Laser-spectroscopic investigation of OH-radical concentrations in the exhaust plane of jet engines

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Abstract. Hydroxyl radical (OH) emissions are relevant for oxidation reactions in the post flame chemistry of exhaust gases emitted from jet engines. No direct measurements of OH concentrations are available to date due to the low abundance and the short lifetime of this radical species. The first application of a combined technique based on Raman scattering and laser-induced fluorescence (LIF) spectrometry is presented here for measurements in the exhaust gases of a commercial jet engine operated in a test rig. From the measurements, upper limits for OH concentrations in the exit plane were determined in the range of 90 ppbv for take off and 80 ppbv for ap-idle. The values are significantly below the predictions of model calculations based on HONO and HNO_3 in-flight concentration measurements presented recently. Possibilities for further increase of the detection sensitivity for OH are discussed.

1. Introduction

Aircraft emissions at flight altitude are a major contributor to pollutants around the tropopause (*Schumann*, 1994). Emissions from jet engines were investigated within the last years both, during in-flight and test rig measurements. Special attention is paid to oxidized nitrogen and sulfur species which are considered to be responsible for aerosol formation in the plume (*Miake-Lye et al.*, 1993) and soot activation (*Schumann et al.*, 1996). Hydroxyl radicals play an important role in oxidation processes in the plume of jet engines. Due to their large reaction cross sections they are the main contributors to the production of acidic gases like H_2SO_4 and HNO_3 upon oxidation of SO_x and NO_x emitted from the flame (*Curtius et al.*,1998, *Tremmel et al.*, 1998). Despite their importance to date no direct measurements of OH concentrations in jet engine exhaust gases are available. Probe measurements are not feasible because of short lifetimes due to the high reactivity of OH radicals. Optical measurements on the other hand have shown to be difficult in harsh environments like jet engine test rigs. Absorption measurements in the uv wavelength range have been carried out within a NASA project but OH concentrations were found to be below the detection limit of the system used which were estimated to be 10^{12} cm^{-1} (i.e. 110 ppbv @ 800 K) (*Brasier et al.*, 1996). Therefore only upper limits were obtained. *Tremmel et al.*, 1998, deduced OH concentrations from measurements of different oxidation stages of nitrogen compounds in the exhaust gases in in-flight experiments. Two different sets of simulation calculations were carried out either starting

at the exit plane of the entire jet engine assembly or from the combustion chamber exit within the assembly. The latter case shows, that due to post-combustion reactions the OH concentrations are reduced by a factor 350 (*Tremmel et al.*, 1998) by the time the exhaust gases exit the engine. It is crucial to know the OH concentration in the exhaust gases quantitatively to validate the current kinetics scheme that is used to model the formation of nitrogen and sulfur containing species in the exhaust plume (*Tremmel et al.*, 1998). A set of different calculations were presented and discussed by Lukachko et al. (*Lukachko et al.*, 1998). Depending on the specific model that was used and input parameters, the predicted OH levels range over several orders of magnitude. They point out the urgent need for measurements. Quantitative measurements of OH radical concentrations are frequently performed within flames and in hot gases using laser-induced fluorescence (LIF) (*Eckbreth*, 1996 and references therein). With LIF, small concentrations down to the ppb range can be measured as long as background signals can be sufficiently suppressed. The dynamic range of LIF provides a possibility to measure OH radical concentrations in the flame at concentrations of 10^4 ppm to the exhaust gases at concentration levels of 10^{-2} ppm. In the study presented here a tunable excimer-laser based OH-LIF/Raman system was set up in the harsh environment of a jet engine test rig. Selective excitation of OH radicals was achieved by tuning the excimer laser to an OH resonance at 308.15 nm (OH A-X(0,0) band) (*Ketterle et al.*, 1992). Background signals, originating from fluorescence of unidentified broadband-absorbing species, were acquired at off-resonant positions. The signal emitted from the probed volume was spectrally resolved by a spectrometer, thus allowing spectral separation of OH-LIF and Raman signals. In flames the signal upon excitation at 308.15 nm is by far dominated by OH fluorescence. Elastically (Rayleigh) and inelastically (Raman) scattered light is weaker than the fluorescence signal by several orders of magnitude. In the absence of OH-LIF on the other hand, Raman signals emitted from the majority species (nitrogen, oxygen, water, fuel) can be detected upon laser excitation. In systems with low OH concentrations OH-LIF and Raman intensities (i.e. N_2-Raman) are of the same magnitude. The ratio can then be used directly for calibration of the OH-LIF signals because the cross sections for both processes are well known, as is the nitrogen number density in the probed gas volume. Additionally, basing the calibration procedure on the evaluation of ratios of LIF and Raman signals makes the transfer of calibration information from one object (well known calibration flame: McKenna burner (*Kaiser et al.*, 1986)) to another (i.e. the exhaust gases in the test rig) much more robust. Within the tuning range of a XeCl excimer laser OH can be excited via a rotational line ($Q_1(3)$) in the strong $A^2\Sigma^+$, v' = 0 ← $X^2\Pi$, v" = 0 band. For this excited level, the most intense fluorescence is observed resonantly in the same band which is usually used to detect OH in clean environments. At low OH

