

Acetylene measurements in fuel-rich premixed methane/air flames

S.Gersen¹, A.V. Mokhov^{1*} and H.B. Levinsky^{1,2}

¹Laboratory for High Temperature Gas Kinetics, University of Groningen
Nijenborgh 4, 9747AG Groningen, The Netherlands
Groningen, The Netherlands

²Gasunie Research, N.V. Nederlandse Gasunie,
P.O. Box 19, 9700 MA Groningen, The Netherlands

Abstract

Measurements of acetylene in fuel-rich premixed atmospheric-pressure methane/air flames using spontaneous Raman and extractive sampling probe techniques are reported. Axial profiles of acetylene in a flame with $\phi = 1.5$ are in good agreement for both diagnostic methods, but are shifted by ~ 1.5 mm. Substantial disagreement is observed between the experiment and numerical predictions based on the GRI-Mech 3.0 chemical mechanism. Increasing the pre-exponential factor of the rate coefficient of the reaction $C_2H_2 + OH \rightarrow CH_2CO + H$ results in good agreement between the measured and calculated axial profiles of acetylene in all flame investigated.

Introduction

Predictions of the flame structure by numerical simulations facilitate further progress in increasing efficiency and minimizing pollutant emissions of combustion devices. Because of the complexity of the chemical mechanisms, the predictive power of the numerical simulations can be tested only by comparing calculated and measured flame parameters under well-defined experimental conditions. In particular, the measured profiles of different intermediate species in flat premixed flames are used for these purposes. One of these intermediates is acetylene (C_2H_2), which plays important role in many high temperature processes, such as the formation of polyaromatic hydrocarbons and soot in hydrocarbon combustion [1-3].

Acetylene was extensively investigated in both atmospheric- and low-pressure flat premixed hydrocarbon flames [4-10]. However, all acetylene measurements in these investigations were performed using extractive probe sampling technique, which has a serious drawback - composition and temperature perturbation of the flame. Correct estimations of the magnitude of these perturbations, such as chemical reactions on the probe surface or accelerating the combustion products into the probe orifice are rather difficult [11]. It requires verifying the methods based on extractive probe sampling by an independent technique.

Recently, after incorporating an improved laser setup we were able to measure native C_2H_2 in a fuel-rich methane/air flame with equivalence ratio $\phi = 1.55$ by using the spontaneous Raman scattering [12]. This gives us the possibility to validate the extractive probe

sampling technique for acetylene detection and deliver reliable experimental results regarding C_2H_2 formation and destruction in atmospheric-pressure methane/air flames, where large discrepancies were observed [13] between experiment and calculations based on the C_2H_2 submechanism derived from Miller and Mellius [14].

Towards this end, C_2H_2 mole fraction profiles in flat atmospheric-pressure rich-premixed methane/air flames are measured using spontaneous Raman spectroscopy and microprobe gas sampling followed by tunable diode laser absorption spectroscopy (TDLAS). In addition, the flame temperature profiles are measured using coherent anti-Stokes Raman Scattering (CARS) and the experimental observations are compared with one-dimensional flame calculations.

Experimental

The measurements were performed in atmospheric-pressure methane-air flames stabilized above a McKenna Products sintered bronze burner of 60 mm diameter. To prevent air entrainment in the combustion products, a nitrogen shroud was used. A cylindrical chimney with a 60 mm inner diameter was installed approximately 30 mm above the burner surface. The flame temperature was varied by changing the mass flux through the burner and determined by broadband planar BOXCARS for nitrogen thermometry. Details of the CARS optical setup are described elsewhere [15]. The flow rates of methane and air were measured by calibrated mass flow meters and the equivalence ratio was determined [16] by measuring the methane concentration in the fuel-air mixture. The accuracy of determining the mass flow rates and equivalence ratios

* Corresponding author: a.v.mokhov@rug.nl

Associated website: <http://www.chem.rug.nl/flame>

Proceedings of the European Combustion Meeting 2005

are estimated to be better than 5% and 2%, respectively. Measurements were obtained at different vertical positions in the flame by moving the burner with a precision positioner relative to the laser beams and sampling probe in steps of 1 mm. The temperature measurements showed that all flames under investigation had a domain with constant temperature extending from the height of 3 mm up to 15 mm above the burner surface in vertical direction and from the flame center up to radial position of 20 mm in horizontal direction. Moreover, the temperatures in this domain were in excellent agreement with calculations, indicating marginal radiative heat losses in these flames.

