \rightarrow \) OH + M and photon emission OH* \( \rightarrow \) OH + hv, corresponding to the transition \( \Sigma^+ \rightarrow \Pi \) observable at 305.4 nm. The rate constants for these steps were taken from Refs. [16,17], with the heat of formation for OH* set at 93 kcal/mol above that of the ground-state OH.

GRI-MECH 3.0 [18] was used to calculate the \( \text{H}_2/\text{CH}_4/\text{He} \) flames. Helium was added to the mechanism simply by assuming the role of argon, and CH* (heat of formation set at 66.3 Kcal/mole above that of ground-state CH) was added with a set of formation and destruction reactions with appropriate rate constants recommended in Ref. [7]. With the introduction of CH₄, OH* is initially assumed to be produced through reaction R1 even with trace of methane [19], and CH* is produced through reaction \( \text{C}_2\text{H}_4 + \text{O} \rightarrow \text{CH}^* + \text{CO} \). The CH* or CH (A-X) emits at 431.5 nm and attributes to the transition \( \Sigma^\Delta \rightarrow \Sigma^\Pi \). Subsequent calculations included reaction R2 to describe OH* formation.

Results on Hydrogen Flames

Figure 3 shows the computational prediction of the flame structure. The close agreement between the measured and computed locations of the maximum temperature is to be noted. The normalized experimental and computed OH* intensity profiles are shown in Fig. 4. It is seen that the experimentally measured OH* profile is slightly wider than the computed one, with the peak slightly shifted outward by 0.06 cm. The comparison is nevertheless very favorable, suggesting not only that the degree of spherical symmetry for the flame is high, but also that the experimental measurements of the flame structure are quantitatively valid and the approach can be extended to multidimensional flame structures. The normalized heat release rate is also plotted in Fig. 4 to show that it is rather wide and its peak is closer to the burner when compared with the OH* emission profile. In Ref. [8], it was demonstrated through microgravity droplet flame experiments and simulations that these two peaks actually coincided at 0.25 atm. Hence, the hydrogen flame was simulated at 0.25 atm and the two profiles were compared. The two peaks were indeed closer and the shape of the heat release rate profile becomes more confined to a narrower region similar to that obtained in Ref. [8]. This also implies that this broadening of the heat release peak is mainly due to the drop in the third-body efficiency in the reaction \( \text{H} + \text{O}_2 + \text{M} \), at low pressures. In fact, the inner heat release peak shown in Fig. 4 is due to these H radicals diffusing inwardly, which would have been consumed far away from the burner near the location of the peak temperature at higher pressures.

Results on Hydrogen/Methane/Helium Flames

The flame displayed a green color, roughly corresponding to wavelengths between 520 and 540 nm. Referring back to Figs. 2c and 2d, relative concentrations of OH* and CH* can be inferred from comparing the brightness of these two images. For the purpose of illustration the intensity of both images
Figure 5 depicts the computed flame structure, without including reaction R2, while Fig. 6 compares the experimental and computed OH* and CH* radial profiles normalized by the corresponding maximum intensity of OH*. The comparison identified several significant differences between the experimental and computed profiles. First, the experimental OH* profile has a double peak while the computed profile has only a distinct peak, which is also located closer to the peak of the simulated CH* profile. Second, the magnitude of the peak CH* is about 23% of that of OH* experimentally, while it is 115% computationally. Finally, the experimental emissions all peak closer to the burner compared to the simulation.

By inspecting the computed flame structure shown in Fig. 5, it is reasonable to suggest that the inner OH* peak observed experimentally is likely due to reaction R2 between the two radicals, O and H, that was neglected in the computation. This is further substantiated by noting that there is negligible amount of CH present in the region around the inner OH* peak, and hence the role of reaction R1 in producing OH* is small. The possible thermal excitation route of OH to form OH* [8] is also unlikely for the present flames because the OH profile is too wide and its peak location is too far away from the inner peak. Consequently, without reaction R2, the computed result showed only one distinct OH* emission profile.

The computation was then repeated by including reaction R2 [16]. Fig. 7 then shows that while the overall flame structure is not affected by these chemiluminescent species kinetics, as expected, the computed profile of OH* now exhibits two peaks. Furthermore, the relative magnitude of the peak CH* compared to that of OH* also matches closer to the experiment. To demonstrate that the two OH* peaks coincide for a methane flame, methane was added to the system computationally and experimentally. Results showed that the profiles of OH* and CH* gradually approached each other and the two OH* peaks indeed merged eventually. This explains why previous studies on methane flames were
able to predict OH* both qualitatively and quantitatively by using reaction R1 alone, with appropriate reaction parameters.

The final issue that needs to be addressed is the apparent shift between the experimental and computed emission profiles for the hydrogen/methane flames. After having considered various assumptions and uncertainties associated with the mechanism and transport components of the simulation, such as using the collision parameters of argon for helium, the fact that the GRI-MECH 3.0 was optimized for natural gas combustion, and the uncertainties of the diffusivity parameters of H, we recognized that the leading order effect in the shift of the experimental peaks toward the burner is the relatively stronger induced buoyant flow associated with the hydrogen/methane flames. The presence of a weak buoyant flow inside the chamber can be inferred from noticing a five degree difference in temperature from top to bottom of the chamber and the faint outer OH* ring near the top shown in Fig. 2c. The overall flame is also shifted upward relative to the burner, resulting in a concentricity that is smaller than 0.9. This slight change in the flame shape and hence location led us to the second part of the study, to be reported next.

