Investigations by Mid-IR QCLAS of pollutant emissions in high temperature exhaust gases released from plasma-assisted combustion

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Nanosecond Repetitively Pulsed (NRP) discharges have been used to stabilize lean methane-air flames, which have the advantage of producing reduced NOx in comparison with stoichiometric flames. Here the effect of NRP plasmas on the nitric oxide and carbon monoxide pollutant emissions was studied. Quantum Cascade Laser Absorption Spectroscopy (QCLAS) was used to measure in situ densities of CO at 2055.4 cm⁻¹ and NO at 1900.076 cm⁻¹, with detection limits below 1 ppm. For the first time the absolute density of NO was measured at high temperatures (up to 1100 K) in the combustion exhaust gases. The NRP discharge studied here was found to not modify the CO density, and to maintain NO densities comparable to those of stoichiometric flames.

1. Introduction

Lean combustion is known to release fewer pollutants, in particular lower NOx emissions. Its drawback is the occurrence of flame instabilities that can lead to flame extinction, hence to unburned hydrocarbons (loss of energy) and the release of pollutants. The use of short-pulsed discharges to ignite and to enhance flame stability has been of great interest during last decade. Particularly, the use of nanosecond repetitively pulsed (NRP) discharges to stabilize lean combustion types is a very promising approach [1,2]. These discharges produce large amounts of atomic oxygen [3,4], a key radical for the flame stabilization mechanism for an average power (∼ 100 W) of a small percentage of the flame power (∼ 10 kW). However, little is known on NO, CO and unburned hydrocarbons emissions.

Absolute in situ measurements of NO and CO densities in plasma-flame environments are very challenging. Complex techniques such as Laser Induced Fluorescence [5] can be intrusive, need difficult calibration methods and are strongly dependent on the knowledge of the quenching of the excited states (especially at atmospheric pressure). The quenching rates are strongly dependent on the density, temperature and nature of the species, and those can be very different for plasmas and flames. Other techniques such as probe sampling Chemiluminescence analysis [6] undergo also quenching, or the ex-situ UV, IR absorption based gas analysers can lead to errors in particular for radicals.

These difficulties were overcome here by using high resolution (10⁻³ cm⁻¹) rotation-vibration resolved absorption spectroscopy. Measurements were carried out at the exhaust of a confined combustion system where the output temperature spatial profile and absorption length were well defined. Nitric oxide and carbon monoxide production was measured using Mid-IR Quantum Cascade Absorption Spectroscopy at 1900.076 cm⁻¹ and at 2055.40 cm⁻¹, respectively. The CO transition in the electronic ground state, the fundamental band ν₁₁₁ (P₂₁), permit measurements at 1100 K with a negligible spectral overlapping even at atmospheric pressure. The selection of the NO transition was very challenging due to very large amounts of hot water and carbon dioxide presence in the exhaust gases (19 % H₂O and 9.5 % CO₂). The electronic ground state X₁₂₂, fundamental band ν₁₁₁ (R₂₅) transition allow measurements of NO if the background absorption is known. Based on the Hitran data base (HITEMP-2010, high temperature data base) accurate line strengths were obtained to correct for the Boltzmann population redistribution over the rotational-vibrational level system at high temperatures [7]. The background absorption was also simulated considering the mole fractions, line strengths and line profiles (collisional and Doppler broadening).

2. Experimental set-up

Figure 1 shows a scheme of the QCLAS (a QMACS system) and plasma-assisted combustion setups. Lean CH₄-air premixed flames were stabilized by the NRP discharges at total flow rates of 4 - 5.8 m³/h. For efficient stabilization the discharge was placed in the recirculation zone, behind a bluff body. The NRP discharges were generated using a pin-to-pin electrode configuration (gap distance 4 mm), by 10-ns high voltage pulses (4-7 kV) at pulse repetition frequencies of 30 kHz.
Figure 1. QCLAS and plasma-assisted combustion experimental set-up.

Experiments were performed with the flame confined in a metallic tube of 50 cm length and 8 cm diameter. The measurements were done at the tube outlet. The temperature of the burned gases at the tube outlet was measured by thermocouples and was found to be 1100 (±70) K with small variations function of experimental conditions. A multi-pass White cell (up to 28 passes) was used to improve the sensitivity of the absorption system.

2. Results

Carbon monoxide is one major combustion intermediate species. Emitted in large amounts it is also a toxic pollutant and its presence in the exhaust gases is an indication of combustion incompleteness. The density of CO was corrected for the line strength temperature dependency (at 1100 K the line strength of the P21 transition increases by a factor 5.5 compared to 300 K) [8]. As shown in figure 2 the spectral interferences with water and carbon dioxide molar fractions were negligible even at 1100 K. The spectrum was simulated for 100 ppm CO, 1.5 m absorption length and the typical water and the carbon dioxide molar fractions (19 % H2O and 9.5 % CO2). In figure 3 the absolute CO density at the tube outlet in the exhaust gases is represented. For equivalence ratios (ER) ≥ 1 (ER=1 represents the stoichiometric composition) the measurements were done with one laser path while for ER < 1 a White multi-pass cell was used. From Abel-inverted one-pass lateral scan absorption measurements the absorption length was found to be equal to the tube diameter. No CO density was measured if the laser beam was not passing above the tube exit.

From figure 3 we can see that using NRP discharges in lean condition produces no significant change of the CO density. For rich flames, about 20-30 % more CO was measured. The typical CO density for lean flames (equivalent ratio ER= 0.7 - 0.95) was on the order of 5x10^{13} cm^{-3} and 6 x 10^{16} cm^{-3} for the rich flame (ER=1.05).