concentrations however, the emitted light can not be discriminated from elastically scattered light i.e. off soot particles or from Rayleigh scattering. From the excited $A^2\Sigma^+$, v' = 0 level alternatively the transition to the vibrationally excited ground state level $X^2\Pi$, v'' = 1 can be monitored at 343-349 nm (*Ketterle et al.*, 1992). The cross section of this process is smaller by about a factor of 200 but due to the red-shifted signal, OH fluorescence can now be spectrally separated from resonantly scattered light. A slightly stronger signal than in the (0,1)-band can be found upon collisionally induced population of the first vibrational level $A^2\Sigma^+$, v' = 1 with subsequent emission in the (1,0) band around 288 nm. Since the transfer to the v' = 1 level depends on collision processes and therefore on gas composition, pressure and temperature, quantitative interpretation of this blue-shifted fluorescence signal is difficult. Therefore, detection of this signal for quantitative measurements in the present study was not considered.

2. Experimental

Two sets of experiments were conducted. A laboratory experiment using a calibration flame was performed to investigate the OH detection scheme best suited for detection of OH concentrations in the sub-ppm range. Furthermore, calibration measurements were done using the optical setup that was designed and built for the measurements in the test rig measurements. A second set of experiments was carried out in the jet engine test rig HAM 2 (Lufthansa, Hamburg) with a Pratt & Whitney 4152 engine. In both experiments the unfocussed beam of a tunable XeCl excimer laser (Lambda Physik, EMG 150 EST, wavelength: 308 nm, tunable ± 0.3 nm, spectral bandwidth: 1 cm^{-1} (full width at half maximum), 17 ns pulse duration, 300 mJ pulse energy) was directed either through a calibration flame (McKenna) or the exhaust gases in a plane 50 cm behind the jet engine exit. After approximately 6 m path length between laser and probe volume, the laser beam expanded to a cross section of 3 x 5 cm resulting in an energy density of 0.8×10^6 W/(cm^{-1}cm^2). The laser was tuned on and off resonance during the jet engine measurements to enable background corrections. Proper tuning of the laser was checked via OH fluorescence obtained from a small Bunsen flame inserted in the laser beam path. OH-LIF from this flame was detected using a photo-multiplier and maximized before performing on-resonant measurements in the exhaust gases of the jet engine.

