

# Comparison and investigation of selected aromatic and ketone fluorescent tracers considering possible self-quenching effects

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## Abstract

This paper presents an investigation of the dependence of the laser-induced fluorescence (LIF) signal intensities on the concentrations of selected organic tracers. We focus primarily on the aromatic tracer toluene vaporized in a mass-flow controlled evaporator and investigated in a steady turbulent jet. In addition, the ketone tracer acetone will be considered. Either nitrogen or air was used as carrier gas. Excitation was accomplished by a Nd:YAG laser (266 nm) with a pulse length of 7 ns. Spectrally filtered fluorescence radiation was recorded with an intensified CCD camera. The results suggest a non-linear relation between LIF signal intensity and tracer concentration well below saturation concentrations, which is attributed to self-quenching and observable for both the aromatic and the ketone tracer. Effective fluorescence lifetimes upon short-pulse UV-laser excitation were determined for toluene to determine room temperature self-quenching rates. In these experiments, a picosecond-laser at 266 nm, a spectrometer, and a streak camera with sub-ns time resolution were used to record temporally and spectrally resolved fluorescence. Preliminary results indicate that the fluorescence lifetime decreases with increasing tracer concentration.

## 1. Introduction

Laser-induced fluorescence (LIF) can be used for spatio-temporally resolved imaging of gas-phase mixing processes, temperatures, and concentrations in internal combustion engines and other combustion applications. For quantitative measurements, fluorescent tracers may be added to a non-fluorescing surrogate fuel. Ketones and aromatics are two commonly used groups of compounds [1]. For example, since the evaporation characteristics of toluene and naphthalene are comparable to those of gasoline [2] and Diesel [3], respectively, they can serve as tracers for those fuels. Recent comparisons of different tracers are presented in [4] and [5].

In measurements in which the quantity of interest is the tracer number density  $n_{tr}$  (or a derived quantity like mixture fraction), it is usually assumed that, all else being equal, the LIF signal intensity  $S_{fl}$  scales linearly with that number density (as well as absorption cross section  $\sigma_{abs}$ , and fluorescence quantum yield  $\phi_{fl}$ ):

$$S_{fl} \propto n_{tr} \sigma_{abs} \phi_{fl} \quad (1)$$

Suitable corrections for background offset and the response of the imaging system then allow simple conversion of the measured LIF intensity into at least a relative local value of tracer concentration.

The current work is motivated by the recent results of a LIF imaging experiment that could not be reconciled with the simple linearity expressed by Eq. (1). Therefore, in this work, we investigated the dependence of the LIF signal intensities on the concentration of the aromatic tracer toluene, with either

$N_2$  or  $O_2$  present in the gas mixture. Some results for the ketone tracer acetone in  $N_2$  are also included. The experiment was typical for LIF-imaging: quantitative two-dimensional measurement of the mixture-fraction field in a turbulent jet. Section 2.1 and 3.1 describe experiment and results.

Additionally, the effective fluorescence lifetime of toluene at different concentrations was measured in  $N_2$ . These measurements, based on a picosecond excitation and detection with a spectrometer and a streak camera with sub-ns time resolution, are described in Sections 2.2 and 3.2.

