CH(A-X) and OH(A-X) Optical Emission in an Axisymmetric Laminar Diffusion Flame

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Steady-state concentrations of electronically excited $CH(A^2\Delta)$ and $OH(A^2\Sigma^+)$ are extracted from previous quantitative measurements of optical emission from an axisymmetric laminar diffusion flame [K. T. Walsh, M. B. Long, M. A. Tanoff, and M. D. Smooke, *Twenty-Seventh Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1998, pp. 615–623]. The flame is modeled with a two-dimensional transport and detailed chemistry explicitly augmented with the reactive, radiative, and energy transfer collisional processes to produce and remove electronically excited CH(A) and OH(A). Computations predict concentrations of CH(A) and OH(A) which agree with the measurement within a factor of 6 or better, a significant improvement compared to the earlier report.   © 2000 by The Combustion Institute

INTRODUCTION

Even though the practical diagnostic uses of the optical emission from flames have been long apparent, very little work quantitatively investigating the intensity of the optical emission from excited molecules in flames has been published since Gaydon [1] in 1974. Joklik et al. investigated CH(X) and CH(A) concentrations in a low-pressure acetylene flame [2], and Deviendt et al. [3] measured CH(A) production rates. Recently, Walsh et al. [4] quantitatively measured the optical emission intensity from the CH(A-X) transition near 431 nm and the OH(A-X) transition near 308 nm; they found very poor agreement between these measurements and model calculations for a methane/air diffusion flame.

In the work reported here, we correct two errors in the published analysis of Ref. 4. First, the removal of the excited molecules by collisional quenching was double counted by both adding collisional removal into the model and then additionally correcting the observed emission for quenching. This double-counting resulted in an overprediction of measured CH(A) and OH(A) by factors of 176 and 327 respec-

tively. Second, Ref. 4 used a branching fraction of unity for $CH + O_2 \leftrightarrow OH(A) + CO$; this ignores the dominant product channel $OH(X) + CO$. Using more appropriate branching ratio reduces predicted OH(A) by a factor of 540. In this paper, we redetermine the steady-state concentrations of CH(A) and OH(A) from the emission intensities measured in Ref. 4, and we compare these concentrations with values predicted from the same model including two-dimensional transport and modified chemistry for CH(A) and OH(A).

THE EXPERIMENT

The lifted axisymmetric laminar methane/air diffusion flame studied here has been extensively characterized both experimentally and computationally [4–8]. Walsh et al. [4] measured the optical emission from CH(A) and OH(A) on a cooled CCD camera with a f/4.5 UV camera lens using narrow bandpass filters (10 nm FWHM at 431 nm and 307 nm respectively). Emission intensity measurements are line-of-sight-integrated and the two-dimensional, in-plane intensity distribution is recovered with an Abel deconvolution [9, 10].

The number density of electronically excited molecules in the flame is a balance between production by chemiluminescent reactions and removal by electronic energy transfer collisions,

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reactive collisions of the excited molecules, and the observed optical emission. Thus, a steady-state concentration of excited radicals is observed in the flame and will be predicted by any model that includes both production and the removal pathways. This concentration produces optical emission at the radiative rate. The emission, S_{em}, from this steady-state concentration for a specific electronic transition between an excited state u and a ground state g during the time interval τ is given by:

$$S_{em} = A_{ug}\tau F_{if}n_{exc}V_{em}\frac{\Omega\epsilon\eta}{4\pi} \qquad (1)$$

where A_{ug} is the Einstein's emission coefficient of the observed vibrational band (s^{-1}), F_{if} is the fraction of the vibrational band transmitted by the interference filter, n_{exc} is the steady-state number density of excited species (cm^{-3}), and V_{em} is the observed volume. The remaining factors are given by the optics and electronics in the detection of the collected light where Ω is the solid angle, ϵ is the transmission efficiency of the optics, and η the photoelectric conversion. The factor $\Omega\epsilon\eta$ is determined by Rayleigh calibration [11]. The volume observed in the emission measurement and the laser-illuminated volume observed by the Rayleigh scattering are not in general equal. This difference in volume is accounted for in the line-of-sight deconvolution [9, 10].