The flames were sampled by a quartz microprobe having a design similar to that described in [17] with an orifice diameter of about 100 μm . With exception of the probe tip the quartz probe was cooled over a distance of 35 cm by water at 12°C. After passing an ice-cooled water trap the sampled gas was purged through a 1 m-length stainless steel tube sealed on both ends with quartz windows. The pressure in the tube was monitored by an electronic pressure transducer and kept constant at 100 mbar by a vacuum pump installed in the exit of the sampling system. Estimates of the sample cooling process, performed using the SENKIN code from the CHEMKIN suite [18] with the GRI-Mech 3.0 chemical mechanism [19], showed that in the present experimental setup conversion of acetylene in the probe is less than 10% when sampling is made at heights higher than 3 mm above the burner surface. These estimates are also supported by measurements performed at different suction back pressures varying from 0.05 to 0.3 Bar, which showed no significant change in the measured C_2H_2 concentrations.

Radiation from a New Focus 6326 tunable diode laser with a linewidth less than 100 MHz was directed through the tube. Before entering the tube, part of the laser radiation was deflected to produce the reference signal. The powers of the reference and sample beams were measured by New Focus 2033 large area photodiodes with internal amplifiers. The photodiodes' signals were digitized and processed by a PC. The laser wavelength was swept over the span of 30 GHz with a scan rate 150 MHz/s by applying the voltage to a piezoceramic plate that moved a grating inside the laser. The measurements were performed in the region around wavelength of 1530 nm where a P(9) absorption line of the $\nu_1 + \nu_3$ band is located [20]. This line was selected because of its relatively high oscillator strength [21] and lack of interference from other radiative transitions in flame molecules.

Whereas it is possible to derive absolute values of acetylene concentration from the measured integral absorption coefficient, to increase the accuracy direct calibration by a gas with known C_2H_2 concentration was used in present work. It allowed circumventing the uncertainties arising from the non-infinite limits of integration when deriving the integrated absorption coefficient and converting the voltage applied to the

piezoceramic plate to a wavelength shift. As a typical example, Fig. 1 shows dependence of the logarithm of the ratio of the reference and transmitted signal upon the applied voltage when the measurements were performed in mixture containing 5000 ppm C_2H_2 in N_2 .

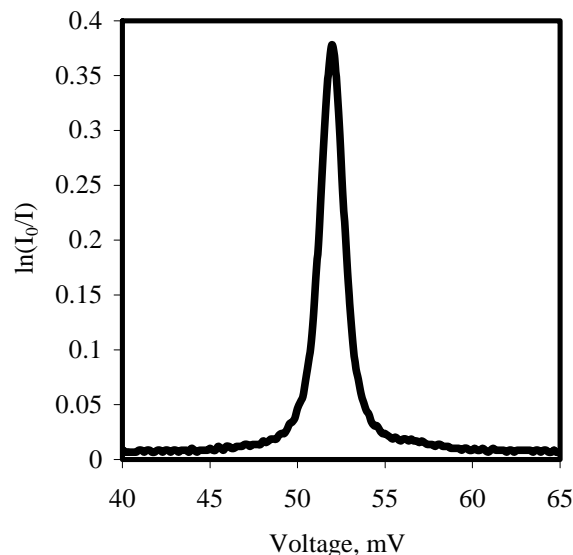


Fig. 1. Dependence of logarithm of ratio of reference to transmitted signal upon voltage applied to piezoceramic plate. Measurements were performed in mixture containing 5000 ppm C_2H_2 in N_2 in the vicinity of the P(9) line of the $\nu_1 + \nu_3$ band of acetylene.

When comparing the measurements performed in the calibration gases and combustion products, no differences were found in shapes of the absorption coefficients. This implies that the line profile function is independent of the gas composition in the present experimental conditions. This result is rather expected because the broadening efficiency for the acetylene lines is of the same order for C_2H_2 and N_2 [22], while the concentration of the other gases with unknown broadening efficiency is low.

