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Energy Fuels, Just Accepted Manuscript • DOI: 10.1021/acs.energyfuels.7b03484 • Publication Date (Web): 02 Apr 2018 Downloaded from http://pubs.acs.org on April 3, 2018

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Quantitative measurements of chemiluminescence in a laminar methane-air premixed flame and comparison with numerical methods

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ABSTRACT: Quantitative measurements of chemiluminescence emissions due to CH^{*}, OH^{*}, C₂^{*} and CO₂^{*} were conducted in CH₄/air premixed flames at different equivalence ratios ($\theta = 0.7-1.33$) and numerical results based on one-dimensional flames simulations were compared to these data. A wavelength-dependent and optical-path-corrected emission calibration method was applied to quantify the emission of each excited species. The numerically simulated emission intensities of OH^{*} and CH^{*} are within the same order of magnitude as the experimental values for

the same flame conditions. Taking into account self-absorption and cooling water thermosteresis, the simulated OH^{*} values are 1.0 to 1.4 times greater than the experimental results, while the CH^{*} values are approximately 2.3 to 4.1 times greater. These findings suggest that more work is required to refine the temperature dependence factors for the CH^{*} formation rate coefficients at high temperatures.

KEYWORDS: Chemiluminescence, Equivalence ratio, Laminar premixed flame

1. Introduction

Flame chemiluminescence monitoring is an efficient, reliable technique and is widely employed in combustion diagnostics. Excited state species such as CH^{*}, OH^{*}, C₂^{*} and CO₂^{*} are the main sources of chemiluminescence in methane–air flames,¹⁻³ and the relative concentrations of these species are correlated with various flame properties. As an example, both flame structure and location can be characterized by imaging CH^{*} and OH^{*} chemiluminescence.⁴⁻⁷ Verissimo et al.⁶ demonstrated that the structure of the main reaction zone changes along with the excess air coefficient based on OH^{*} imaging, while CH^{*} chemiluminescence has immediate value as a feedback parameter for reducing NO_x emissions from a premixed gas turbine engine.⁸ In combustion heat release studies, chemiluminescence is often used to study overall temporal fluctuations and measure local distributions of heat release .⁹ Tinaut et al.¹⁰ examined OH^{*} and CH^{*} concentrations on an experimental basis during the combustion of

different primary fuels and found that the maximum OH* chemiluminescence coincided with the highest rate of heat release.

The numerical modeling of chemiluminescence can provide a flexible approach to understanding the excited state chemistry in flames, and has also been widely studied. Kathrotia et al.¹¹ produced simulations of combustion under fuel lean to fuel rich conditions and at different pressures and found that OH^* and CH^* are important indicators of the heat release zone, while C_2^* is a poor predictor. Hossain et al.¹² examined heat release rate in non-sooting counterflow diffusion flames based on C1– C3 hydrocarbon reaction mechanisms. They concluded that the chemiluminescence intensity is linearly correlated with the total heat release rate under low-velocity conditions while a non-linear relationship appears at higher velocities. Lauer et al.¹³ presented a model-based means of generating a correction factor that accounts for the nonlinear relationships between OH^* intensity, heat release rate and strain rate. However, the reaction pathways that generate chemiluminescent species such as OH^* , CH^* , C_2^* and CO_2^* are still being debated and cannot be modeled using standard flame simulation codes.¹⁴