Both CH(A) and OH(A) occur in a very thin region on the order of 200 μm thick as shown in the insets of Figs. 1 and 2. To facilitate direct comparison between experiment and computations, the CH(A) and OH(A) concentrations are integrated through the flame front (viewed according to the inset of Fig. 1 or 2; the integration is 100 μm along z by 100 μm into the page by 1 cm along r. Note the excited radicals only are present in a narrow region along r). This eliminates differences in spatial resolution and radial position between measurement and model, and one can easily compare measurements and predictions of excited state radicals versus height in the flame. However, the integration produces an ordinate scale in Figs. 1 and 2 with units of molecules instead of the more familiar number density. The resulting integrated steady-state CH(A) and OH(A) profiles
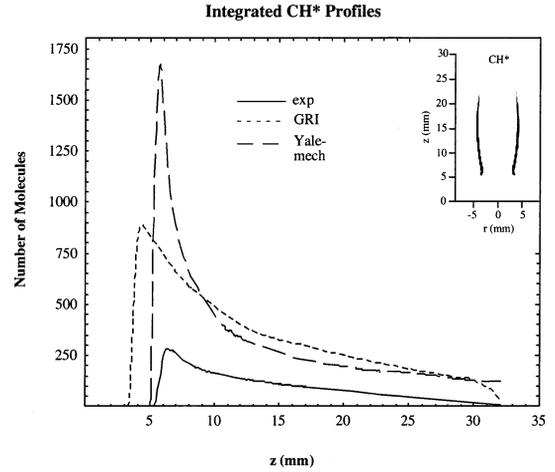
Fig. 1. Integrated, steady-state CH(A) versus height above the burner: measured (solid line), predicted with GRI-Mech 2.11 (dashed line), and predicted with the mechanism of Ref. 7 (long dashed line). The Abel inversion of the measured optical emission provides the two-dimensional CH(A) distribution shown in a gray scale in the upper right corner.

are shown as a function of height above the burner in Figs. 1 and 2, respectively. Both the CH(A) and OH(A) profiles peak at the base of the flame and steadily decline along the flame length to the tip of the flame 3 cm above the burner.
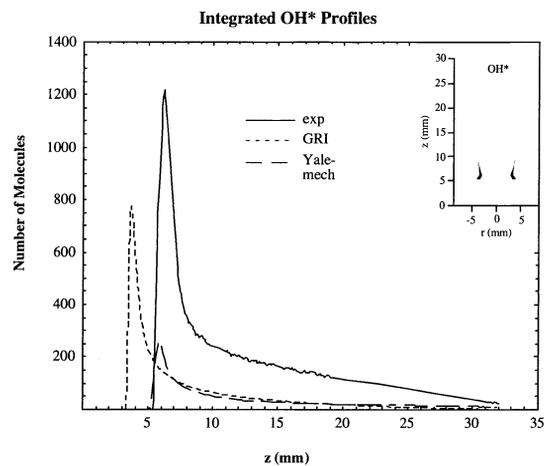
Fig. 2. Integrated, steady-state OH(A) versus height above the burner: measured (solid line), predicted with GRI-Mech 2.11 (dashed line), and predicted with the mechanism of Ref. 7 (long dashed line). The measured, two-dimensional OH(A) distribution is shown in a gray scale in the upper right corner.