Low-Gr Flame Scaling

There are two objectives for this project. First, we aim to establish the scaling law for low-Gr flames. In particular, while the scaling for high-Gr flames has been well established [20,21], very little has been done on low-Gr scaling. For classical heat transfer problems [22,23], the scaling has been found to be $Gr^{1/2}$, which has also been corroborated by scaling based on the droplet burning rate [24]. However, there has not been any correlation based on the dimension of the flame, which is the natural length scale of the problem while the flame itself is also the driving force for the buoyant flow. The second objective is to use the scaling and hence the correction factor to show that the deviation between the experimental and computational profiles for the methane flames is likely due to buoyancy rather than deficiencies in chemistry.

**Experimental**

Flames were established by ejecting standard air (21% O$_2$/79% N$_2$) at four mass flow rates, $m = 0.063, 0.067, 0.070$, and 0.075 g/s, into a pure methane environment at pressures ranging from 0.07 to 0.3 atm. Methane was chosen because OH* displays only a single, distinct peak and that peak roughly coincides with that of the CH* profile. Furthermore, the peak location corresponds to that of the maximum temperature. Consequently, the flamefront position was assumed to correspond to that of the peaks of the OH* profiles obtained from the two-dimensional deconvoluted projections. A typical methane OH* flame image and its deconvoluted image are shown in Figs. 2e and 2f, respectively.

**Results and Discussion**

As in Ref. [20] for the boundary layer flame, Gr scaling was examined at the lateral and stagnation regions of the flamefront. Specifically, the lateral radius of the flame, $R_l$, was measured horizontally from the center of the burner to the side flamefront, while the stagnation radius, $R_s$, was measured vertically from the center of the burner to the bottom flamefront.

Neglecting the dependence of the flame temperature on pressure and gas composition, $Gr$ of the flame is proportional to the square of the pressure and the volume $(V)$ enclosed by the flame. Hence, the $Gr$ dependence of the flame deviation from its steady-state radius can assume the form

$$\frac{1}{R_{ls}} = \frac{1}{R_{ss}} + b \frac{Gr}{V}$$

where $b'$ and $c$ are the fitting constants. It may be noted that the peak location of OH* actually increases slightly with increasing pressure, although this increase is negligible compared to the corresponding decrease due to the increased buoyant intensity.

To determine the fitting constants $b'$ and $c$, the experimental data were least square fitted, with $V$ being the volume bounded by the OH* boundary, subject to the following constraints. For any given mass flow rate, the extrapolated steady-state radius ($R_{ss}$) at zero $Gr$ is the same for $R_l$ and $R_s$. Additionally, the extrapolated steady-state radius for different mass injection conditions must be proportional to the mass flow rate. Finally, the fitting parameter, $c$ is constrained to be identical for all curve fits.

Extensive experiments were performed to determine the lateral and vertical flame radii by varying $p$. The resulting fitting, shown in Fig. 8, collapses the experimental data into a fairly tight regime of correlation, with $c = 0.50$, and $b'$ remaining fairly constant around 0.5 for the lateral radii, where $R$ is in centimeters and $p$ in pascals. We have therefore demonstrated that low-Gr scaling based on the flame dimension remains at $1/2$. Furthermore, using the Gr scaling obtained, the zero $Gr$ radius ($R_{ss}$) for the hydrogen/methane flame was determined by substituting for appropriate pressure and volume of the flame. As a result, a 2 mm shift was obtained for the situation of Fig. 7, which is very close to the deviation of 3 mm between the experimental and computational locations of the maximum OH* as well as CH*. Thus, the differences between the experimental and computational profiles of OH* and CH* are
Fig. 8. Correlation for the scaling of low-Gr flames. Note that the independent parameter plotted is proportional to the Gr number, which is defined as \((g/v^2)(\Delta \rho V/\rho)\), where \(g\) is the gravitational constant, \(\Delta \rho\) is the density difference between the hot product and ambient gases, \(V\) is the volume of the flame, and \(v\) is the coefficient of kinematic viscosity.

likely consequences of weak buoyant motion rather than any deficiency in the description of the flame chemistry and structure.

Concluding Remarks

In the present study, we first experimentally acquired the OH* emission profiles of almost spherical hydrogen flames, which were then compared to those from the one-dimensional simulation with detailed chemistry and transport. The close agreement substantiates the validity of our experimental technique to measure flame structures quantitatively and the applicability of this technique to quantify the structure of more complex flames. The subsequent investigation of the hydrogen/methane flames, and the result on the presence of double luminescence peaks, not only demonstrates the importance of reaction R2, \(H + O + M \rightarrow OH^* + M\), but it also highlights the care needed in interpreting the flame structure and dynamics on the basis of flame chemiluminescence. Specifically, the presence of double luminescence peaks would give the impression of a thickened flame, which to an unsuspecting observer could imply a state of weakened burning. Furthermore, since the location of the chemiluminescence peak could change as a result of the reaction processes within the flame structure, analysis of the flame dynamics based on the fine movement of the luminescence front could either complicate or even falsify the subsequent interpretation.

The project on the scaling of low Grashof number flames, while initially being auxiliary to the study on the flame structure, turned out to be equally fruitful in that we have demonstrated, possibly for the first time based on the responses of flames, that the scaling remains to be \(1/2\), in accordance to the same exponent as that of heat transfer phenomena.

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