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Toluene LIF at elevated temperatures: implications for fuel–air ratio measurements

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ABSTRACT Toluene laser-induced fluorescence (LIF) was investigated for 266- and 248-nm excitation in the temperature range of 300–650 K in a nitrogen/oxygen bath gas of 1 bar total pressure with oxygen partial pressure in the range 0–400 mbar. Contrary to a popular assumption, the toluene LIF signal is not directly proportional to the fuel–air ratio (termed the FAR-LIF assumption) for many conditions relevant to reciprocating IC engines. With increasing temperature, a higher oxygen partial pressure is required to justify the FAR-LIF assumption. The required oxygen pressure becomes unrealistic (> 5 bar) for $T > 670$ K at 266-nm excitation and for $T > 625$ K at 248-nm excitation.

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1 Introduction

The performance of modern engine concepts like direct-injected spark ignition (DISI) or homogenous charge compression ignition (HCCI) largely depends on the exact control of the mixing process of air, gasoline and residual gases. A widely used technique to improve the understanding of this mixing process is imaging of the laser-induced fluorescence (LIF) signal of a fuel tracer added to a non-fluorescing base fuel (e.g. iso-octane). The two most widely used fuel-tracer classes are ketones (e.g. 3-pentanone [1–6]) and aromatics (e.g. toluene [7–9]), with toluene being especially suited as it also forms a constituent of commercial gasoline. A current review article on fuel tracers is available [10].

Whereas the ketone signal is almost insensitive to the presence of oxygen and commonly used to determine the fuel number density, aromatic fluorescence is strongly quenched by oxygen and thus offers the potential to track oxygen concentrations. In fact, as long as oxygen quenching is the dominant de-excitation pathway, the fluorescence signal will be proportional to the fuel–air ratio. This concept (so called FAR-LIF) was introduced by Reboux and Puechberty [11], who found that this is the case for toluene LIF at room temperature with 248-nm excitation and air pressures above 3 bar. Similar results were found for benzene [12]. Despite the relatively sparse experimental evidence, the concept of aromatic fluorescence being proportional to the fuel–air ratio became quickly generalized for the whole range of temperatures and pressures present in the compression stroke of an IC engine.

The study presented in this paper is the first thorough investigation of the FAR-LIF assumption at elevated temperatures. The results for toluene absorption and fluorescence in nitrogen at high temperatures were published in [13]. More details about the fluorescence in the presence of oxygen including a photophysical model can be found in [14], and temperature-imaging techniques using toluene will be presented in [15]. Although this study focuses on toluene, we believe that our findings can be generalized in a qualitative manner for many aromatic fuel tracers as the photophysics of other one- and two-ring aromatics is similar.

2 Background

The integrated toluene LIF signal S_{fl} is proportional to the product of number density n_{tracer} and absorption cross section σ (i.e. number of excited molecules) times the fluorescence quantum yield ϕ_{fl} (i.e. the fraction of excited molecules that actually fluoresce):

$$S_{\mathrm{fl}} \sim n_{\mathrm{tracer}} \sigma_{\mathrm{abs}} \phi_{\mathrm{fl}} \,. \tag{1}$$

A simple rate-equation analysis of a single excited electronic state yields an expression for the quantum yield in the presence of a quenching species (in this case oxygen):

$$S_{\mathrm{fl}}(T, n_{\mathrm{oxy}}) \sim n_{\mathrm{tracer}} \sigma_{\mathrm{abs}}(T) \frac{k_{\mathrm{fl}}(T)}{k_{\mathrm{tot}}(T) + \tilde{k}_{\mathrm{q}}^{\mathrm{oxy}}(T) n_{\mathrm{oxy}}} \,, \tag{2}$$

with k_{fl} denoting the rate of spontaneous fluorescence [s^{-1}] and k_{tot} the rate for the sum of all intramolecular decay pathways [s^{-1}]. The oxygen-quenching rate is the product of oxygen number density n_{oxy} [cm^{-3}] and the bimolecular quenching rate coefficient $\tilde{k}_{\mathrm{q}}^{\mathrm{oxy}}$ [$\mathrm{cm}^3\,\mathrm{s}^{-1}$]. If oxygen quenching is much stronger than intramolecular processes, k_{tot} can be neglected and the

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signal becomes proportional to the fuel–air ratio ϕ:

$$S_{\mathrm{fl}}(T, n_{\mathrm{oxy}}) \sim g(T)\frac{n_{\mathrm{tracer}}}{n_{\mathrm{oxy}}} \sim g(T)\phi$$
$$\text{if} \quad k_{\mathrm{tot}}(T) \ll \tilde{k}_{\mathrm{q}}(T) n_{\mathrm{oxy}}\,. \tag{3}$$

Thus, the FAR-LIF technique relies on two assumptions:

1. Oxygen quenching is the dominating de-excitation pathway at all temperatures,
2. Temperature-dependent variables (like the absorption cross section and the T-dependent parts of the quantum yield expression) can be separated into an experimentally accessible function $g(T)$, which can be used to correct the signal.