## 2. Methods

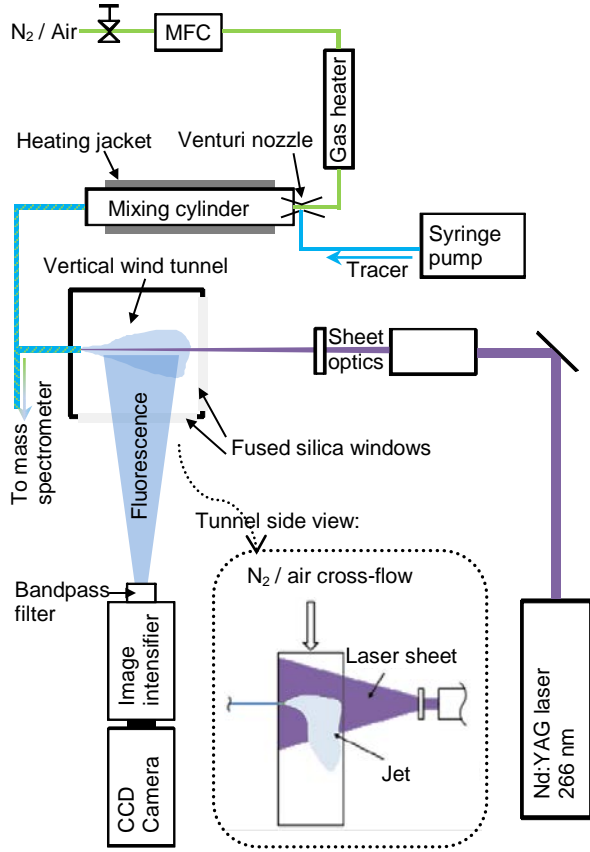
### 2.1. Jet imaging experiment

Fig. 1 shows a schematic view of the experiment. The flow rate of the liquid tracer is set by a syringe pump. In a venturi nozzle, the tracer is injected into a pre-heated and mass-flow controlled flow of either  $N_2$  or air. The volumetric flow rate of the carrier gas was set to 0.6 L/s. To avoid condensation of the tracer at 293 K, the maximum tracer flow rates are 66.5 mg/s (corresponding to a volume fraction of 2.85 vol%) in case of toluene and 471 mg/s (24.81 vol%) in case of acetone.

After atomization in the venturi nozzle, the tracer evaporates and mixes with the carrier gas in a heated plenum with 2.25 L volume. In a wind tunnel, the mixture issues from a nozzle with 4 mm diameter into a slightly heated cross-flow of  $N_2$  or air. The resulting turbulent jet has a Reynolds number of about 10 000. Upstream of the nozzle, a small amount of the mixture can be diverted into a mass spectrometer.

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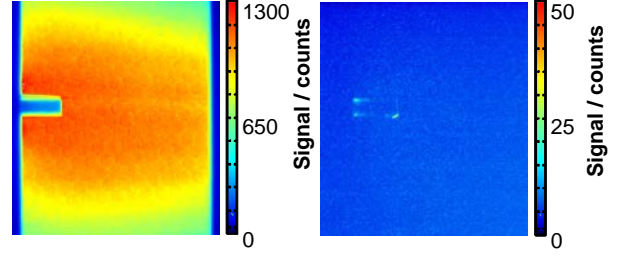
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**Fig. 1.** Schematic diagram of the jet experiment.

The turbulent jet downstream of the nozzle is imaged by LIF. For this purpose, the beam from a frequency-quadrupled Nd:YAG laser at 266 nm with a pulse duration of 7 ns is formed into a light sheet, aligned with the jet's central plane of symmetry. The measurements were performed with “weak” recitation, ( $< 3$  mJ/pulse), i.e., the LIF signal scaled linearly with laser pulse energy. The fluorescence was spectrally filtered by means of band pass filters (Semrock BrightLine 292/27 for toluene, 417/60 for acetone) and recorded with an intensified CCD camera.

In linear approximation, the inevitable spatial non-uniformity of laser illumination and LIF detection efficiency can be accounted for by a so-called flat-field correction, i.e., by imaging a field  $I_{FF}$  with uniform tracer concentration, by which the measured image is then divided on a pixel-by-pixel basis. The flat-field image was obtained by blocking imaged section of the wind tunnel and filling it homogeneously with a defined tracer/carrier gas mixture with known tracer concentration. Also, a set of background images  $I_{BG}$  were captured in the absence of fluorescent tracer. Fig. 2 shows examples of ensemble-averaged flat field and background.

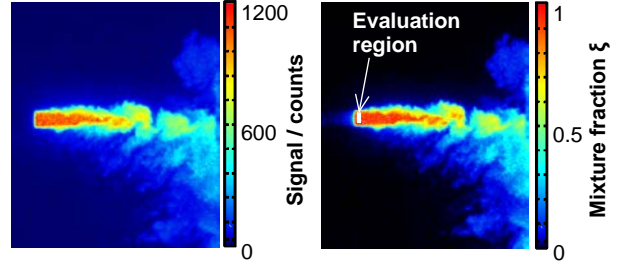


**Fig. 2.** Example flat-field  $\langle I_{FF} \rangle$  (left) and background  $\langle I_{BG} \rangle$  (right) images, ensemble averaged over a series of 50 images.

The left panel of Fig. 3 shows a single-shot jet image  $I$  with toluene as the tracer. If the tracer concentration in the flat-field image is the same as in the jet measurement, this raw LIF image can be converted to mixture fraction  $\xi$  (right panel) according to:

$$\xi = \frac{I - \langle I_{BG} \rangle}{\langle I_{FF} \rangle - \langle I_{BG} \rangle}. \quad (2)$$

If the tracer concentration is increased with respect to that used in the flat field, Eq. (1) would suggest that the right side of Eq. (2) yield proportionally higher values.