In present experimental setup, at acetylene concentrations above 1000 ppm, the accuracy of the C_2H_2 concentration measurement was determined mainly by the uncertainty in the calibration gas concentration and was better than 5%, while at low C_2H_2 concentrations the uncertainties in the measured integral absorption coefficient became dominant, which resulted in deterioration of the accuracy up to 15% at 100 ppm C_2H_2 . To verify the possible influence of nonlinearity in the detection system, the integral absorption coefficient was measured in calibration gases with different C_2H_2 concentrations. As can be seen from Fig. 2, where the results of these measurements are presented, the detection system possesses an excellent linearity – differences between the linear fit and experimental values of the fitted and experimental values are less than 5%.

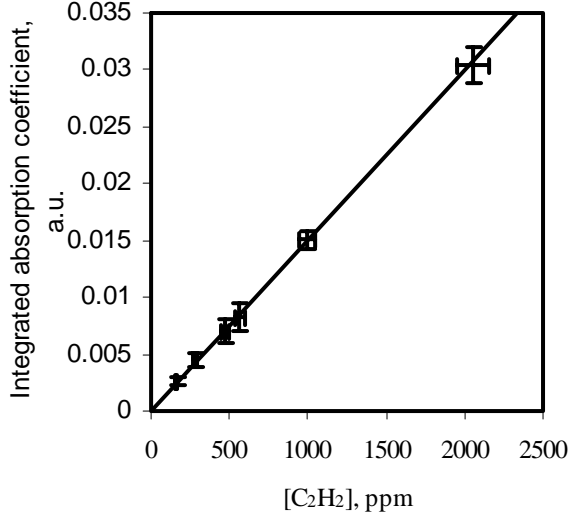


Fig. 2. Integrated absorption coefficient of C₂H₂ P(9) line of the $\nu_7 + \nu_3$ band as a function of acetylene mole fraction in N₂ dilution gas. Solid line is a linear fit.

The optical scheme for spontaneous Raman measurements is described in detail in [12]. Briefly, the exciting beam of the Nd-YLF laser (Spectra Physics Merlin, 1 kHz repetition rate, average power of 10 W at wavelength 527 nm) was focused in the flame center by a lens with focal length of 500 mm. The scattered radiation was collected at right angles by a f/2.8 lens with focal length of 300 mm and dispersed by an f/4 spectrometer (Acton Research Spectra Pro 150), whose entrance slit was oriented parallel to the exciting laser beam. An intensified 1024 x 256 pixel CCD camera was mounted at the exit plane of the spectrometer. To increase the signal/noise ratio, 256 vertical pixels were binned, which corresponds a distance of 16 mm along the laser beam. This loss of spatial resolution does not introduce significant errors because of the flatness of the flames. The Raman spectrum was obtained by subtracting the signals measured with the laser shutter open and closed. Both signals were measured by taking 20 accumulations with 25 s exposure time.

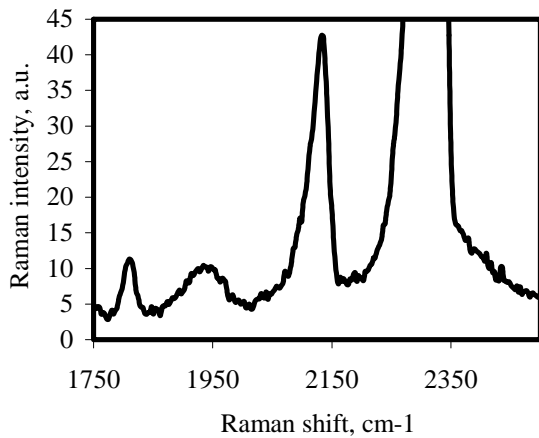


Fig. 3. Raman spectrum measured at height of 2 mm in methane/air flame, $\phi = 1.5$ and $\rho\nu = 0.008 \text{ g}/(\text{cm}^2\cdot\text{s})$.