Many studies of chemiluminescence using experimental data combined with chemical modeling have implied a strong correlation between emission intensity and equivalence ratio (θ) in premixed flames. An early comparison of experimental data with a numerical model was published by Dandy et al.,¹⁵ who determined that chemiluminescent intensity was most sensitive to the reaction O + OH \leftrightarrow O₂ + H. Panoutsos et al.¹⁶ studied the effects of flow strain rate and θ on both CH^{*} and OH^{*}

and on the ratio of these two species. Eight detailed models were proposed and compared to experimental measurements obtained from premixed laminar counterflow flames. In these models, the OH^{*}/CH^{*} ratio was a monotonic function of θ , but only five of the eight mechanisms were within the same order of magnitude as the experimental data. No quantitative agreement was identified for any given excited state species. In fact, the OH^{*}/CH^{*} ratio is evidently independent of many experimental parameters,¹⁷ such as flame speed and flame area. This is because the intrinsic parameters are eliminated by the ratio of OH^{*}/CH^{*}, and so the predictions for individual species typically do not match the experimental results, although the predicted OH^{*}/CH^{*} ratios may exhibit good agreement with experimental data. More importantly, the ability to accurately model quantitative emissions from specific species such as OH^{*} or CH^{*} could provide key parameters for the computational fluid dynamics (CFD) analysis of experimental data in the field of supersonic combustor studies.¹⁸ Recently, combustion diagnostic based on the computed tomography of chemiluminescence (CTC)¹⁹⁻²¹ and digital inline holography²² have been found capable of providing the three-dimensional structures of flames. Therefore, the quantitative comparison of results for various species is important in chemiluminescence studies and is indispensable for the verification of modeling. The predicted and experimental values of the chemiluminescence signal normalized by the fuel mass flow have been previously compared by Venkata et al.^{17 23} for methane and Jet-A flames, although this work did not provide quantitative emission information regarding excited state species.

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The present study attempted to obtain quantitative chemiluminescence data by investigating the relationship between the emission intensities of excited species and the θ values in methane-air premixed laminar flames. The wavelength responsivity of the optical detection system employed in this work was calibrated using a quartz tungsten halogen lamp. In addition, a Monte Carlo photon tracing method was developed to correct calibration errors caused by variations in the detection distance between experimental and calibration conditions. The corresponding analysis involved a chemical model that generated simulations of one-dimensional, adiabatic, premixed laminar flames.

2. Experimental

Directly-measured emissions are known to differ significantly from the true chemiluminescence output due to the wavelength-dependent responsivity of spectrometers, collection solid angle and losses throughout the detection system (including losses as light passes through the lens, attenuation by fibers and losses in the spectrometer). Therefore, in the present work, calibration of the instrumentation was necessary and а standard lamp capable of producing known wavelength-dependent irradiance was utilized.

The experimental results presented herein were obtained using the experimental setup shown in Figure 1. A flat flame burner was used to generate a stable laminar premixed methane-air flame under atmospheric pressure conditions, so as to allow a direct comparison with numerical modelling. The diameter of the burner was 50 mm

and the mass flow rate of air through the burner was maintained at 18 sLpm while varying the methane flow rate to obtain θ values from 0.7 to 1.33. Accordingly, the mass flow rate per unit area spanned the range from 20.6 to 21.3 mg/cm^2 -sec. The accuracy of the mass flowmeter used for flow rate measurements (Shengye, SY-9322D) was 1.5% F.S in conjunction with ranges of 6 sLpm for CH₄ and 60 sLpm for air. Therefore, the largest possible θ error was 0.11. The apparatus also incorporated a fiber lens based optical collection section coupled to a spectrometer (Andor, SR-500i). Eleven fused silica fibers, each with a numerical aperture of 0.22, were arrayed as a bundle at a distance of 20 mm behind the lens. The focal length and diameter of the resulting lens were 50.8 mm and 10 mm, respectively. Finally, a quartz halogen tungsten filament lamp (Newport, 63355) combined with a radiometric power supply (Newport, 69931) was utilized to calibrate the optical measurement responsivity. The specific irradiance produced by the standard lamp at a distance of 500 mm was determined in advance of the experimental work.



Quartz tungsten halogen lamp

Figure 1. A schematic diagram of the experimental setup.