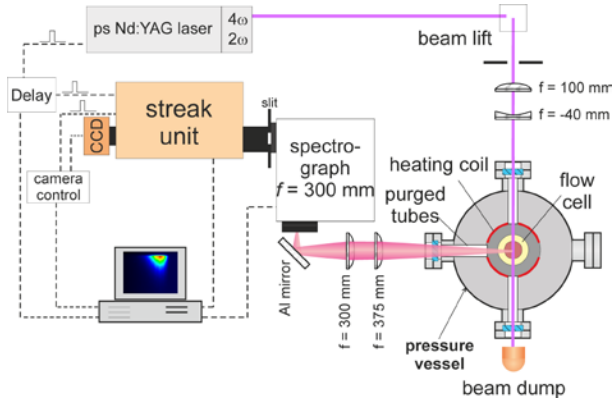


**Fig. 3.** Example single-shot raw LIF image  $I$  (left) and the same image after conversion to mixture fraction  $\xi$  by background and flat-field correction (right).

Turbulent jets have a “potential core” just downstream of the nozzle, where the jet’s fluid has not mixed at all with the surrounding fluid, such that the mixture fraction is unity. For quantitative evaluation of the signal intensity we evaluated a region of interest, covering 400 pixels, in this potential core. The white rectangle indicates this region in Fig. 3, right panel.

## 2.2. Fluorescence lifetime measurements

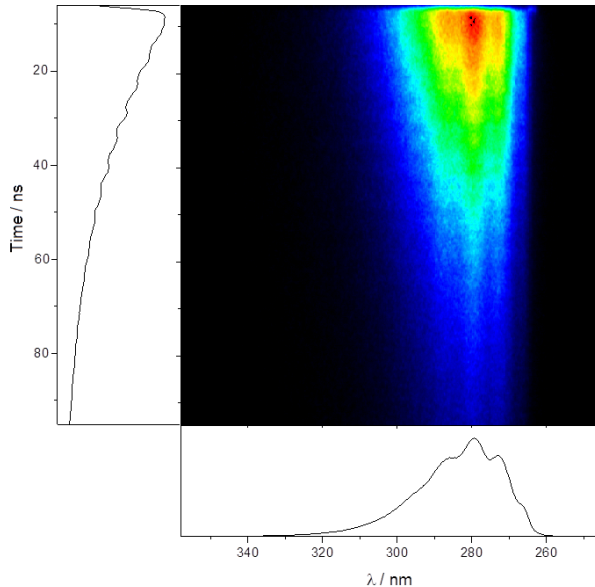
The experiment is schematically depicted in Fig. 4. A detailed description can be found in [6]. Briefly, a high pressure pump metered the liquid tracer before it was evaporated and mixed with part of the main carrier gas  $N_2$  in a commercial evaporator (CEM, Bronkhorst). The rest of the carrier gas was then admixed before the mixture entered a pressure cell (flowing perpendicularly to the drawing plane in Fig. 4).



**Fig. 4.** Sketch of the fluorescence lifetime experiment.

A flashlamp-pumped frequency-quadrupled Nd:YAG laser delivered a pulse energy of 1 mJ at 266 nm with a pulse duration of 26 ps. A combination of quartz lenses focused fluorescence from the cell onto the entrance slit of a spectrograph ( $f = 300$  mm, 150 l/mm grating). The spectrally resolved signal was then imaged on the entrance slit of a streak camera (Hamamatsu) consisting of a streak module and a CCD camera, which provided a minimum time resolution of 20 ps.

For each condition, 1000 individual measurements were corrected for temporal jitter and background signal and then averaged. A resulting sample image is shown in Fig. 5, where wavelength is along the horizontal and time along the vertical axis, respectively. Such images yield either spectrally selected temporal profiles (horizontal binning of columns), or fluorescence spectra for specific time intervals after laser excitation (vertical binning of rows).