As a typical example, the measured Raman spectrum in the flame with the equivalence ratio $\phi = 1.5$ and mass flux $\rho\nu = 0.008 \text{ g}/(\text{cm}^2\cdot\text{s})$ at a height of 2 mm above the burner surface is presented in Fig. 3. We assign the broad feature around 1950 cm^{-1} as the ν_2 band of C₂H₂ and associated hot bands. This assignment is substantiated by additional experiments described in detail in [12]. In that work, Raman measurements at room temperature in a gas containing acetylene were compared with those in a flame with $\phi = 1.3$ and $\rho\nu = 0.005 \text{ g}/(\text{cm}^2\cdot\text{s})$ in which low C₂H₂ concentrations in the post-flame zone are expected (suggested by both numerical simulations and probe measurements); this feature completely disappeared in the flame. To derive acetylene mole fractions, the measured acetylene Raman feature was frequency-integrated and compared with the integrated intensity from the 1670 ppm mole fraction of acetylene in nitrogen at room temperature, applying density and Boltzmann factor corrections using the double-harmonic approximation for the intensity of the Raman vibrational transitions [23].

Results and discussion

The measurements were performed in a set of fuel-rich flames with different equivalence ratios and mass fluxes. The flame parameters (equivalence ratios, mass fluxes and temperatures at a height of 5 mm above the burner surface) are presented in Table 1.

Table 1. Flame parameters

Flame	ϕ	$\rho\nu \text{ (g}/\text{cm}^2\cdot\text{s})$	T (K)
A	1.5	0.005	1763
B	1.5	0.007	1835
C	1.5	0.008	1852
D	1.45	0.0085	1885
E	1.4	0.0085	1850

Vertical profiles of the acetylene mole fraction measured by the Raman and probe techniques in flame C with $\phi = 1.50$ and $\rho\nu = 0.008 \text{ g}/\text{cm}^2\cdot\text{s}$ are presented in Fig. 4. The acetylene mole fraction, determined by the Raman technique, reaches its maximum at a height of $\sim 2 \text{ mm}$ and then decrease to $\sim 500 \text{ ppm}$ at 8 mm . Two sets of Raman measurements are presented in Fig. 3 indicating good reproducibility of the method. The difference at 2 mm can be explained by a sharp C₂H₂ gradient in the flame front, for which a very small axial shift results in a large difference in C₂H₂ concentration. The probe profile appears to be shifted approximately 1.5 mm downstream of the Raman profile. This shift is the result of the acceleration of the combustion products into the probe orifice [24]. A similar shift between probe and optical measurements was observed in temperature and hydroxyl profiles in other flames [25,26]. Shifting the probe profile results in good agreement with the Raman profiles, which substantiates the extractive probe technique for the experimental determination of the acetylene in measurements presented below.

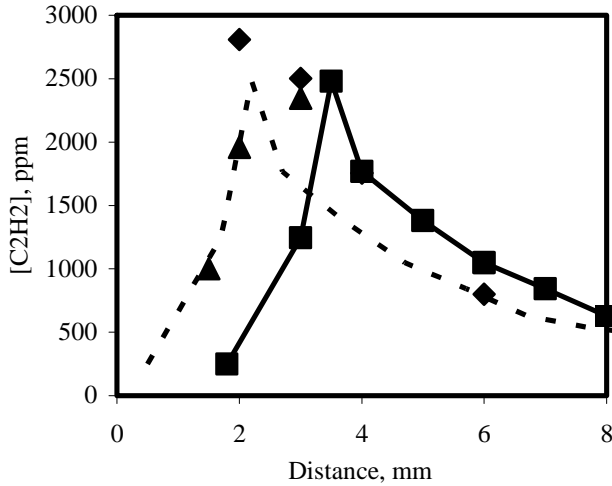


Fig. 4. Vertical profiles of acetylene in methane-air flame, $\phi = 1.5$ and $\rho v = 0.008 \text{ g/cm}^2\text{s}$. Symbols denote Raman (triangles and diamonds) and probe (squares) measurements; dashed line denotes shifted probe measurements.

At acetylene concentrations below 500 ppm the measured Raman spectrum was barely recognizable in the noise, while for the absorption TDLAS spectrum the signal-to-noise ratio remained higher than 10 at C_2H_2 concentrations above 100 ppm. This high detectability limit of the present experimental setup precluded us from measurements of acetylene by the Raman technique in the flames with low C_2H_2 concentrations in the post-flame zone.

