

Structure of H₂/O₂/N₂ Flames at Atmospheric Pressure Studied by Molecular Beam Mass Spectrometry and Modeling

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Abstract

Structure of laminar premixed flat H₂/O₂/N₂ flames with different equivalence ratios at atmospheric pressure is investigated experimentally and by numerical modeling. Concentration profiles of stable species (H₂, O₂, H₂O) as well as of H atoms and OH radicals in the flames were measured using molecular beam mass-spectrometry with soft ionization by electron impact. A good agreement between the obtained experimental data and the results of numerical simulation using three different detailed kinetic mechanisms indicates the robustness of these models in predicting the structure of hydrogen-oxygen flames at atmospheric pressure.

Introduction

Through many years and up to now, mechanism and chemistry of combustion of hydrogen-oxygen mixtures have been the subject of many investigations [1-10, 27]. Chemical kinetic mechanism of combustion of H₂/O₂ mixtures is of great importance because it is an integral part of kinetic models for hydrocarbons oxidation. The progress in development of these mechanisms is based on a comparison of experimental data (on burning velocity, ignition delay, flame structure etc.) obtained over wide range of conditions (pressure, temperature, composition of fresh mixture) with the results of numerical simulation performed using the testable kinetic mechanism. In kinetic mechanisms, the reactions with active species, atoms and radicals, play a key role. Therefore, the most important, while a challenging task is to measure their concentration and concentration profiles in the flames. Probing molecular beam mass-spectrometry with soft electron-impact ionization is one of the most appropriate tools for this purpose. Eltenton [8] as well as Foner and Hudson [9] were the pioneers, who applied this technique for detection of atoms and radicals in low-pressure flames. Probing molecular beam mass-spectrometry (pMBMS) is the most useful technique allowing all species in the flame (including atoms and radicals) to be measured simultaneously. It was widely used for studying the structure of flames, including the flames of hydrogen-oxygen mixtures.

The structure of such flames was studied mostly at subatmospheric pressures [10-13]. Only a few works [14-16] were focused on studying the structure of hydrogen-oxygen flames at atmospheric and higher pressures, due to the difficulties of measurements of species concentration profiles by pMBMS at these conditions. The concentration profiles of stable species only were measured in fuel-rich [14-15] and stoichiometric [16] flames. To validate thoroughly a chemical kinetic mechanism for combustion of hydrogen at 1 atm, one needs the data on spatial

variation of concentration of active species (particularly, H and OH) in the atmospheric hydrogen flames.

Specific Objectives

This work aims to investigate the structure of H₂/O₂/N₂ flames over the range of equivalence ratios at atmospheric pressure by molecular beam mass spectrometry and by modeling for validation of the kinetic mechanisms developed earlier. One of the key emphases of this study is to validate the pMBMS-system with soft electron-impact ionization for determining the structure of hydrogen flames, in particular, for measurement of concentration profiles of the key flame species (H and OH).

Experimental method

The flames studied were stabilized under near-adiabatic conditions on a perforated plate burner using the heat flux method [17, 18]. The burner consists of a burner head mounted on 35-cm-high tube with water jacket. The burner head represents 3-mm-thick copper plate 24 mm in diameter perforated with the holes 0.5 mm in diameter (centers of the holes are equally spaced 0.7 mm apart) and heating jacket. The heating jacket of the burner head is supplied with thermostated water to maintain the temperature of the burner plate constant at 333 K. The water jacket of the burner tube is supplied with circulating water at 308 K, which controls the temperature of a fresh gas mixture. The idea of the heat flux method is based on finding of the flow velocity of the fresh mixture through the burner when the heat losses into the burner are compensated by the controlled heating of the fresh mixture, and the balance of the heat losses to the burner surface is close to zero. The balance of the heat losses at the burner surface is determined by measuring the radial temperature distribution on the burner plate. For this purpose, six copper-constantan thermocouples were soldered into the burner holes at 0, 2.4, 4.5, 7, 10 and 12 mm from the

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Table 1. Summary of different parameters for the flames studied.