Figure 2. Simulation using the Hitran data base for atmospheric pressure 1100 K combustion exhaust with 100 ppm CO, 19 % H2O, 9.5 % CO2 and 1.5 m absorption length.

Figure 3. CO density measured at tube outlet in the exhaust gases with and without plasma function of the equivalence ratio (ER).

Because the burned gases flow in the confinement tube at temperatures in the range of 1100 – 2000 K and the combustion of CO is very efficient (CO+1/2O2→CO2) at high temperature, the CO density strongly decreases (to 8 ppm). In rich flames, large amounts of CO (<1%) are measured because the methane combustion in the confinement tube is not complete.

Detection of NO in exhaust gases at high temperature is particularly challenging. In reference
[9] A few transitions were identified around 5.2 μm wavelength, with a relatively small overlap with water lines. The reported experiments were carried out below 700 K. In order to perform measurements of NO fundamental band transitions at higher temperatures, accurate background absorption must be subtracted from the transmittance spectra. Figure 4 shows simulations of water and carbon dioxide background together with 100 ppm NO at 300 and 1100 K and for 1.5 m absorption length. These simulations were obtained using HITEMP data.

Figure 4. Atmospheric pressure H₂O and CO₂ combustion exhaust simulations at 300 and 1100 K for 1.5 m absorption length and for 100 ppm NO.

It can be seen that the absorption at 1900.076 cm⁻¹ decreases by a factor 3.9 from 300 to 1100 K, however it is still suitable for NO detection.

Figure 5 shows a typical NO measured spectrum when NRP plasma was generated in ambient air. A very good fit was obtained with a synthetic spectrum calculated using the Hitran database. All NO absorption measurements were performed using a White multi-pass cell at the tube outlet.

Figure 5. Typical atmospheric pressure NO transmittance spectrum at 300 K generated by NRP discharge and fitted by a synthetic spectrum calculated using Hitran data.

Figure 6. NO absolute density as a function of ER. The highest NO was found to be in the range of 2.3 x 10¹⁵ cm⁻³ and was obtained when the NRP was running in pure air (black triangles). Air was injected at the same flow rates as in the combustion ER experiments. The measurements were performed at room temperature. No significant temperature changes at the tube exit were observed. The pulse energy was measured by integrating the voltage and current waveforms (using a high-voltage probe, Lecroy PPE 20 kV, and a Pearson coil, model 6565), however with a significant uncertainty due to run-to-run variations. The energy per discharge pulse was about 2.3 mJ and the repetition frequency was 30 kHz, yielding an average discharge power of about 70 W. For all experiments shown in figure 6 the pulse energy in air and air-fuel mixtures was assumed to remain the same, and of the order of one percent of the flame power.

For the flame with plasma we see that the NO density is in the range of 1.4 - 2.3 x 10¹⁴ cm⁻³. A factor of 3.7 decrease relative to the discharge in ambient air, is explained by the total density reduction due to temperature increase at the tube exit (from 300 to 1100K). The additional decrease of a factor 4 represents the NO reduction due to combustion.

In the flame case, the NO densities are found in the range of 8.6 x 10¹² - 1.7 x 10¹⁴ cm⁻³ for equivalence ratios between 0.75 and 1.05. This
corresponds to an NO reduction from rich to lean by a factor 20, a typical reduction for methane-air flames. For 0.7 ER the NO density was below the detection limit.

3. Discussions and conclusions

Mid-IR QCLAS has proven to be a suitable technique highly selective and sensitive, capable of in situ, absolute NO and CO density measurements in harsh environments such as plasma-assisted combustion and at high exhaust temperatures of up to 1100 K. QCLAS can be used as an endpoint detection sensor, for instance to quantify the combustion completeness. A few orders of magnitude increase of CO density were measured when going from lean to rich flames. For lean flames, the NRP discharges do not increase the CO density while for rich flames a 20-30 % increase was observed.

NRP discharges in pure air produce high NO densities, and those are strongly reduced when NRP discharges are used in the flame. The measured NO densities in the exhaust gases in case of NRP air discharge and in air/methane flame+NRP were found to be larger than in case of unassisted flames. The main NO formation mechanism given by the Zel’dovich reactions (thermal NO): N_2+O → NO+N, N + O_2 → NO + O, and N+OH → NO+H, cannot explain the large NO increase when plasma is added to the flame. According to reference [5] the kinetics of NO formation must be completed by plasma-induced reactions such as:

\[ \text{N}_2(X, v \geq 12) + \text{O}(^3\text{P}) \rightarrow \text{NO} + \text{N}(^4\text{S}) \]
\[ \text{N}(^4\text{S}) + \text{O}_2(b^3\Sigma) \rightarrow \text{NO} + \text{O}(^3\text{P}) \]

which are shown an important role.

As shown in references [3,4] the NRP discharges were found also to produce large amounts of atomic oxygen, e.g. up to 50 % dissociation of molecular oxygen. Consequently an important fraction of atomic oxygen formed during the 10 ns discharge will lead to NO formation. In the presence of a flame atomic oxygen is consumed through oxidation processes. As a confirmation, the measurements from figure 6 show a strong reduction of the NO emitted by the plasma+flame compared to the NO emitted by the plasma alone.

For the discharge conditions studied here the NO density in lean flames was found to be lower than in plasma-assisted combustions. The current measurements show that the NO emissions in lean flames stabilized by the NRP discharge remain close to the unassisted stoichiometric flames. Recent results obtained using a gas analyzer indicate that NO density below the stoichiometric level can be obtained with reduced pulse frequencies [10]. Thus, optimization of plasma-assisted combustion must be further studied with discharges at lower power, lower frequencies, and probably well controlled reduce electric field (E/N) conditions. For a better understanding of NO formation mechanisms, advanced plasma-combustion kinetic models will be necessary.

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References