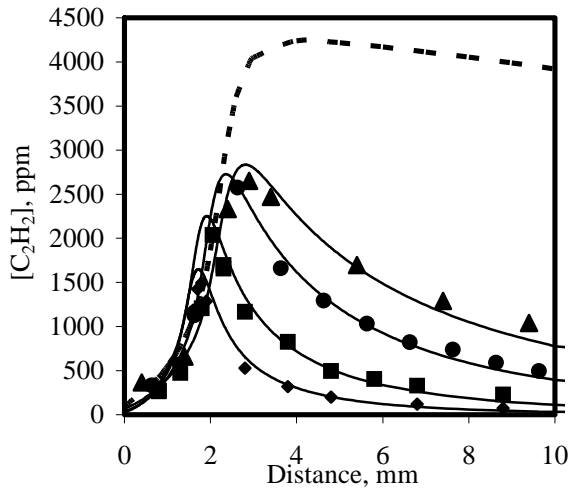


Fig. 5. Vertical profiles of acetylene in methane-air flames, $\phi = 1.5$ and $\rho v = 0.008 \text{ g/cm}^2\text{s}$. Symbols denote probe measurements in flames A (triangles), B (circles), D (squares) and E (diamonds). The dashed and solid lines denote flame calculations with unchanged and increased rate constant of reaction $\text{C}_2\text{H}_2 + \text{OH} \rightarrow \text{CH}_2\text{CO} + \text{H}$, respectively.

Fig. 5 shows the vertical acetylene profiles measured by the probe technique in the flames A, B, D

and E. All profiles have been shifted 1.5 mm closer to the burner surface, as discussed above. As can be seen from Fig. 4, increasing the equivalence ratio from $\phi = 1.4$ to 1.45 at fixed mass flux $\rho v = 0.085$ maintaining constant flame temperature (flames D and E), significantly increases the peak C_2H_2 concentration. In contrast, increasing the flame temperature at fixed equivalence ratio by changing the mass flux (flames A and B) has marginal influence on the peak C_2H_2 concentration. Further, the Fig. 5 shows that acetylene concentration decreases in the post-flame zone faster in flame B than in flame A, indicating acceleration of the C_2H_2 conversion in the post-flame zone with increasing the temperature.

In addition, we note substantial discrepancy between the measured acetylene profiles and those derived from the flame calculations, which show substantially higher peak concentrations and slower decay in the post-flame zone. The calculations have been performed for all flames, and all showed the same discrepancy; to avoid clutter in the figure results are presented only for the flame A. This discrepancy has been observed previously [27], where it was attributed to the rate of the reaction $\text{C}_2\text{H}_2 + \text{OH} \rightarrow \text{CH}_2\text{CO} + \text{H}$ used in the GRI-Mech 3.0. Following the suggestion made in ref. [10], we increased the pre-exponential factor of the rate coefficient to $1.7 \cdot 10^{12} \text{ cm}^3/(\text{mole} \cdot \text{s})$ and repeated the calculation. The calculated acetylene profiles are now in excellent agreement for all flames studied here. Whereas the limited range of the parameter variation in the present work an unambiguous recommendation regarding increasing the rate coefficient of this reaction, the agreement between experiment and calculations favours this conclusion.

Conclusions

We report the measurements of acetylene in fuel-rich atmospheric-pressure methane/air flames using spontaneous Raman and extractive probe sampling techniques. Excepting the shift of approximately 1.5 mm resulting from the acceleration of the combustion products in the probe orifice, the vertical Raman and probe profiles are in very good agreement. This result validates using the extractive probe sampling technique as a diagnostic tool for measurements of acetylene in atmospheric-pressure hydrocarbon flames. Substantial disagreement is observed between the experimental profiles of acetylene and those obtained from calculations based on GRI-Mech 3.0, which predict higher acetylene concentrations and slower decay in the post-flame zone. Increasing the pre-exponential factor in the rate coefficient for the reaction $\text{C}_2\text{H}_2 + \text{OH} \rightarrow \text{CH}_2\text{CO} + \text{H}$ to the value of $1.7 \cdot 10^{12} \text{ cm}^3/(\text{mole} \cdot \text{s})$ brings the calculated acetylene profiles into excellent agreement with those derived experimentally. Further improvement of the sensitivity of both spontaneous Raman and extractive probe techniques will provide more information on acetylene chemistry in fuel-rich

methane-air flames. These improvements are currently in progress in our laboratory.

