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Measurements and modelling of HCN and CN species profiles in laminar $CH_4/O_2/N_2$ low pressure flames using LIF/CRDS techniques

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Abstract

In the present work, measurements of absolute mole fraction profiles of CN and HCN were jointly performed in low pressure (5.3 kPa) premixed $CH_4/O_2/N_2$ flames of three equivalent ratios ($\phi = 0.8$–1.25). These species were the missing link of the database comprising CH, NCN, NCO and NO species previously acquired in Lille to improve detailed mechanisms of prompt-NO formation. For that purpose, LIF and pulsed CRDS techniques were implemented to measure in the flames absolute mole fraction of CN by probing the B-X(1,0) vibrational band around 356 nm. This combination of techniques allows reaching a detection limit as low as tenth of ppbv that was necessary to measure CN in lean flame condition could be achieved. HCN molecules were measured by using *cw*-CRDS technique around 1.5 μm (in the (200)–(000) vibrational band) after gas probe sampling. The required sensitivity equal to 15 ppbv of HCN was achieved using a long absorption cell (about 1 m). These CN and HCN profiles were simulated by considering two detailed mechanisms of prompt-NO formation from literature (Konnov0.6 (Combust. Flame 156 (2009) 2093–2105) and GDFkin®3.0_NCN (Combust. Flame 157 (2010) 1929–1941)).

Keywords: HCN; CN; Laser diagnostics; Flame; Prompt-NO formation

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1. Introduction

During the last decade thanks to the theoretical work performed by Moskaleva and Lin [1] demonstrating that the reaction between CH radicals and N_2 yields NCN and H-atoms, the prompt-NO chemistry has been revisited. Theoretical calculations have been performed in order to determine the rate constant values of reactions where NCN radicals are involved: (1) $CH + N_2 = NCN + H$ [1–3], (2) $NCN + H = HCN + N$ [1,3], (3) $NCN + O = CN + NO$ [4], (4) $NCN + OH = HCN + NO$ [5] and (5) $NCN + O_2 = NCO + NO$ [6]. The rate constant values of the first three reactions have also been determined from experiments performed in shock tube apparatus [7,8], but at

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higher temperature than the ones encountered in low pressure flames. The experimental and theoretical rate constant values are in overall good agreement except for the reaction (2) that is one of the most sensitive reactions for the prediction of prompt-NO formation. The implementation of the NCN route in the prompt-NO sub-mechanism relies on the knowledge of both the rate constant values of these reactions and the thermochemistry of the involved species. The influence of NCN thermochemistry has recently been highlighted [9]. In the limit of uncertainties reported in the literature for NCN, the increase of its heat of formation (from 445.7 to 466.5 kJ mol^{-1}) decreases by a factor of 2.5 the maxima values of NCN or NO profiles.

This is why the new prompt-NO sub-mechanism requires to be validated against experimental data such as species profiles measured in premixed flames. Up to date, the NCN route is only implemented in two detailed kinetic schemes: konnov0.6 [10] and GDFkin®3.0_NCN [11]. During the five last years, in Lille, extensive experimental work in low pressure flames has been conducted in order to measure profiles of trace species involved in prompt-NO formation, essentially at level of a few tens of ppbv. Not only CH and NO species, but NCN and NCO species profiles have already been measured in low pressure $CH_4/O_2/N_2$ flames [11,12]. According to the kinetic scheme of the prompt-NO formation, two other species are important in this process of validation: CN and HCN. They are generated from NCN consumption reactions (2–4) and are then oxidised yielding NCO.

Most of the quantitative measurements of HCN and CN have been performed in flames seeded with nitrogen species in which their concentration is increased due to the conversion of nitrogen-containing species. For instance, HCN was measured in absolute concentration after probe sampling by using Molecular-Beam Mass Spectrometry (MBMS) [13] in morpholine/O_2/Ar low pressure flames (with a peak value of 5%). Meantime, radical species profiles (CH, NH_2 and CN) were obtained in situ by Cavity Ring-Down Spectroscopy (CRDS) [14]. Much less works report on HCN or CN measurements in flame free of nitrogen-containing species except N_2, referred in the following as undoped flame. In undoped flames, the sole optical techniques applied to the quantification of HCN rely on absorption measurements. To avoid possible interfering absorption coming from stables species present around the flame (especially in confined vessel), the absorption measurement of HCN after probe sampling is beneficial. HCN measurements were performed by *cw*-CRDS (continuous wave-CRDS) [15,16] or by WMAS (Wavelength Modulated Absorption Spectroscopy) [17,18] after gas probe sampling from atmospheric diffusion flames or from atmospheric premixed flames, respectively. In these experiments, measurements were achieved in the (200)–(000) band around 1.5 μm, with a sensitivity limit in the cell equal to 1.0×10^{10} molecule cm^{-3} and 2.4×10^{12} molecule cm^{-3}, corresponding to a mole fraction in the flame of 43 ppbv and 1 ppmv, respectively. To detect HCN in low pressure flames, we initially implemented pulsed CRDS technique in the (300)–(000) band around 1.0 μm after gas probe sampling [19], but were not able to obtain a sensitivity limit better than 20 ppmv of HCN in the flame (i.e. 1.6×10^{13} molecule cm^{-3} in the cell). Consequently, the applicability of the technique was limited to flames doped with nitrogen-containing species. Up to date, absolute HCN measurements have never been reported in undoped low pressure flames.

CN radical has previously been measured twice in absolute concentration in premixed undoped $CH_4/O_2/N_2$ low pressure flames by pulsed CRDS [20,21]. Measurements were performed by probing the P-branch of the B-X(0,0) band around 388 nm. From integrated spectral absorptivity measurements, the CN peak value in a rich premixed flame at 5.33 kPa was found equal to 22 ppbv, with a detection limit estimated to be a few ppbv [20]. Similarly, the CN peak value in a nearly stoichiometric premixed flame at 3.36 kPa was measured equal to 8 ppbv, with a limit of detection equal to 1.4 ppbv [21]. In those flames, the CN peak value is 3 orders of magnitude lower than in morpholine flame [14].

We report here the first joint measurements of CN and HCN in premixed low pressure (5.3 kPa) $CH_4/O_2/N_2$ flames of three equivalent ratios ϕ (0.8, 1.0, 1.25). HCN mole fraction profiles have been measured by using *cw*-CRDS technique after gas probe sampling at 1.5 μm with a sensitivity limit similar to that previously reported [15,16]. LIF (Laser induced fluorescence) and CRDS techniques have been combined to achieve the required sensitivity (lower than 1 ppb) for measuring the CN mole fraction profiles. Experiments were completed with temperature profiles measurements in order to compare the experimental species profiles with the simulated ones using Chemkin code. For that purpose, two recent detailed kinetic sub-mechanisms for the prompt-NO formation were considered [10,11].

2. Experimental

2.1. Low pressure burner and gas supply

Experiments were undertaken in laminar $CH_4/O_2/N_2$ premixed flames stabilized at 5.33 ± 0.01 kPa (40 Torr) on a 6-cm diameter bronze water-cooled McKenna burner. Details concerning the burner and gas supply were given in