Flame	Rich flame	Near-stoichiometric flame	Lean flame	Calibration flame
Equivalence ratio $\phi = ([\text{H}_2]/[\text{O}_2])/([\text{H}_2]/[\text{O}_2])_{\text{stoichiometry}}$	2	1.1	0.47	1.1
Dilution ratio $D = [\text{O}_2]/([\text{O}_2] + [\text{N}_2])$	0.077	0.09	0.209	0.14
Flow velocity of fresh mixture at burner surface (in the experiments), cm/s	40.7	42.5	34.24	49.1
Measured burning velocity of free propagating flame, cm/s	41.1	47	55	
Burning velocity of free propagating flame calculated using kinetic mechanism [2], cm/s	39.6	38.3	36.2	141.6

center of the burner. The flow velocity of the fresh mixture whereby the above conditions are satisfied is adiabatic burning velocity by definition.

Compositions and flow rates of the fresh mixtures studied were set by mass flow controllers (MKS Instruments Inc.). The stated purity of gases (H_2 , O_2 , N_2) was 99.95%. Three flames of different compositions were studied in this work and a flame called “calibration flame” was used to calibrate the MBMS-setup for measurements of absolute concentrations of H and OH radicals. Table 1 shows the compositions, equivalence and dilution ratios for all four flames. Linear velocities of the fresh mixtures at the burner surface as well as measured and calculated (using PREMIX code [19-21] and chemical kinetic mechanism [2]) burning velocities of these flames are also given in the Table 1. To stabilize reliably the flames during the flame structure measurements, the flow velocities of the fresh mixtures were set somewhat below the burning velocities of these mixtures. The lean flame ($\phi=0.47$) had a cellular structure when the flow of the fresh gas mixture is close to the burning velocity. Thus, to eliminate this effect, the flame was stabilized with the fresh mixture flow 40% lower than the burning velocity of the flame in this mixture. Temperature profiles in the flames were measured using Pt/Pt+10%Rh thermocouple made of wires 0.02 mm in diameter and coated with SiO_2 (total diameter of the coated thermocouple was ~ 0.04 mm). Concentration profiles of the species were obtained using molecular beam sampling system coupled with quadrupole mass-spectrometer MS-7302 with soft ionization by electron impact [22]. Sampling was performed at different heights above the burner surface using a quartz “sonic” probe. The opening angle of the probe was 40° , the orifice diameter was 0.08 mm, and the wall thickness near the orifice was 0.08 mm.

A sampling probe is known to perturb a flame structure. The total probe effect on the flame is a combination of thermal and gas-dynamic perturbations of the flame. To take into account the thermal perturbations, temperature profiles measured in the flame by a thin thermocouple at a certain distance “probe tip - thermocouple” in front of the probe tip are usually used in the calculations of concentration profiles of flame species. In our experiments, the distance “probe tip - thermocouple junction” was chosen to be 0.2 mm. To validate this choice we have preliminary measured temperature profiles in the near-stoichiometric flame with the thermocouple positioned

at different distances from the probe tip (0.1, 0.2, 0.3 and 0.4 mm). The obtained results are shown in Fig. 1. Using these profiles and the detailed chemical kinetic mechanism [23] we simulated the flame structure. A criterion for choosing the most appropriate distance “probe tip – thermocouple junction” was as following: position of H and OH maximums on corresponding measured concentration profiles should be in agreement with those on calculated profiles obtained using the appropriately measured temperature profile. We find this criterion to be justified, because in this case the accuracy of absolute concentration of the species does not need to be perfect. In addition, position of the maximum on the measured H and/or OH concentration profile is far easier to recognize and to compare with the numerical results. Figure 2 shows H and OH concentration profiles measured in the near-stoichiometric flame as well as calculated ones using the temperature profiles given in Fig. 1 (the calculations were performed using PREMIX code [19-21] and chemical kinetic mechanism [23]). Comparing the experimental and modeling results shown in Fig. 2 one can conclude that for the near-stoichiometric flame the appropriate distance “probe tip – thermocouple junction” is somewhere between 0.15 and 0.2 mm. Since the conditions (post-flame temperature, velocity of the flow riding on the probe) for lean ($\phi=0.47$) and rich ($\phi=2.0$) $\text{H}_2/\text{O}_2/\text{N}_2$ flames studied are very similar to those for the near-stoichiometric flame ($\phi=1.1$), the