3 Experimental

The temperature dependences (300–700 K) of toluene absorption and fluorescence were studied with varying oxygen concentrations (2%–35%) at 1 bar total pressure. Since further details of the experimental setup can be found in [13], only a brief summary will be given here.

Experiments were carried out in an optically accessible, stainless-steel flow cell placed in a Thermolyne 48 000 furnace. Nitrogen was percolated through two bottles of liquid toluene to produce a toluene-saturated gas. A thermocouple and a pressure gauge at the exit of the second bottle allowed for the calculation of the toluene concentration. Toluene (0.2%–2%), oxygen (2%–35%) and nitrogen concentrations were controlled by mixing the toluene-saturated nitrogen flow with additional flows of oxygen and nitrogen (1–8 l/min). The flow was preheated in a metal tube section before it entered the cell. A type-K thermocouple in the center of the cell measured the gas temperature. Residence times were kept below 0.5 s. Chemical stability was a concern, so fluorescence signals were always confirmed to be independent of gas flow rate (e.g. residence time). Absorption cross sections were also confirmed to be the same in the presence of oxygen as within pure nitrogen. Above 700 K the fluorescence signal in the presence of oxygen became dependent on the flow rate and laser absorption was significantly reduced compared to the results within pure nitrogen, indicating the onset of chemical degradation of the tracer.

Laser light was provided at 248 nm by a Lambda-Physik Compex 102 krypton fluoride (KrF) excimer laser (30-ns pulse length, 5 Hz) and at 266 nm by a Spectra Physics GCR 300 quadrupled Nd:YAG laser (6-ns pulse length, 10 Hz). Incident pulse energies were kept at about 0.1 mJ with beam diameters of about 2 mm, thus ensuring weak (linear) excitation.

The fluorescence-signal light was collected with an achromatic lens ($f = 100$ mm), spectrally resolved with an Acton Research Spectra Pro 150-mm spectrometer (300-lines/mm grating, blazed at 300 nm) and detected with a Princeton Instruments I-Max-512-T intensified CCD camera. Signals were then integrated from 260–400 nm and 270–400 nm for 248- and 266-nm excitation, respectively, to exclude elastically scattered laser light.

4 Results

The toluene LIF signal dependence on the inverse oxygen concentration is displayed for various tem-