The signal emitted from the probe volume (calibration flame or exhaust gases) was collected with a large aperture quartz lens (f = 600 mm, f$_\#$ = 4) and imaged on the entrance slit of a spectrometer
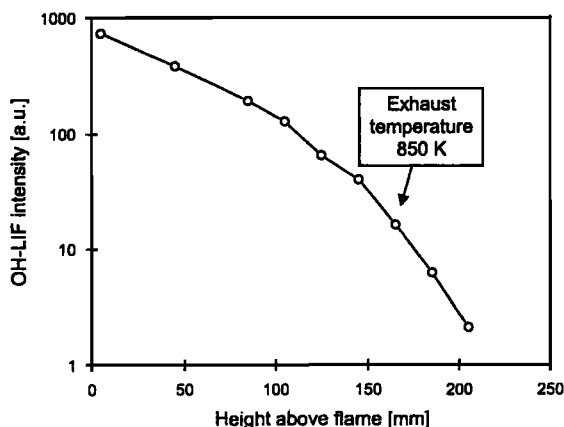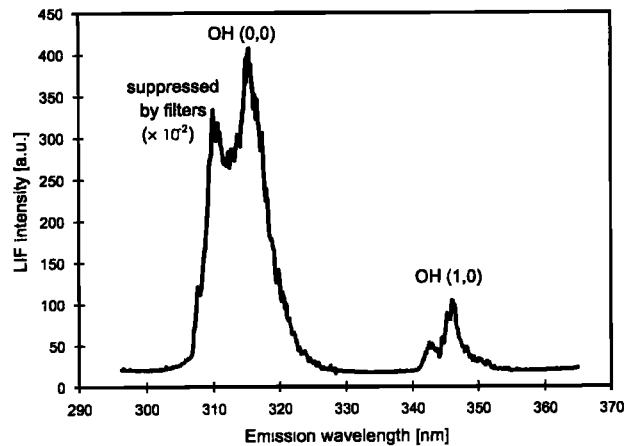
Figure 2. Spectrally resolved OH-laser-induced-fluorescence obtained from a calibration flame mounted in the jet engine test rig.

(Acton Research, ARC SpectraPro 150, f = 150 mm, f$_\#$ = 3.8). The spectrometer was equipped with a 1200 grooves/mm grating. An image-intensified CCD camera (LaVision FlameStar III) mounted in the exit plane of the spectrometer recorded the spectrally resolved light on a single laser shot basis. The setup provided a spectral resolution of 0.07 nm per pixel. Mirrors for beam direction and optics for signal detection had to be fixed very rigidly in the wind tunnel because they were exposed to high air speeds and vibrations. To protect the optical system, spectrometer and camera were mounted in a closed housing equipped with a quartz window. To enhance the signal-to-noise ratio in the exhaust gas measurements the laser was operated at maximum repetition rate (10 Hz) and signal was acquired on-chip for several thousand single laser pulses. Since the standard test procedure for jet engines include take-off conditions for five minutes only, data acquisition in these cases was limited to approx. 1500 laser pulses for both, on and off resonant excitation.

3. Results and discussion

In the calibration flame upon excitation at 308.15 nm it was found that the red- and blue-shifted emissions are weaker by a factor of 200 and 100 resp. compared to resonant emission. Because of high levels of scattering particles the use of the resonant emission at 308 nm is not feasible in jet engine exhaust measurements. The red shifted emission was chosen for all the measurements presented here, as it offered the best possibility to quantify the LIF data. Figure 1 shows the signal intensity of OH-LIF measured in the exhaust gases of the calibration flame at various heights above the burner matrix. With increasing height, the temperature drops and therefore OH equilibrium concentrations are decreasing. Emission spectra were taken with the laser tuned on and off an OH resonance. The OH-LIF signal was obtained from the difference of both spectra. OH radicals could be measured up to heights of 20 cm above the burner at temperatures of around 800 K. Therefore at temperatures expected to be present in the jet engine exhaust immediately behind the exit plane (approx. 850 K) equilibrium OH concentrations were expected to be easily detectable. Figure 2 shows the OH emission spectrum (resonant and red-shifted emission) measured in the test rig in the calibration flame that was mounted at the location for the jet engine exhaust measurements. This proved that the optical setup in the test rig was suited for OH-LIF detection at the expected OH concentration levels (300-700 ppbv as in *Tremmel et al.*, 1998).

Figure 1. OH-LIF intensity at different heights above the calibration flame.