To ensure that the entire flame was within the collection solid angle of the fiber lens, we positioned the lens 170 *mm* from the flame center and employed an optical axis pitch angle of approximately 17° . The burner was prevented from overheating by a coil through which cooling water flowed, and N₂ was used to purge ambient air from the immediate area during flame experiments. The standard lamp was placed 500 *mm* from the burner along the optical axis to obtain the appropriate specific irradiance. Consequently, unlike the flame (which was a thin layer with a diameter of 50 *mm*) the standard lamp was much further away from the lens and so can be considered as a point source. Therefore, the photon quantity ratios sent to the spectrometer from the lens were different for the two light sources and so a correction factor was required to allow for quantitative measurements.

Figure 2 shows the chemiluminescence signal acquired by the spectrometer over the wavelength range of 250–600 *nm*. The primary emission from the flame was due to the transitions of OH ($A^2\Sigma^+ \rightarrow X^2\Pi$, appearing at 309 *nm*), CH ($A^2\Delta \rightarrow X^2\Pi$, at 430 *nm*), C₂ ($d^3\Pi_g \rightarrow a^3\Pi_u$, at 516 *nm*), and CO₂ (representing a continuum emission). ²⁴ ²⁵ However, it should be noted that other transitions also made a contribution but were excluded from our quantitative analysis, including the 473 *nm* line from C₂^{*} and the 390 *nm* line from CH^{*}.



Figure 2. Flame spectra acquired at various equivalence ratios.



Figure 3. The wavelength-dependent responsivity of the experimental system.

The responsivity calibration results are shown in Figure 3, acquired using a consistent set of experimental parameters and at the required distance (500 *mm*). The quantitative emission from an excited state species is given by

$$P_{\lambda} = S_{\lambda} \cdot \Phi_{\lambda c} \cdot \varepsilon / R , \qquad (1)$$

where S_{λ} is the detected signal (*counts*), $\Phi_{\lambda c}$ is the wavelength-dependent responsivity ($\mu W/counts$) of the detection system calibrated using the standard lamp, R is the photon collection coefficient for the lens (which varies with the collection solid angle of the lens relative to the flame), and ε is the calibration deviation

between the lamp and flame that results from changing the detection distance and the size of the optical source. To ensure accurate data, this deviation parameter was necessary, because light collection by the fiber behind the lens varied while changing the radial distance and the object distance along the optical axis.

In this study, we used the Monte Carlo method to trace the path of random photons from a point source at the position of the standard lamp, and integrated the collection of photons from each position of the burner source in combination with lens imaging theory. The proportional number of photons entering the fiber behind the lens could be calculated separately for these two geometries, and the deviation parameter was the ratio of these two values. With an object distance of 170 *mm*, the coefficient *R* for the lens was 2.163×10^{-4} and the correction factor, ε , for the transmission of photons from the lens to the fiber was 1.224.

The emission values were calculated by integrating the spectrum area. As shown in Figure 2, the continuous spectrum of CO_2^* from 250 to 600 *nm* first increases and then decreases under all experimental conditions. Therefore, we were able to use a polynomial to fit the CO_2^* data between 250 and 600 *nm*. To ensure accuracy, fifth order polynomial fittings were used for all CO_2^* curves, and then applied as the baselines for all other species. The integration range for all spectral lines was not fixed with θ to ensure that the wavelength width of each spectral line was covered.

Figure 4 presents the experimental results for CO_2^* and C_2^* emissions, based on the spectral integration described above. Here, we used units of μW to quantify the emission intensity of the chemiluminescence and the number of emitted photons

(*mole-photons* s^{-1}) could be calculated based on the Planck–Einstein relationship. As illustrated by these curves, the C₂^{*} intensities were only significant under fuel rich conditions.²⁶ The entire CO₂^{*} continuum emission band was not collected, but band integration was performed between 250 and 600 *nm* and plotted against the equivalence ratio.



Figure 4. Experimental results for CO_2^* and C_2^* chemiluminescence intensities versus the equivalence ratio.