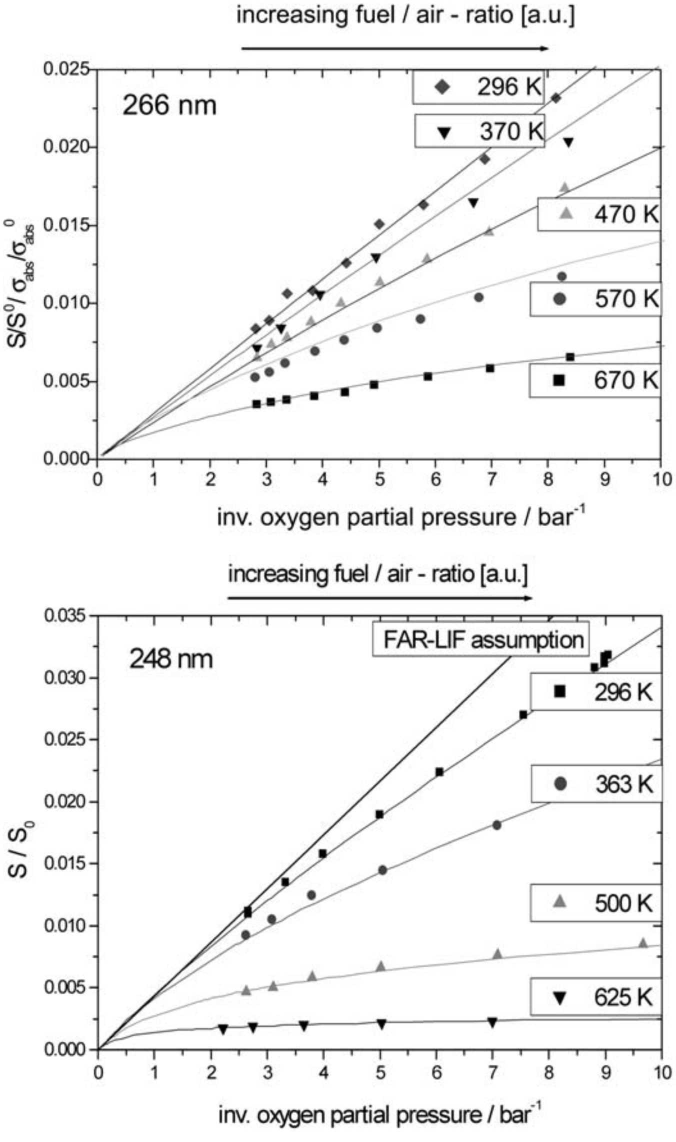

FIGURE 1 Toluene LIF signal vs. inverse oxygen pressure, which is proportional to the fuel–air ratio ϕ since the tracer concentration is constant. Total signals are corrected for the T-dependence of the absorption cross section [13] (note that at 248 nm the absorption cross section is constant). *Symbols* are experimental data, *solid lines* are extrapolations. The assumption for the FAR-LIF technique, that the signal is proportional to fuel–air ratio, is applicable only in the case of moderate temperatures and 266-nm excitation. Note that in this case the slope depends strongly on temperature (see also (3))

peratures in Fig. 1. The tracer concentration is constant, and thus the x axis scales with the fuel–air ratio ϕ. The absolute value of ϕ depends on the actual amount of fuel. However, this plot remains the same for all fuel concentrations as the photophysics depends on the amount of oxygen only. In the case of 266-nm excitation we corrected the absolute signals for changes in the absorption cross section so that only the change in fluorescence quantum yield is shown. For 248-nm excitation, the absorption cross section does not change within this temperature range [13]. The solid lines are extrapolations to higher oxygen pressures. This can be reliably done as the signal dependence on oxygen partial pressure is strong and characteristic. For the exact algebraic form please refer to [14].

For 266-nm excitation we find that the LIF signal is proportional to ϕ for temperatures up to ~ 500 K. The slope, however, varies with temperature (see (3)). Above 500 K, a deviation from linearity becomes obvious. Above 650 K, more than ~ 4 bar of oxygen (i.e. 20 bar of air) is required to make the signal proportional to the fuel–air ratio (e.g. where the deviation is $< 10\%$). Thus, for 266 nm the FAR-LIF concept works only for $T < 500$ K and only with additional temperature corrections. For 248-nm excitation the FAR-LIF concept breaks down even at moderate temperatures. At room temperature the signal is proportional to ϕ for pressures above 400 mbar of oxygen (or 2 bar of air, corresponding to the literature [11]). This minimum oxygen pressure required to make the FAR-LIF concept work increases significantly with increasing temperatures. It is 2 bar oxygen at 500 K and ~ 5 bar oxygen (e.g. 25 bar of air) at 625 K. In the extreme case of high T and low oxygen concentrations the signal is insensitive to oxygen; that is to say, the signal intensity is simply proportional to the tracer number density, as is the case for tracers like 3-pentanone. At most engine-related pressures and temperatures, the signal behavior is in between the two extreme cases of $S_{\mathrm{LIF}} \sim$ fuel–air ratio and $S_{\mathrm{LIF}} \sim$ fuel number density.