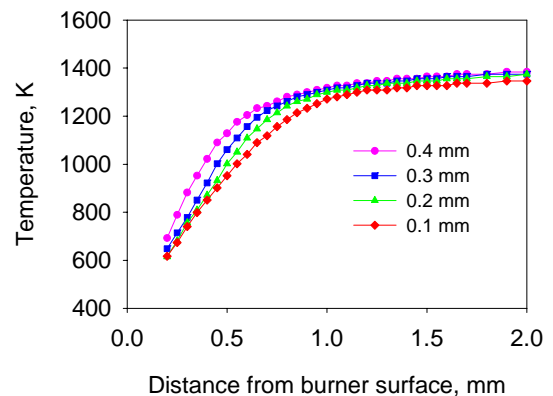


Fig. 1. Temperature profiles measured in presence of the sampling probe by the thermocouple positioned at different distances “probe tip – thermocouple junction” in near-stoichiometric $\text{H}_2/\text{O}_2/\text{N}_2$ flame ($\phi=1.1$, $D=0.09$).

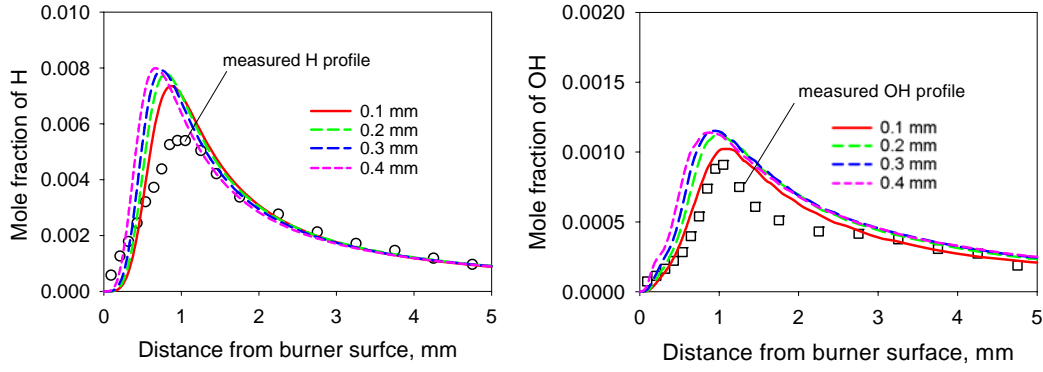


Fig. 2. Concentration profiles of H and OH radicals. Symbols: measurements; lines: modeling (using kinetic mechanism [23]) with temperature profiles measured at different distances “probe tip - thermocouple”.

appropriate position of the thermocouple relative to probe tip can be assumed to be the same.

To take into account the gas-dynamic perturbation of the flames by the sampling probe, the upstream shift ΔZ of all measured concentration profiles was made. The value of ΔZ was estimated using the following semiempirical formula proposed earlier [24]:

$$\Delta Z = 0.37 \cdot d \cdot \sqrt{\frac{Q}{S \cdot V}},$$

where d is the probe orifice diameter, Q is gas flow rate through the probe orifice, S denotes probe orifice area, V is the velocity of incoming gas flow.