**Fig. 5.** Sample image of time-resolved toluene fluorescence spectra (296 K, 1 bar,  $N_2$  bath).

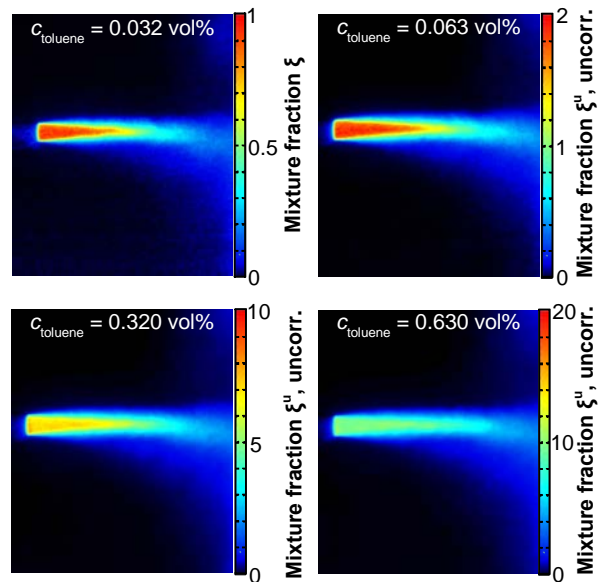
### 3. Results

#### 3.1. Jet imaging experiment

Different toluene mixtures were set via the syringe pump, resulting in toluene volume fractions  $c_{\text{toluene}}$  from 0.032 vol% to 1.864 vol%. The temperatures of jet and cross-flow were set to about 315 K.

In Fig. 6, ensemble-averaged LIF images of the jet with different tracer volume fractions are shown for the case of nitrogen as carrier gas. The images are background and flat-field corrected according to Eq. (2). For Eq. (2) to yield mixture fraction, the tracer concentration in flat field and jet fluid would have to be equal. Here, however, we converted all jet images using the flat-field measured at a concentration of  $c_{\text{toluene}} = 0.032$  vol%. According to Eq. (1), this should yield values that are higher than the mixture fraction in proportion to the jet's concentration. In return, the color scale has been adjusted in each image by the factor by which the jet's tracer concentration has been increased with respect to  $c_{\text{toluene}} = 0.032$  vol%. Therefore, we would expect all four images in Fig. 6 to be equal in appearance.

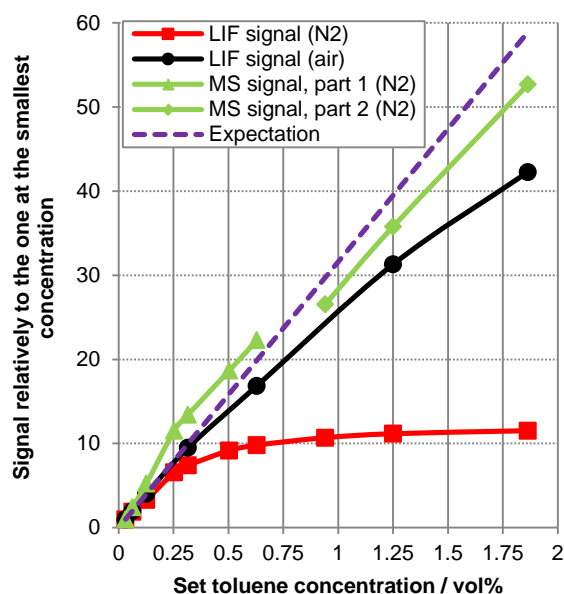
From the left to the right images, the tracer concentration increases by a factor of 2, while from the top to the bottom the factor is 10. When increasing the concentration from 0.032 vol% to 0.063 vol%, the LIF signal is doubled, as expected according to Eq. (1). However, increasing the concentration further does not result in a proportional increase in LIF signal. When increasing the concentration by a factor of 20 from 0.032 vol% to 0.63 vol%, the LIF signal increases only by a factor of 11.



**Fig. 6.** Ensemble-averaged, background, and flat-field corrected jet LIF images for different toluene volume fractions  $c_{\text{toluene}}$ . For the flat-field correction, the tracer concentration was always 0.032 vol% .

Fig. 7 shows the LIF signal averaged over the area indicated in Fig. 3 (right panel, white rectangle) as a function of toluene concentration. The carrier gas was either  $N_2$  or air and in each case the signal is normalized by that at 0.032 vol%. Data points have been connected by straight lines to guide the eye. The dashed line represents the expected increase in LIF signal relatively to the one at 0.032 vol% assuming a proportional dependence according to Eq. (1).