Acknowledgements

We are thankful to V.V. Toro for experimental assistance and the Dutch fund for 'Ecology, Economy and Technology' (EET) for financial support of this work.

References

1. J. Warnatz, H. Bockhorn, A. Mozer, H.W. Wenz, *Proc. Combust. Inst.* 19 (1982) 197-209.
2. P. Lindstedt, *Proc. Combust. Inst.* 27 (1998) 269-285.
3. H. Richter, J.B. Howard, *Prog. Energy Combust. Sci.* 26 (4-6) (2000) 565-608.
4. C.P. Fenimore, G.W. Jones, *J. Chem. Phys.* 41 (7) (1964) 1887-1889.
5. J. Vandooren, P.J. van Tiggelen, *Proc. Combust. Inst.* 16 (1977) 1133-1144.
6. J.D. Bittner, J.B. Howard, *Proc. Combust. Inst.* 19 (1982) 211-221.
7. E.W. Kaiser, *J. Phys. Chem.* 94 (11) (1990) 4493-4499.
8. I.T. Woods, B.S. Haynes, *Combust. Sci. Technol.* 87 (1-6) (1993) 199-215.
9. I.T. Woods, B.S. Haynes, *Proc. Combust. Inst.* 25 (1994) 909.
10. E.W. Kaiser, T.J. Wailington, M.D. Hurley, J. Platz, H.J. Curran, W.J. Pitz, C.K. Westbrook, *J. Phys. Chem. A* 104 (35) (2000) 8194-8206.
11. E.L. Knuth, *Combust. Flame* 103 (3) (1995) 171-180.
12. A.V. Mokhov, S. Gersen, H.B. Levinsky. Submitted to *Chem. Phys. Lett.*
13. E.W. Kaiser, T.J. Wailington, M.D. Hurley, J. Platz, H.J. Curran, W.J. Pitz, C.K. Westbrook, *J. Phys. Chem. A* 104 (35) (2000) 8194-8206.
14. J.A. Miller, C.F. Melius, *Proc. Combust. Inst.* 22 (1988) 1031.
15. A.V. Mokhov, H.B. Levinsky, C.E. vanderMeij, *Appl. Opt.* 36 (15) (1997) 3233-3243.
16. A.V. Mokhov, H.B. Levinsky, *Proc. Combust. Inst.* 26 (1996) 2147-2154.
17. R.M. Fristrom, A.A. Westenberg, *Flame structure*, McGraw-Hill, New York, 1965.
18. R.J. Kee, F.M. Rupley, J.A. Miller, *CHEMKIN II: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics.*, Sandia National Laboratories, (1989).
19. G.P. Smith, D.M. Golden, M. Frenklach, N.W. Moriarty, B. Eiteneer, M. Goldenberg, C.T. Bowman, R. Hanson, S. Song, W.C. Gardiner, V. Lissanski, Z. Qin, http://www.me.berkeley.edu/gri_mech/.
20. Q. Kou, G. Guelachvili, M.A. Tamsamani, M. Herman, *Can. J. Phys.* 72 (11-12) (1994) 1241-1250.
21. R. El Hachtouki, J. Vander Auwera, *J. Mol. Spectrosc.* 216 (2) (2002) 355-362.
22. A.S. Pine, *J. Quant. Spectrosc. Radiat. Transfer* 50 (2) (1993) 149-166.
23. D.A. Long, *The Raman effect*, Wiley, Chichester, 2002.
24. E.L. Knuth, *Combust. Flame* 103 (3) (1995) 171-180.
25. R.J. Cattolica, S. Yoon, E.L. Knuth, *Combust. Sci. Technol.* 28 (5-6) (1982) 225-239.
26. A.T. Hartlieb, B. Atakan, K. Kohse-Hoinghaus, *Combust. Flame* 121 (4) (2000) 610-624.
27. E.W. Kaiser, T.J. Wailington, M.D. Hurley, J. Platz, H.J. Curran, W.J. Pitz, C.K. Westbrook, *J. Phys. Chem. A* 104 (35) (2000) 8194-8206.