To verify the experimental results, the behavior of C_2^*/CH^* peak intensities was compared to data in the literature,²⁷ as in Figure 5, although no calibration of responsivity for these two species was available in the literature. The curves show similar monotonic trends and ratio values when the equivalence ratios are above 1.1, which confirms the validity of using chemiluminescence to determine θ in this range. In addition, the values plateau at ratios from 0.9 to 1.1. Lower equivalence ratios have also been assessed previously, but the results exhibit significant scatter, as was also

evident in our own experiments. This is attributed to the very low C_2^* emission intensity at θ values below 0.9, as discussed above. These calibrated C_2^*/CH^* are close to the uncalibrated values because the responsivities of the CH^{*} (430 *nm*) and C_2^* (516 *nm*) emissions are very close, not to say the calibration is negligible. In contrast, the responsivity of the OH^{*} (309 *nm*) emissions is quite different and so calibration is essential. The intensity of the C_2^* chemiluminescence emissions becomes relevant under fuel rich conditions, which is also in agreement with the work of Tatiana et al.²⁸



Figure 5. C_2^*/CH^* peak ratios as functions of the equivalence ratio (θ)

3. Chemical kinetics model

Quantification by numerical methods is based on a one-dimensional premixed flame reaction simulation, and many researchers have attempted to model the formation and destruction of chemiluminescence species, applying different mechanisms. Herein, we used the model in Table 1, which integrates 19 reactions from other studies,²⁹⁻³¹ as a sub-mechanism, and combined it with the basic methane mechanism (GRI-Mech 3.0).³² This model was selected because its excited species sub-mechanism has been

thoroughly tested.^{16,33} The same sub-mechanism was also used by Panoutsos et al.¹⁶ to

identify the general structures of laminar premixed counterflow flames.

NO.	Reaction	А	В	Ea
1	$CH+O_2 \le OH^*+CO$	6.000E+10	0.00	0
2	$OH^* \ll OH + hv$	1.450E+06	0.00	0
3	$OH^* + N_2 \le OH + N_2$	1.080E+11	0.50	-1238
4	$OH^{*}+O_{2} <=>OH+O_{2}$	2.100E+12	0.50	-482
5	$OH^* + H_2O \le OH + H_2O$	5.920E+12	0.50	-861
6	OH*+H2<=>OH+H2	2.950E+12	0.50	-444
7	$OH^*+CO_2 \le OH+CO_2$	2.750E+12	0.50	-968
8	OH*+CO<=>OH+CO	3.230E+12	0.50	-787
9	OH [*] +CH ₄ <=>OH+CH ₄	3.360E+12	0.50	-635
10	$C_2H+O \leq >CH^*+CO$	1.080E+13	0.00	0
11	$C_2H+O_2 \leq CH^*+CO_2$	2.170E+10	0.00	0
12	$CH^* \ll CH + hv$	1.850E+06	0.00	0
13	$CH^* + N_2 \le CH + N_2$	3.030E+02	3.40	-381
14	$CH^{*}+O_{2} <=>CH+O_{2}$	2.480E+06	2.14	-1720
15	$CH^* + H_2O \le CH + H_2O$	5.300E+13	0.00	0
16	CH*+H2<=>CH+H2	1.470E+14	0.00	1361
17	$CH^*+CO_2 \le CH+CO_2$	2.400E-01	4.30	-1694
18	CH*+CO<=>CH+CO	2.440E+12	0.50	0
19	CH [*] +CH ₄ <=>CH+CH ₄	1.730E+13	0.00	167

Table 1. Sub-reaction mechanism used to model OH^* and CH^{*16}

Note: The reaction rate coefficient is expressed as $k = AT^{B}exp(-E_{a}/RT)$, where E_{a} is in cal/mole and R is in cal mole⁻¹ K⁻¹.