The absolute concentrations of the measured species were determined using the corresponding calibration coefficients. These coefficients for H_2 , O_2 and H_2O were obtained by direct calibration. For this purpose, the measurements of the intensities of the base mass peaks (m/z) 2, 32 and 18 in the gas mixture of known composition consisting of air and hydrogen and containing the water vapor heated to the temperature of 200 °C were performed. Peak intensity of argon presenting in the air was used as a reference. The calibration coefficient k_i relating to argon was evaluated using the following formula:

$$k_i = C_i \times I_{40} / C_{Ar} \times I_i, \quad (1)$$

where I_i and I_{40} are the intensities of the base peak for i -species and for argon, respectively; C_i and C_{Ar} are mole

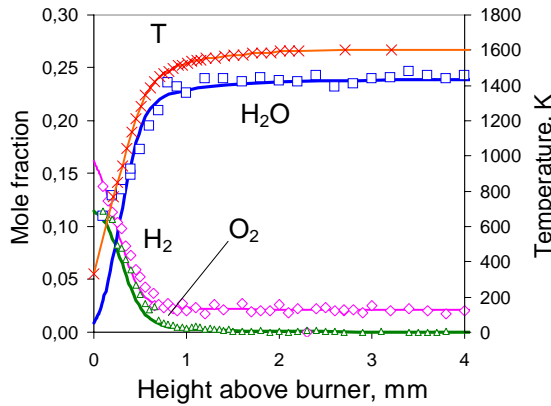
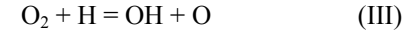


Fig. 3. Temperature profile and concentration profiles of stable species in calibration flame $H_2/O_2/N_2$ flame ($\phi=1.1$, $D=0.14$). Symbols are experimental data; lines are modeling using kinetic mechanism [23].

fractions of the species being calibrated and argon, respectively.

The measurements of H atoms and OH radicals in the flames were carried out with the energy of ionizing electrons of 16.2 eV, which allowed the contribution from other species to the corresponding mass spectra to be excluded. Calibration of H and OH radicals was performed using a well known method proposed earlier [25]. We have already employed it for subatmospheric hydrogen-oxygen flames [26]. This method is based on a fact that in the post-flame zone of hydrogen flames partial equilibrium of three “fast” reactions takes place. These three reactions are the following:



The equilibrium constants K_1 , K_2 and K_3 [23] corresponding to the aforementioned reactions are given below:

$$K_1 = 0.113 \times T^{0.0839} \times e^{7680/T} \quad (2)$$

$$K_2 = 1.8 \times T^{0.027} \times e^{-917/T} \quad (3)$$

$$K_3 = 302 \times T^{-0.374} \times e^{-8620/T} \quad (4)$$

The expressions for H, O and OH in this approximation are of the following form:

$$[OH] = \sqrt{K_2 \times K_3 \times [O_2] \times [H_2]}, \quad (5)$$

$$[O] = \frac{K_1 \times K_3 \times [H_2] \times [O_2]}{[H_2O]}, \quad (6)$$

$$[H] = \frac{K_1 [H_2]}{[H_2O]} \sqrt{K_2 \times K_3 \times [O_2] \times [H_2]}. \quad (7)$$

In the post flame zone (1.5-4 mm above the burner) of all hydrogen flames with $\phi=0.47$, 1.1 and 2.0 ($D=0.209$, 0.09 and 0.077, respectively) studied in this work, the concentrations of H and OH calculated by both methods using PREMIX and the detailed kinetic mechanism [23] and using the above formulas differ. This is because of relatively low post-flame temperature (1200-1350 K). For this reason, to carry out the calibration of radicals we used hotter flame (calibration flame) with the post-flame temperature of 1600 K (see Table 1). To determine the calibration coefficients for H and OH radicals and hence to obtain their absolute concentration, concentration profiles of H_2 , O_2 and H_2O , as well as temperature profile were measured. They are shown in Fig. 3. In this figure, the measured profiles are

