Brief Communication

A note on chemiluminescence in low-pressure hydrogen and methane–nitrous oxide flames

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Abstract

Absolute OH(A) and CH(A) concentrations were determined in low-pressure H_2–air and CH_4–N_2O flames, respectively, by measuring absolute chemiluminescence yields at 310 and 430 nm. From spatial profiles and intensities in these and other flames, we deduce that two reactions are responsible in each case, and derive rate constants for all.

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1. Introduction

We have recently reexamined visible flame luminescence—OH(A–X) at 310 nm, CH(A–X) at 430 nm, and C_2(d–a) [1,2]—as a useful diagnostic for application where more complex laser methods are inconvenient, such as microgravity. Our method involves determinations of excited-state concentrations via calibrated measurements of emission intensities in well-characterized and modeled low-pressure methane–air laminar premixed flames. A quantitative analysis of such measurements with a chemical kinetics interpretation requires knowledge of the excited-state production and loss reaction rates. Since loss rates were directly measured in related decay lifetime studies using pulsed laser-induced fluorescence (LIF) on the same electronic transitions [2,3], production rate constants can be determined. Use of a low-pressure flame also provides good spatial resolution to validate the flame and chemiluminescence chemistry.

Previously we determined a rate constant of 1.8×10^{11} $cm^3/(mol\,s)$ for $CH + O_2 \rightarrow OH(A) + CO$ near 1700 K [1] which is somewhat larger than the recent measurement of 0.5×10^{11} at 300–500 K by Carl et al. [4]. Rates for CH(A) production also were deduced, but we were unable to distinguish between the reactions $C_2H + O$ or $C_2H + O_2$ as the source. Two alternatives and a recommendation were offered. Our original estimate, based on the ambiguous literature values discussed there, had overpredicted the amount of CH(A) emission. In this note we report results for CH(A) chemiluminescence from CH_4–N_2O flames [5] which contain higher relative amounts of O atoms, and hence allow a partitioning of the emission yield between the two reactions.

A second, although minor, source of OH(A) emission in hydrocarbon–air flames was included in our mechanism but not examined—the recombination of H and O atoms. This could become an important quantitative diagnostic. The OH(A–X) emission will be the strongest near-visible signature for monitoring combustion in any future hydrogen economy.

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Also the initial SOFBALL spherical flame ball experiments [6,7] on the space shuttle involved H_2–O_2 flames monitored by weak visible radiation, but the OH(A–X) ultraviolet signal offers an alternative. Previous low-pressure flame studies by Kaskan [8] and Davis et al. [9] have provided rate constants, assuming partial equilibrium, for the reaction $H + OH + OH \rightarrow OH(A) + H_2O$, or alternately the inverse predissociation reaction $O + H + M \rightarrow OH(A) + M$. We report here spatially resolved OH(A–X) emission studies in our 38 Torr H_2–air flame [10] to remeasure and partition this rate between these reactions.

2. Experimental

Conditions characterizing the five premixed flames studied are copied from the previous referenced studies and they are shown in Table 1. The methane flames were featured in our LIF studies of methane flame chemistry [11]. Details of the experiments, temperature distributions from OH LIF rotational excitation scans, and absolute CH profiles versus height above the burner may be found in that work. Chemiluminescence results for these flames and details of those experiments have been presented [1]. The next-to-last column of Table 1 gives the flame temperature at the height of maximum chemiluminescence, measured by LIF of OH rotational levels using 14 lines of the R branch of the (0, 0) transition near 307 nm. We remeasured temperature values, peaks, and height profiles for the last three flames. Since some change in position of the temperature rise can occur compared to old measurements, the new temperature expressions given below were used for model runs.

Operation at low pressure allows good spatial resolution of the flame structure of each species, and thus the progress of the flame chemistry can be followed via LIF or chemiluminescence. The flames are supported on a 6-cm-diameter sintered plug McKenna burner, housed inside a vacuum chamber designed for optical probing. A concentric flow of argon is used to isolate and stabilize the flame. The burner translates vertically with respect to the optical axis of the laser and detection system. A servo control valve maintains the chamber and flame pressure, while massflow controllers regulate the fuel, oxidizer, and nitrogen. A laser beam traverses the chamber through Brewster angle windows for the LIF OH temperature measurements. A large silica window, through which light may be imaged onto either spectrometer or CCD camera detection systems, lies perpendicular to the laser path.

The chemiluminescence concentrations and distributions were measured, as in the prior work [1], by imaging the flame emissions through 430- or 310-nm interference filters onto a gated intensified CCD camera operating in simple shutter mode (Princeton Instruments, ICCD 576G.RBT, 14 bits dynamic range, 384×576 pixels). Pixel resolution is 0.0187 cm. An Abel inversion is performed to deconvolute the line-of-sight integrated signal, and determine flame-center excited-state concentration height profiles from the 2-D images. Absolute amounts are obtained by comparison with the previously measured near-stoichiometric methane flame values [1].

We performed one-dimensional flame model calculations using the Sandia code Premix [12] and the GRI-Mech 3.0 chemical mechanism for methane oxidation [13]. Measured flow rates and temperature profiles are also inputs. A few reactions involving C and C_2 species were added, beyond the requirements of GRI-Mech; they were included and described in the previous chemiluminescence study [1], as trace species involved in the production kinetics relating to CH(A–X) chemiluminescence.

3. Hydrogen flame emission

Aside from weak water vibrational overtone emissions that give a faint red color, emissions from hydrogen–air flames consist of OH(A–X). Levels are much lower than hydrocarbon flames, without the

Table 1
Flame conditions

Flame	Φ	P (Torr)	Fuel flow (slm)	Oxidizer	Nitrogen	T (K)[a]	Ref.
CH_4–air	1.28	30	0.78	1.22	2.78	1940	[11]
CH_4–air	1.07	25	0.45	0.84	1.93	1730	[11]
CH_4–N_2O	1.07	25	0.45	1.70	0.84	2400[b]	
CH_4–N_2O	1.07	14	0.49	1.87	0.0	2500[c]	[5]
H_2–air	1.54	38	2.36	0.76	2.87	1150[d]	[10]

[a] Values at peak of chemiluminescence. $T = A + B[1 - \exp(Ch^D)]$ height h in mm.
[b] $A = 280$, $B = 2447$, $C = -0.011$, $D = 2.031$.
[c] $A = 277$, $B = 2488$, $C = -0.036$, $D = 1.657$.
[d] $A = 401$, $B = 869$, $C = -0.346$, $D = 0.931$.