In our study, the methane-air mixtures were at 298 K and atmospheric pressure under inflow conditions. The numerical results for mole fraction profiles at $\theta = 0.9$ and 1.27 using the same fuel mass flow conditions as in the experimental work are presented in Figure 6. The quantities of excited states (OH^{*} and CH^{*}) are small compared to the number of ground state species. As an example, the OH^{*}/OH peak ratio is only 1.4 × 10^{-8} at $\theta = 0.9$, and a similar ratio is obtained at $\theta = 1.27$. Therefore, the added sub-mechanism had only a minimal effect on the basic reactions of the other species. When θ was increased, the peak positions of all species (OH, CH, HCO, OH^{*} and

CH^{*}) moved upstream for $\theta < 1.1$ and downstream for $\theta > 1.1$, while the relative positions changed only slightly. The distributions of CH and CH^{*} increased with increases in θ , while there was a remarkable reduction in the OH distribution. In addition, both the heat release rate and the temperature increased when θ was increased from 0.9 to 1.27.



Figure 6. Mole fraction profiles and heat release rates at $\theta = 0.90$ and 1.27.

The source reactions for C₂ ($d^3\Pi_g \rightarrow a^3\Pi_u$) emissions are not certain³⁴ compared with the OH^{*} and CH^{*} kinetic models, and we were unable to identify any thermodynamic properties for C₂ ($d^3\Pi_g$). As a result, C₂^{*} was excluded from modeling, as was CO₂^{*} for the same reason.

The distributions of OH^{*} and CH^{*} in Figure 6 indicate that the OH^{*} emissions increased earlier than the CH^{*} emissions at both θ . However, the peak values, the wave breadths and the peak-to-peak distances of the CH^{*} and OH^{*} emissions changed very differently with θ . In the case of $\theta = 0.90$, the OH^{*} chemiluminescence breadth was slightly wider than that of CH^{*}, which agrees with the experimental results of Kojima et al.,²⁶ and the FWHM values were 0.15 and 0.14 mm for the OH^* and CH^* distributions. The peak-to-peak distances between excited species and the heat release rates were approximately 28 μm for OH^{*} and 67 μm for CH^{*}, which are similar to the results of Hardalupas et al.³⁵ At $\theta = 1.27$, both the OH^{*} and CH^{*} intensities increased, although the CH^{*} values varied more significantly than those for OH^{*}, while the CH^{*} FWHM became 0.23 mm and so was wider than that of the OH*, for which the FWHM was 0.18. At this same θ , the position of the heat release rate peak value moved downstream by approximately 240 μm , and the peak-to-peak distances between excited species and the heat release rate were approximately 55 and 100 μm for OH^{*} and CH^{*}.

4. Results

The chemiluminescence emission intensity (*mole-photons* s^{-1}) will be directly proportional to the excited state population. To compare the spatially integrated chemiluminescence results with the experimental data, the measured emission values (*mole-photons* s^{-1}) were also integrated spectrally, according to:

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$$P_E = \int_{\lambda_1}^{\lambda_2} P_{\lambda} d_{\lambda} , \qquad (2)$$

where λ_1 and λ_2 are the margin wavelengths for which there are no obvious emission for each excited species. The emissions for modeling calculations were obtained using the equation:

$$P_{S} = A_{f} * \int_{0}^{L} i_{c} dx * A_{E}, \qquad (3)$$

where L is the burner distance (the entire numerical length), i_c is the concentration (mol cm⁻³), A_f is the flame area, and A_E is the Einstein coefficient (1.85 × 10⁶ s⁻¹ for CH^{*} and 1.40 × 10⁶ s⁻¹ for OH^{*}).³⁰







Figure 7. Simulated and experimental results for (a) OH^{*} and (b) CH^{*} chemiluminescence intensities (Y-left axis) with ratios of simulated to experimental results (Y-right axis) versus the equivalence ratio. (c) Simulated and experimental results for CH^{*}/OH^{*} (Y-left axis) with ratios of simulated to experimental results (Y-right axis) versus the equivalence ratio.