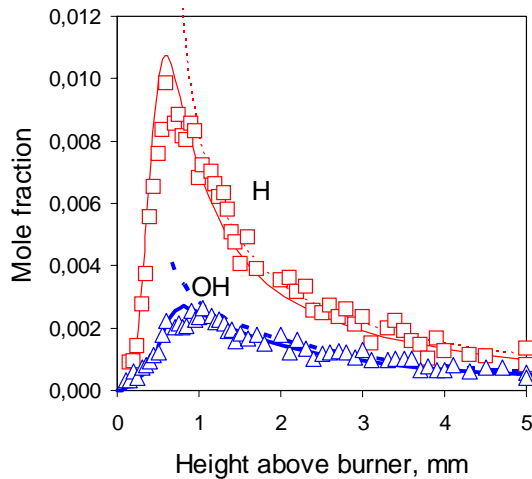


Fig. 4. Concentration profiles of radicals in calibration flame $H_2/O_2/N_2$ flame ($\phi=1.1$, $D=0.14$). Symbols are experimental data; solid lines are modeling with the detailed chemical kinetic mechanism [23]; dashed lines are calculation using the approach of partial equilibrium on three “fast” reactions.

compared with those calculated using kinetic mechanism [23].

Inserting the values of concentrations of stable species and equilibrium constants into the formulas (5) and (7), the concentrations of H and OH in the post-flame zone (at 1.2-1.5 mm) of the calibration flame ($\phi=1.1$, $D=0.14$) above the burner were evaluated. The concentration profiles of H and OH calculated using the detailed kinetic mechanism [23] (and measured temperature profile with the distance “probe tip – thermocouple junction” of 0.2 mm) and using the approach of partial equilibrium on three fast reactions are compared in Fig. 4. A good agreement clearly observed between them demonstrates a correctness of selection of the experimental conditions for calibration of the MBMS-system. Thus, using the data obtained in the “hot” calibration flame, the calibration coefficients for H and OH were determined. These coefficients were used in the following for quantification of absolute concentrations of H and OH in all flames studied (lean, near-stoichiometric and rich). Due to a very low concentration of atomic oxygen in the post-flame zone, calibration coefficient for it was not determined with adequate accuracy, so we do not provide in the following measured concentration profiles of O radicals. Relative error in determining the concentrations of the species from the measured mass peak intensities of H and OH radicals was within the range 40 - 60 %.

Modeling

Flame structure and burning velocity were simulated using PREMIX and CHEMKIN-II codes [19-21] taking into consideration thermodynamic and transport properties of all species, as well as a detailed chemical kinetic mechanism.

Three different reaction mechanisms for hydrogen oxidation proposed earlier by Li et al. [1], O’Conaire et al. [2] and Konnov [23] were used for the modeling.

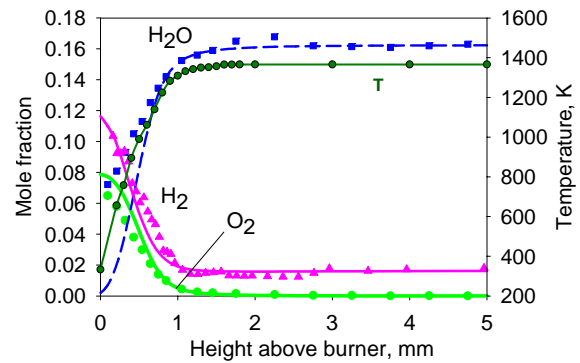


Fig. 5. Temperature profiles and concentration profiles of stable species in near-stoichiometric $H_2/O_2/N_2$ flame ($\phi=1.1$, $D=0.09$). Symbols are experimental data; lines are modeling using the kinetic mechanism [23].