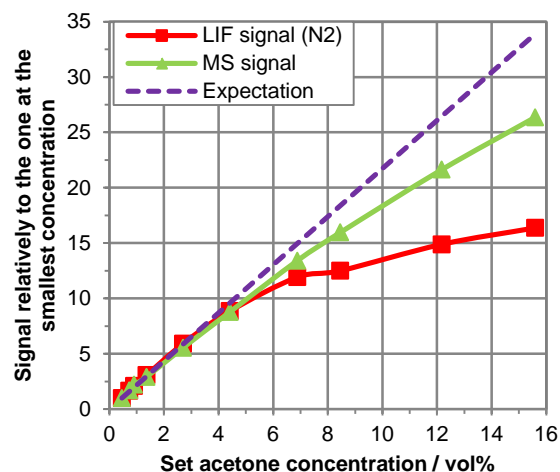
Also shown is the signal of a mass spectrometer (MS) probing the toluene/carrier gas mixture immediately upstream of the nozzle (see Fig. 1). Like the LIF signal, the MS signal at a mass number corresponding to toluene is plotted relative to the MS signal at 0.032 vol% fraction. Relative to that data point we can thus validate that the toluene concentrations set via syringe pump and MFC are indeed the true gas-phase concentrations. The mass spectrometer was accidentally infiltrated by external air before acquiring the last three data points. Although the leakage was stopped immediately, a slight offset between the two sets of measurement remains. Nevertheless, the mass spectrometer measurements confirm that intended concentration is indeed reached. In particular this confirms that the tracer toluene is completely evaporated in the mixing cylinder.



**Fig. 7.** The LIF and mass spectrometer (MS) signals of toluene relatively those at 0.032 vol% versus toluene concentration in either nitrogen or air as carrier gas. The dashed line represents proportional scaling with respect to 0.032 vol% as expected from Eq. (1).

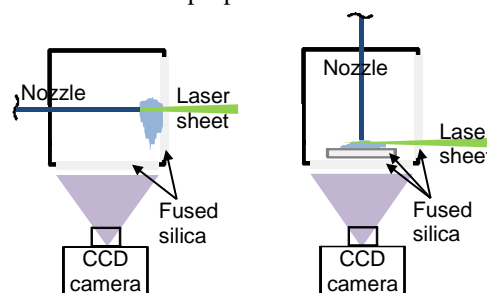
As opposed to the MS measurement, the LIF signal clearly deviates from linearity. In the presence of nitrogen, the LIF signal of toluene exhibits significant deviation from linear scaling for concentrations beyond 0.25 vol%, which is still quite far from the vapor-pressure limited maximum concentration of 2.85 vol%. Also for air carrier gas some non-linearity is visible, but it starts later and is much weaker.

In addition to the aromatic tracer toluene, acetone was investigated at concentrations from 0.46 vol% to 15.6 vol%. Due to risk of explosion, the measurements were performed in nitrogen only. The result is shown in Fig. 8. We see that also for acetone there is a deviation from linear signal increase that clearly exceeds the also-present non-linearity of the actual concentration as measured by the MS.



**Fig. 8.** LIF and mass spectrometer (MS) signals of acetone in  $N_2$  relatively those at 0.46 vol%.

The non-linearity observed will be investigated further in the following. Since a general malfunction of the vaporizer was excluded by the mass spectrometer measurements, the focus is now put on photophysical effects. First, we assessed possible effects of laser absorption and signal re-absorption (“signal trapping”). Fig. 9 illustrates two variations of the experiment that we performed for this purpose.



**Fig. 9.** Left: Reduced laser path length. Right: Reduced LIF-signal path length.

First, the nozzle was positioned close to the laser entrance window, which reduces the path length the *laser light* propagates through the tracer mixture (left panel). Second, the nozzle was positioned close to the observation window, which reduces the path length the *LIF signal* travels through the tracer mixture. However, both of these configurations yielded results similar to those shown in Fig. 1, i.e., the signal did not increase linearly with concentration. We therefore conclude that neither excessive absorption of the incident laser beam nor re-absorption of the emitted fluorescence is the reason why the detected signal does not scale linearly with tracer concentration.

Other possible explanations could be collisional quenching, either by oxygen or by the tracer, i.e. “self-quenching. Quenchers interact with fluorescent tracers by means of a non-radiative process depopulating the excited state without emission of fluorescence light: The fluorescence is quenched. In the presence of quenching by both O<sub>2</sub> and tracer, the LIF signal intensity  $S_{fl}$  is given by:

$$S_{fl} \propto n_{tr} \sigma_{abs} \frac{k_{fl}}{k_{tot} + \tilde{k}_q^{O_2} n_{O_2} + \tilde{k}_q^{tr} n_{tr}}, \quad (3)$$

with  $k_{fl}$  denoting the rate of spontaneous fluorescence emission and  $k_{tot}$  the rate for the sum of all non-radiative intramolecular decay pathways. The oxygen quenching rate is the product of O<sub>2</sub> number density  $n_{O_2}$  and the bimolecular quenching rate coefficient  $\tilde{k}_q^{O_2}$  [7]. Similarly, self-quenching may be represented by the rate coefficient  $\tilde{k}_q^{tr}$  and the tracer number density  $n_{tr}$ .