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Figures 7(a) and (b) plot the overall chemiluminescence intensities of OH^* (for values from 10^{-11} to 10^{-10} *mole-photons* s^{-1}) and CH^* (10^{-12} to 10^{-10} *mole-photons* s^{-1}) in the premixed flat flames of our experimental apparatus. Here, the simulated emissions are on the same order of magnitude as the experimental data. However, the simulated results are larger than the experimental values for both OH^* and CH^* , and the OH^* data are a better match than the CH^* data in terms of equivalence ratio.

The experimental and numerical intensities in Figure 7(a) demonstrate that the OH^{*} emissions increased monotonically with θ over the range of $0.7 < \theta < 1.2$, and decreased thereafter. The ratio of simulated to experimental values ranged from 1.5 to 2.0, and shows no correlation with θ . The intensities in Figure 7(b) show that the CH^{*} emissions increased monotonically with the full course θ for $0.7 < \theta < 1.3$. The ratio of simulated values to experimental values also increased (from 2.4 to 5.1) as θ became larger, indicating that the CH^{*} modeling performance is poor with regard to experimental results for fuel rich flames. Nevertheless, the numerical results still correctly predict the general trend of the CH^{*} chemiluminescence. In Figure 7(c), the absolute values of the CH^{*}/OH^{*} intensity ratios increased monotonically with respect to θ , which suggests the feasibility of determining equivalence ratios using chemiluminescence. This ratio also increased as the fuel equivalence increased, mainly because of the deviation between the experimental and simulated CH^{*} intensities.

5. Discussion

There are certain disagreements between the simulated and experimental values, in that the simulated emissions for both OH^{*} and CH^{*} are greater than the experimental results. In addition, the ratios of simulated to experimental results behave differently, such that the OH^{*}/CH^{*} intensity ratios are greater than the experimental values. Self-absorption and thermosteresis are two possible reasons why the simulation settings may not be in complete agreement with the experimental conditions, and so the effects of these factors on the emissions of OH^{*} and CH^{*} were analyzed.

Self-absorption is related to the Beer-Lambert law. The absorbance coefficient varies linearly with the number density of molecules in the low energy state, which in turn is positively correlated with the concentrations of these species in a given absorbing path length. Figure 8 shows the simulated OH (not OH^{*}) concentrations under the same conditions as employed during experiments. The OH concentration is seen to increase monotonically with θ for $0.7 < \theta < 0.95$ and then decreases. Based on experimental results from the literature [36] for a study using a similar premixed burner, OH^{*} emissions can be 10%-40% self-absorbed for an absorption path of 54 *mm* and the maximum self-absorption is at a θ of 0.9. Under our experimental conditions, with an average self-absorption path length of approximately 26 *mm* (25/cos(17°)), the maximum self-absorption should be about 0.2 at a θ close to 0.95. In contrast, the concentration of CH (not CH^{*}) is on the order of 10⁶ molecule/cm³ in the post-combustion zone, which is ten orders of magnitude less than the OH concentration. Therefore, the effect of CH^{*} self-absorption should be negligible.



Figure 8. Simulated OH concentrations versus the equivalence ratio.

The prediction of CH^{*} emissions is more challenging¹⁴ compared to OH^{*} since it involves intermediates species such as C₂H and O, whose validation is difficult. Berman et al.³³ demonstrated the importance of the temperature dependence of CH radical reactions. As shown in Table 1, the two reaction rate coefficients used in the CH^{*} formation reactions are both constant with changing temperature. There are some other reactions rates that vary with temperature,¹⁴ and Elsamra et al.³⁷ studied the temperature dependence of the rate constant for the reaction C₂H + O₂ \leftrightarrow CH^{*} + CO₂ over the temperature range 316–837 *K*. They found that the rate constant exhibited a positive temperature dependence based on their proposed reaction rate coefficient. In the case of the premixed burner used in the present work, the reaction zone is less than 1 *mm* above the burner, as shown in Figure 6. Thus, thermal transmission to the burner (via the cooling water) is the main thermosteresis effect resulting in a lower temperature.