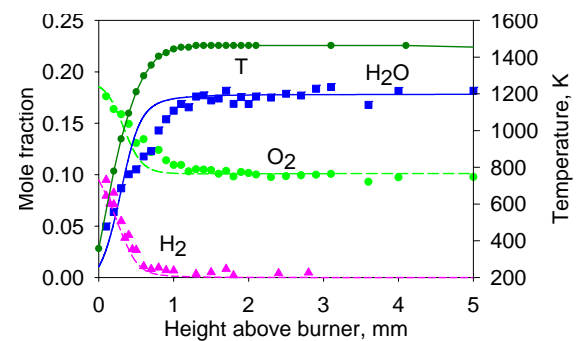


Fig. 6. Temperature profiles and concentration profiles of stable species in lean $H_2/O_2/N_2$ flame ($\phi=0.47$, $D=0.209$). Symbols are experimental data; lines are modeling using the kinetic mechanism [23].

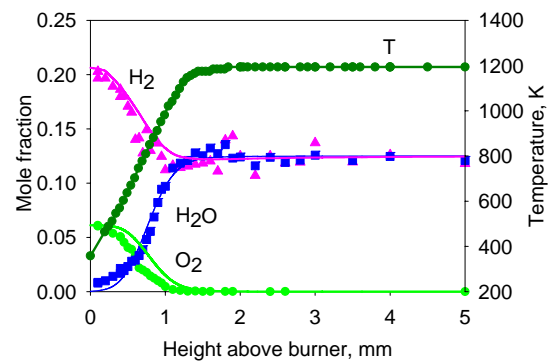


Fig. 7. Temperature profiles and concentration profiles of stable species in rich $H_2/O_2/N_2$ flame ($\phi=2.0$, $D=0.077$). Symbols are experimental data; lines are modeling using the kinetic mechanism [23].

Multi-component diffusion and thermal diffusion options were taken into account. Adaptive mesh parameters were $GRAD = 0.1$ and $CURV = 0.5$.

Results and Discussion

Figures 5, 6 and 7 show measured concentration profiles of stable species (H_2O , H_2 , O_2) in the near-stoichiometric, lean and rich flames, respectively. The profiles simulated using the kinetic mechanism [23] are also given in these figures. The species concentration and temperature profiles predicted by the mechanisms

of Li et al. [1] and of O’Conaire et al. [2] are very close to those predicted by Konnov’s mechanism [23]. They are not shown in Figs. 5-7 to not overcharge them. A comparison of the measured concentration profiles of stable species with the simulated ones (Figs. 5-7) shows

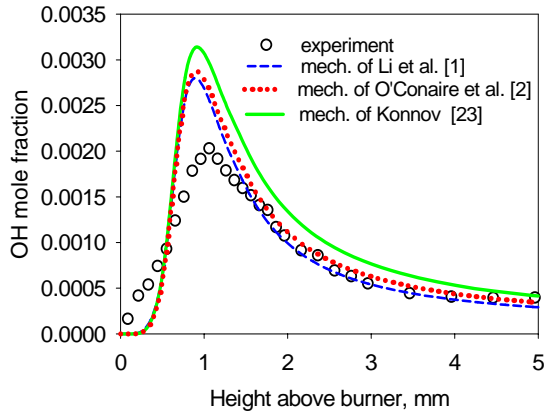


Fig. 8. OH concentration profiles in lean $H_2/O_2/N_2$ flame ($\phi=0.47$, $D=0.209$). Symbols are experimental data; lines are modeling.

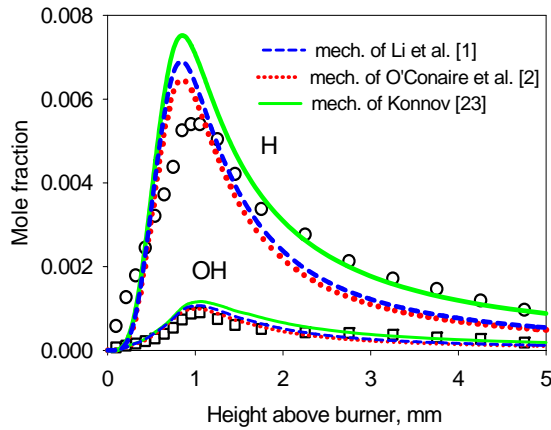


Fig. 9. H and OH concentration profiles in near-stoichiometric $H_2/O_2/N_2$ flame ($\phi=1.1$, $D=0.09$). Symbols are experimental data; lines are modeling.