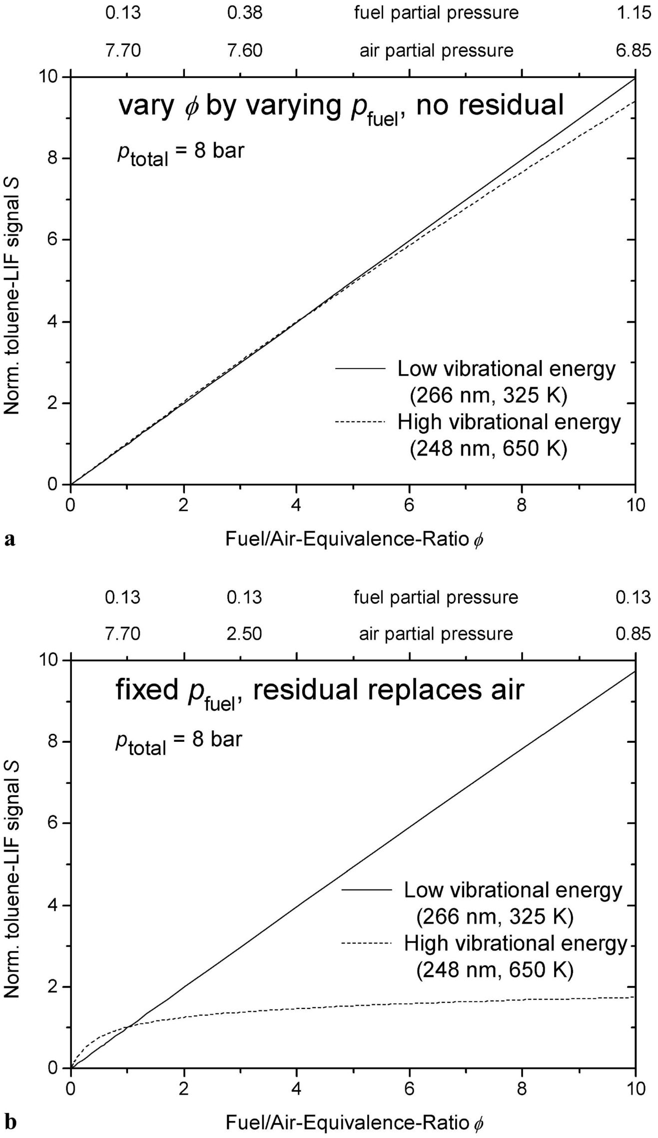

FIGURE 2 Two realistic cases of measurements in an engine environment. **a** Mixing of fuel and air only, **b** mixing of fuel, air and residual gas. In (**a**) variations of the fuel–air ratio are dominated by variations in the fuel concentration since the oxygen concentration barely changes. In (**b**) the oxygen concentration changes significantly and the FAR-LIF technique proves valid only for low vibrational excitation (e.g. low temperature, long excitation wavelength). Total pressure is 8 bar, signals are normalized to 1.0 at $\phi = 1$. Values are based on an extrapolation of the experimental data in Fig. 1

With these results we have shown that the FAR-LIF concept leads to erroneous signal interpretation at most of the interesting temperatures and pressures in the compression stroke of IC engines. How then has the FAR-LIF concept become so popular for measurements in engine environments without this being noticed? The answer can be found in Fig. 2. As it is in the nature of a ratio, there are two ways to vary ϕ. One can change either the fuel (Fig. 2a or case a) or the oxygen concentration (Fig. 2b or case b). Both correspond to situations of practical interest. Figure 2a displays the LIF signal vs. ϕ behavior when fuel concentration is changing and oxygen pressure is well known and nearly constant (changing only slightly to accommodate the increase in fuel with a fixed total pressure). Figure 2b shows the analogous behavior for the case where fuel concentration is fixed and oxygen partial pressure varies. Case (b) could apply in an engine environment with exhaust-gas recirculation. In the few cases where the FAR-LIF concept was critically examined at elevated temperatures, investigators have looked at case (a) only [7, 16]. The apparent linear correlation of ϕ and LIF signal in this case, however, is misleading as changes in ϕ are dominated by changes in the fuel number density. The proportionality found in Fig. 2a is thus nothing more than the trivial linear relation of tracer number density and LIF signal. In fact, any tracer (even oxygen-insensitive tracers like 3-pentanone) could be applied in this case with the same result. Hence, one should not draw conclusions on the dependence of toluene LIF on the fuel–air ratio from plots like Fig. 2a. The true strength of the FAR-LIF concept would be its applicability to a case where the oxygen concentration varies significantly, e.g. when significant amounts of exhaust gas are present. The behavior of toluene LIF under these conditions is shown in Fig. 2b, where the LIF signal will only be proportional to ϕ for moderate temperatures with 266-nm excitation (e.g. low vibrational excitation of toluene). On the other hand, in the case of 650 K/248-nm excitation (e.g. high vibrational excitation) the signal becomes almost insensitive to oxygen for $p_{\mathrm{oxy}} < 1$ bar, and oxygen partial pressures of more than 7 bar would be required to provide a signal that is proportional to the fuel–air ratio. Note that the LIF signal in Fig. 2b is plotted over the fuel/air (equivalence) ratio ϕ. Hence, the plot does not change even if the residual contains oxygen. However, if the residual contains much oxygen (i.e. lean-burn engines), the overall variation of the oxygen concentration (i.e. the variation of ϕ itself) is moderated and thus possible errors in data analysis are somewhat reduced. In general, the effects of temperature and oxygen on the total signal cannot be separated. However, the dependence of toluene LIF on temperature also provides for new diagnostic opportunities. In an upcoming publication we will present a technique based on toluene LIF to measure temperatures in turbulent flows [15].

5 Conclusions and outlook

We investigated the dependence of toluene LIF on the presence of oxygen (0–400 mbar) at elevated temperatures (300–650 K). We have shown that the assumption of toluene LIF being proportional to the fuel–air ratio (FAR-LIF) breaks down for most of the pressure and temperature range present in the compression stroke of an engine. The higher the vibrational energy of the excited toluene molecule (e.g. increasing T, decreasing excitation wavelength), the less important is the influence of oxygen and the characteristic behavior of toluene LIF shifts from signal $\sim$ fuel–air ratio towards signal $\sim$ fuel number density. Unfortunately, for most practically relevant conditions the signal is in a regime in between these two cases where oxygen quenching is neither dominant nor negligible, and thus the effects of temperature and oxygen are not separable. To derive fuel–air ratios from toluene LIF signals, then, one must know or estimate the temperature or oxygen concentration in the experimental flow field.

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