Cooling water was essential in our experiments to maintain a constant inlet gas temperature. To evaluate the heat loss to the burner, we measured the temperatures of

cooling water flowing into and out of the burner for each θ and heat losses were calculated using the heat capacity of cooling water after carefully calibrating the water flux. As shown in Figure 9, the maximum heat loss to the burner was approximately 60 *J/s* at $\theta = 1.2$.



Figure 9. Thermosteresis relative to the burner and the temperature rise of the cooling water.

We subsequently combined the thermosteresis data with the simulation and utilized a new CH^{*} formation mechanism involving temperature dependent reaction rate constants, as shown in Table 2. Based on variations in the thermosteresis with θ , the simulated OH^{*} chemiluminescence values decreased by approximately 17% while the CH^{*} values decreased by 30%. Thus, the CH^{*} formation mechanism in Table 2 gives better agreement with the experimental results.

Table 2. Sub-reaction mechanism for CH^{*} formation³⁷

NO.	Reaction	А	В	Ea	
1	$C_2H+O \leq >CH^*+CO$	6.020E+12	0.00	457.00	
2	$C_2H+O_2 <=>CH^*+CO_2$	6.020E-04	4.40	2285.00	

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To sum up, self-absorption and thermosteresis may have caused the experimental OH^* chemiluminescence results to be up to 33.6% lower than expected. Therefore, $[OH^*]_s$ and $[OH^*]_e$ in Figure 7(a) should be in reasonable agreement with one another, suggesting that the sub-reaction mechanism involving OH^* in Table 1 is credible. In contrast, even taking thermosteresis taken into account, the model overpredicts the CH^{*} emissions, and so the associated reaction rate coefficients at elevated temperatures require correction.

6. Conclusions

Quantitative and spectrally-resolved information regarding excited OH(A), CH(A), and C₂(d) chemiluminescence from CH₄/air premixed flames ($\theta = 0.7-1.33$) was obtained using a fiber system combined with a spectrometer to study a flat flame burner. Spatially integrated OH^{*} and CH^{*} chemiluminescence data were compared with simulation results based on one-dimensional premixed flames, using formation and consumption reaction mechanisms for OH^{*} and CH^{*}.

The results show that the experimental and simulated emission intensities for CH^{*} and OH^{*} were on the same order of magnitude (10^{-12} to 10^{-10} *mole-photons* s⁻¹), and changed along with θ . Increasing θ initially increased and then decreased OH^{*} emissions but continually raised CH^{*} emissions. These results indicate that the chemiluminescence intensity can be used to evaluate θ when employing a well-calibrated system. Considering self-absorption and the thermosteresis of the cooling water, the simulated OH^{*} emissions were approximately 1.0 to 1.4 times the

experimental values while the simulated CH^{*} values were from 2.3 to 4.1 times greater. The simulation accuracy for OH^{*} was therefore better than that for CH^{*}. Thus, we propose that the temperature dependence factors for the rate coefficients for CH^{*} formation at high temperatures should be refined.

The results presented herein were obtained from quantitative comparisons of experimental and simulated values for independent species, and such data are difficult to obtain using OH*/CH* ratios. More importantly, future analysis of the chemiluminescence reaction mechanisms may allow CFD simulations based on the quantification of chemiluminescence, combined with 3D-CTC experiments, to bring new perspectives to the study of complicated chemical reactions.

ACKNOWLEDGMENTS

This work was sponsored by the National Natural Science Foundation of China (Grant No. 11372329) and supported by the Scientific Instrument Developing Project of the Chinese Academy of Sciences (Grant No. YZ201637).

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