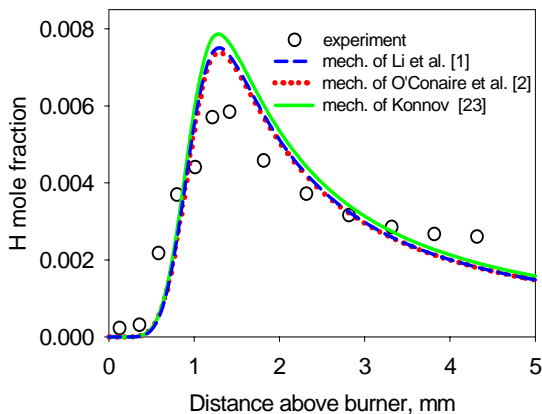


Fig. 10. H concentration profiles in rich $H_2/O_2/N_2$ flame ($\phi=2.0$, $D=0.077$). Symbols are experimental data; lines are modeling.

that the models used provide a good fit of the experimental data. Some small discrepancies observed between the measured and simulated concentrations of H_2O near the burner surface are associated with variation of the H_2O calibration coefficient depending on flame temperature. This is due to formation of H_2O clusters in molecular beam while sampling from the low-temperature zone of the flame. Therefore, an excessive concentration of H_2O measured near the burner surface is related to the experimental errors.

The concentration profiles of H and OH radicals measured in the lean, near-stoichiometric and rich flames are given in Figs. 8, 9 and 10, respectively. The results of numerical calculations using three kinetic mechanisms [1, 2, 23] are also plotted in Figs. 8-10. A satisfactory agreement is observed between the measured and calculated OH concentration profiles in the lean and near-stoichiometric flames (Figs. 8 and 9). It should be noted that maximums of the experimental OH profiles are ~ 0.1 mm shifted downstream relative to the calculated profiles. Maximum measured concentration of OH is 2.0×10^{-3} and 9.1×10^{-4} in the lean and near-stoichiometric flame, respectively. The models over-predict them by about 20 - 30 percents. Measured concentration profiles of H radicals in the near-stoichiometric and rich flames (Figs. 9, 10) are also in a satisfactory agreement with the simulated ones. As it was observed for OH profiles, the measured H concentration profiles are also shifted downstream by ~ 0.1 mm relative to the calculated ones. Such a shift can be associated with the errors of taking into account the probe induced perturbations. Maximum measured concentration of H is 5.4×10^{-3} and 5.9×10^{-4} in the near-stoichiometric and lean flame, respectively. These values are 16-30 percents lower than those obtained in the simulation. Therefore, within the experimental errors, the experimental data obtained in this work are in a fairly good agreement with the calculated results. This indicates the robustness of these models in predicting the structure of hydrogen-oxygen flames at atmospheric pressure.

Conclusions

The structure of laminar premixed $H_2/O_2/N_2$ flames stabilized on a flat flame burner with different equivalence ratios at atmospheric pressure was studied. Probing molecular beam mass spectrometry with soft electron-impact ionization was used to measure species concentration profiles in the flames. In this work, for the first time, concentration profiles of H and OH radicals in the lean ($\phi=0.47$), near-stoichiometric ($\phi=1.1$) and rich ($\phi=2.0$) atmospheric flames were measured. Numerical simulation of the structure of the flames using three detailed kinetic mechanisms for hydrogen combustion proposed earlier was carried out in order to validate them by comparison of the calculated results with our experimental data. The comparison showed that these models reproduce quite well the measured concentration profiles of the species in the flames studied. This demonstrates a good performance of the

models in predicting the structure of atmospheric hydrogen flames.

Acknowledgements

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