In figure 3 spectrally resolved signal light obtained from the jet engine exhaust measurements is shown for both, take-off and ap-idle operating conditions. The spectra were averaged over 1500 subsequent measurements for both, off and on resonant measurements for one operating condition. Main influence on statistics is caused by variations in laser energy (smaller than 10% per single shot) by averaging over 1500 single shots variations are reduced to < 0.3%. It can be seen that the signal is dominated by Raman emissions of oxygen, nitrogen and water. Spectral positions of OH emission from the OH (0,1) band and H_2O Raman signal coincide. Therefore spectra taken at off-OH resonance positions were taken and subtracted. For both operating conditions of the engine, no net signal intensity due to OH fluorescence was detectable within the error limits of the experiment.

From statistical variation of the background signal intensities observed under these conditions the limit of detectable OH-LIF signal intensities was inferred. The detection limits were experimentally determined to 3 σ (approx. 1.7% of the N_2 Raman signal). In the calibration flame operated with methane/air under well-controlled conditions Raman and OH-LIF intensities were measured with the identical optical setup. With the laser tuned to the OH resonance, N_2-Raman signals were too weak and hidden in the slopes of OH fluorescence. Therefore the ratio of OH-LIF and N_2-Raman was obtained from subsequent experiments with the laser tuned on and off resonance. The measured ratio of Raman and LIF signals was then used to calibrate the exhaust gas measurements.

When using the calibration information obtained in a different environment corrections have to be included to account for variations of temperature and gas composition, which alter the signal intensity. Raman intensities depend on the number density of the respective species with only a small temperature dependence (*Eckbreth*, 1996). LIF intensities on the other hand depend strongly on the temperature dependent population $f_B(T)$ of the probed ground state (determined by a Boltzmann distribution). Furthermore, collisionally induced fluorescence quenching Q reduces the fluorescence quantum yield ϕ, which is proportional to

$1/Q$ by non-radiative relaxation of the electronically excited molecules. The total quenching rate $Q(T)$ however, depends on collision frequency and thus on temperature and on the nature of the colliders. Assuming complete combustion in the present case only N_2, O_2, H_2O and CO_2 were included as major contributors. Individual temperature dependent quenching cross sections were taken from *Paul*, 1994 and *Paul et al.*, 1995. Equation 1 shows the transfer of the calibration measurement to the exhaust gas measurements.

$$N_{OH}^{exp} = N_{OH}^{cal} \frac{(I_{LIF}\ N_{N_2})_{exp}}{(I_{LIF}\ N_{N_2})_{cal}} \frac{(I_{Raman}\ f_B(T)\ \phi(T)\ g_\lambda(T))_{cal}}{(I_{Raman}\ f_B(T)\ \phi(T)\ g_\lambda(T))_{exp}} \qquad (1)$$