THE MODEL

This axisymmetric diffusion flame is modeled by a two-dimensional transport code [8] using two different chemical mechanisms: a 26 species C_2 hydrocarbon mechanism developed at Yale [8] and GRI-Mech 2.11 [12]. Both predict values of temperature and major species concentrations in excellent agreement with measurements [8]. It should be pointed out, however, that GRI-Mech predicts a higher methane–air counter-flow extinction strain rate (i.e., higher scalar dissipation at extinction) than the Yale mechanism, which predicts values closer to experimental measurements. As a result, two-dimensional coflow solutions computed with GRI-Mech sit closer to the burner (lower lift-off height) than those computed with the Yale mechanism. Computed peak concentrations of ground state CH, OH, and NO agree with measurements [4, 6, 7] within 25%, 15%, and 30% respectively for either mechanism. Both of these mechanisms are augmented to include the production and loss of excited CH(A) and OH(A).

Chemiluminescent reactions to produce excited state CH(A) and OH(A) are added to both chemical mechanisms. CH(A) is the product of the reactions of C_2H with O and O_2:

$$C_2H + O_2 \leftrightarrow CH(A) + CO_2 \qquad (2)$$

$$C_2H + O \leftrightarrow CH(A) + CO \qquad (3)$$
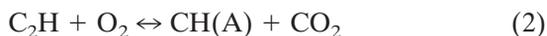
The reported rate constants $k_2 = 3.6 \times 10^{-14}$ $cm^3 s^{-1}$ and $k_3 = 1.8 \times 10^{-11}$ $cm^3 s^{-1}$ measured recently at 298 K are used [3]. CH(A) was assigned a heat of formation of 66.3 kcal/mole above that of ground-state CH, based on the energy of the spontaneously emitted photon. OH(A) is produced by the single reaction:

$$CH + O_2 \leftrightarrow OH(A) + CO \qquad (4)$$

The rate constant $k_4 = 1 \times 10^{-13}$ $cm^3 s^{-1}$ deduced from the flame measurements of Porter et al. [13] is used. The heat of formation of OH(A) was set at 93 kcal/mole above that of ground-state OH. From the rate constant for all products of CH + O_2 measured by Berman et al. [14], a branching ratio of 0.00185 for OH(A) can be inferred. At flame temperatures, we estimate large, factor of 3, uncertainties in the rate coefficients for the production of CH(A) and OH(A).

Radiative and collisional removal of the excited CH(A) and OH(A) are also added to the chemical mechanisms. Spontaneous emission rates of $1.86 \times 10^6 s^{-1}$ and $1.45 \times 10^6 s^{-1}$ are used for CH(A) and OH(A) respectively [4]. Species-specific, temperature-dependent quenching rate constants were taken from Tamura et al. [15] for both CH(A) and OH(A) [following Ref. 4]. The removal rate coefficients for major species in methane flames are known within 10% for OH(A) and 25% for CH(A) [15].

Figures 1 and 2 compare the measured data with the predictions of the model calculations using the Yale chemical mechanism and the augmented GRI-Mech 2.11. The model with augmented GRI-Mech 2.11 predicts concentrations of CH(A) and OH(A) that agree with the measurements within a factor of 4 and 2, respectively. The shape of the variation with height above the burner of both the CH(A) and OH(A) steady-state concentrations is also well predicted by the augmented GRI-Mech 2.11. The calculation using the Yale mechanism does not predict the concentrations as well, overpredicting the peak CH(A) concentration by a factor of 6 and underpredicting the OH(A) by a similar factor of 6. The calculation using the Yale mechanism does not match the variation of the CH(A) concentration as a function of height above the burner as well as the calculation with the augmented GRI-Mech 2.11. However, as noted earlier, the predictions using the Yale mechanism match the flame stand-off height, whereas calculations with the augmented GRI-Mech 2.11 find the flame 0.18 cm too close to the burner, as apparent in Figs. 1 and 2.

CONCLUSION

The revised analysis and the chemiluminescence chemical mechanism result in qualitative agreement between model calculation and measured emission intensity. Although the quantitative agreement is improved more than a factor of 20, uncertainties in the production reaction rate coefficients for excited CH(A) and OH(A) limit

our ability to quantitatively predict the optical emission from methane flames to a factor of 6.

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