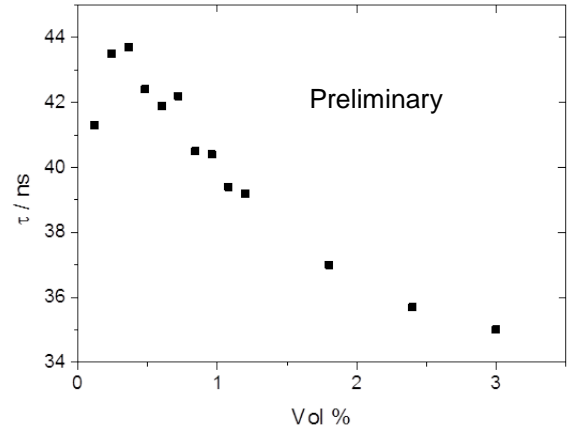
Eq. (3) is consistent with the results presented above. In the absence of self-quenching, the oxygen concentration does not alter the linear dependence of the LIF signal on the tracer concentration (Eq. (1)). If self-quenching occurs, i.e., neither  $\tilde{k}_q^{tr}$  nor  $n_{tr}$  are negligible, the LIF signal is not proportional to tracer concentration any more – the effect we see in our measurements in N<sub>2</sub>. Quenching by oxygen and by tracer molecules are competing mechanisms of depopulation. This is consistent with the observation that for toluene the non-linearity is significantly less distinct in the presence of O<sub>2</sub>: Since O<sub>2</sub> is such an efficient quencher, its influence may exceed that of self-quenching, such that a more linear dependence of the LIF signal on the toluene concentration is expected in the presence of O<sub>2</sub>.

If self-quenching were significant, we would expect the fluorescence lifetime to decrease with increasing tracer concentration. Hence we expected to gain further information from fluorescence lifetime measurements.

### 3.2. Fluorescence lifetime measurements

Here, tracer concentrations from 0.12 vol% to 3 vol% in N<sub>2</sub> were investigated at a temperature of 296 K. The results are presented in Fig. 10.

The data are considered preliminary because they suffer from large uncertainties at the smaller tracer concentrations, which are probably caused by contamination of the measurement cell by residual gases of former experiments. However, the decrease of fluorescence lifetimes with increasing tracer concentration is significant despite these uncertainties. These results confirm the tracer self-quenching hypothesis introduced in Section 3.1.



**Fig. 10.** Fluorescence lifetime of toluene at 296 K in 1 bar nitrogen versus tracer concentration (preliminary data).

### 4. Conclusions

The aromatic tracer toluene as well as the ketone tracer acetone have been vaporized in a mass-flow controlled evaporator using nitrogen or air as carrier gas. The tracer/carrier gas mixture was then investigated in a jet in cross-flow in a wind tunnel by means of laser-induced fluorescence (LIF).

Using nitrogen as carrier gas, there is a significant deviation from a linear dependence of the LIF signal on the tracer concentration observable for both tracers. However, in case of toluene with air as carrier gas, there is a higher degree of linearity. The non-linearity in case of using nitrogen as carrier gas may be attributed to self-quenching effects both tracers are subjected to. Using air as carrier gas subjects toluene to O<sub>2</sub> quenching, which is more efficient than the self-quenching, bringing the scaling closer to linear.

We are planning to also perform measurements for acetone in air, which was not yet possible because of experimental constraints. Because acetone as a ketone does not suffer from O<sub>2</sub> quenching, this would be a valuable cross-check: When self-quenching by O<sub>2</sub> does not dominate, there should be significant non-linearity also in case of air as carrier gas.

These imaging results were confirmed by preliminary data from fluorescence lifetime measurements. Both experiments thus indicate that self-quenching is an effect that has to be accounted for in at least some quantitative measurements based on LIF.

Self-quenching is not fully understood at this point, but it may affect a multitude of LIF-based measurements. We thus think it is important to further investigate the effects of self-quenching in fluorescent tracers.

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