N_{OH}^{cal} is the number density of OH in the calibration flame. I_{LIF} and I_{Raman} are the measured intensities for OH-LIF and N_2-Raman scattering in both environments. $g_\lambda(T)$ represents the excitation efficiency which depends on the overlap of spectral laser line profile and absorption spectrum (*Schulz et al.*, 1997). Nitrogen concentrations in the air and the exhaust gases are known. Thus, from relative Raman signal intensities taken at room temperature (jet engine off) and in the hot exhaust gases, total number densities can be measured. Using the perfect gas law for the atmospheric pressure system local temperatures were computed. For ap-idle conditions, temperatures were found to be in the range of 505 K whereas at take off temperatures of 840 K were measured. These data agree with the temperature data provided by Lufthansa Technik obtained from thermocouple measurements. Temperatures obtained from these measurements were included in the data evaluation. With the analysis procedure as described above, upper limits for the OH concentration in the exhaust gases were obtained. Detection limits depend on the operation condition of the engine due to different temperature levels in the exhaust gases which affects equation 1. Furthermore different background levels caused by scattering particles like soot in the exhaust gases influence the signal-to-background ratios. OH concentrations were found to be below 90 ppbv and 80 ppbv for take-off and ap-idle resp which corroborates the results of *Tremmel et al.* who showed that the main part of OH is consumed between combustion chamber exit and jet exit. The experimentally obtained upper limits are significantly below the OH concentration levels predicted by *Tremmel et al.*, 1998 which are based on in-flight concentration measurements of a variety of nitrogen containing species like NO, HNO_2 and HNO_3 (*Arnold et al.*, 1992). The predicted OH concentrations at the jet engine exit in the range of 300-700 ppbv are significantly above the upper concentration limit obtained from the present experiment. A further reduction of OH concentration in the test rig experiment, however, might be due to higher pressure and higher water content compared to conditions at flight altitude (*Arnold 1999*). Further improvements of the detection limit for OH radical measurements with the technique described here can be achieved. With excimer laser-based systems providing higher pulse repetition rates (could be increased by a factor of 50), signal-to noise ratios could be increased by a factor of 7 with the same duration of a single experiment (i.e. 5 minutes). Using other excitation-detection schemes for the OH radical, higher detection efficiencies can be expected. After exciting OH in the A-X(1,0) band with detection of the subsequent fluorescence from the A-X(0,0) transition, an increase in fluorescence cross-sections by a factor of approx. 20 is calculated. However, the necessary wavelengths (281-285 nm) are not available from tunable excimer laser sources. Therefore dye-laser systems are required which are more difficult to operate in harsh environments like the jet engine test rig. Furthermore, they provide significantly lower pulse energies. But, since the detection limit is mainly determined by the signal-to-background ratio, reduced excitation energies would be no
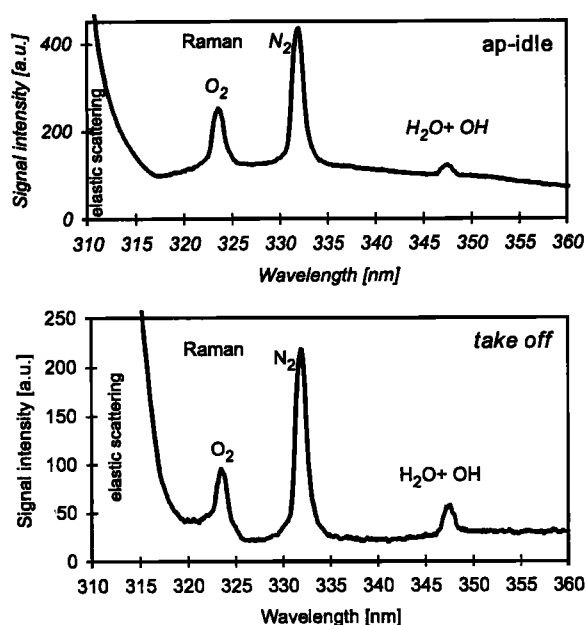

Figure 3. Spectra obtained from laser-induced processes in the jet engine exhaust gases. (The arbitrary intensity scale is different from that used in figure 2). The intensity of the combined H_2O/OH-line would increase by a factor of 3.3 in the presence of 300 ppbv OH..

limitation. An overall improvement of the detection limit is therefore expected in the range of 1 to 1.5 orders of magnitude. Direct measurements of the OH radical concentration in the exhaust plane of jet engines are then possible for concentrations as low as 5 ppbv.

4. Summary and Conclusions

In a jet engine test rig an optical system to assess OH concentrations in the exit plane of jet engines using a combined LIF/Raman technique was set up. With this system an upper limit for the OH concentrations could be inferred. OH concentrations were determined to be below 90 ppbv for take-off and 80 ppbv for ap-idle conditions. These concentrations are significantly below the predictions which are based on simulation calculations using the ratio of concentrations of different nitrogen-containing compounds in the exhaust gases in flight altitude (*Tremmel et al.,* 1998). Lower OH concentrations in the test rig measurements might be due to higher ambient pressure and water content. Especially in view of the wide range of OH concentrations predicted by Lukachko et al., 1998, calculations must be performed for exactly the conditions under which the experiments were performed.

Further experiments are desirable in jet engines with after-burner configuration where OH concentration levels in the exit plane are expected to be much higher. Then, OH measurements at different ages of the exhaust gases could be performed at different distances to the jet engine exit and be compared to the modeling results. A further potential for improving the sensitivity of the measurement technique was outlined and could be implemented in future investigations.

Acknowledgement

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