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# High-temperature shock tube study of laser-induced fluorescence of toluene and its pyrolysis products

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## Abstract

Toluene is frequently used as fluorescence tracer in high-temperature combustion applications, but its optical properties and stability limits under high-temperature conditions are underexplored. Here we present investigations of laser-induced fluorescence (LIF) signals during toluene pyrolysis behind reflected shock waves between 865 and 1750 K at a pressure of 1.2 and 2.9 bar. The species in the gas mixture were excited at 266 nm at fixed times after the arrival of the reflected shock wave and the LIF signal was spectrally resolved between 260 and 700 nm. When increasing temperature, the toluene-LIF signal decreases substantially with a significant red-shift. Above 1600 K, the toluene emission spectrum disappears essentially completely and the spectrum is instead dominated by spectral features that appear far red-shifted compared to the original spectrum and that originate from intermediates and products of toluene pyrolysis. These results highlight the importance of tracer decomposition when interpreting fluorescence signals in high-temperature applications.

## Introduction

In-cylinder tracer-LIF diagnostics are frequently used for quantitative visualization of fuel concentration, equivalence ratio, and temperature in combustion processes [1]. Especially in modern highly energy-efficient internal combustion engines with high compression ratios, however, high in-cylinder temperatures raise concerns about the thermal stability of the tracer throughout the measurement cycle [2]. Under such conditions, the tracer can pyrolyze or oxidize. This behavior can significantly influence the interpretation of the tracer fluorescence signals.

So far, studies of the spectroscopic properties of tracer molecules have been carried out typically in stationary or flow cells [3,4]. However, under combustion conditions, the tracer can be exposed to temperatures well above the upper limit achievable with these setups (<1100 K), leaving a significant gap of understanding of the tracer properties under practical conditions and making it necessary to extend the temperature range beyond this limit. Shock tubes are ideally suited for this purpose, because they enable the rapid gas-dynamic heating of gases within a few microseconds and therefore give access to spectral measurements at high temperatures. They furthermore enable the observation of absorption and fluorescence from products formed via tracer decomposition. The obtained spectra and/or absorption transients not only provide a valuable data base for practical applications in high-temperature environments, but can also serve as validation targets for chemical kinetics modeling of the different reaction steps during the decomposition of the tracer.

Toluene is a common fluorescent tracer for engine applications because of its strong fluorescence signal and its natural occurrence in commercial gasoline. The limited thermal stability of toluene at high temperature has restricted previous experiments on its spectral properties in flow cells to temperatures below 1100 K [3,4] to avoid decomposition on the experimental time scales.

The kinetics and mechanism of the thermal decomposition of toluene in the gas phase (R1)



have been intensively investigated both experimentally and computationally [5]. The main reaction channels are C-H bond fission (R1a) forming an H atom and the resonance stabilized benzyl ( $\text{C}_6\text{H}_5\text{CH}_2$ ) radical, and C-C bond fission (R1b) producing methyl ( $\text{CH}_3$ ) and phenyl ( $\text{C}_6\text{H}_5$ ) radicals:



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Recent high-level theoretical kinetics calculations of Klippenstein et al. [6], which are consistent with many recent results from shock-tube experiments [7-10], predict a high-pressure rate coefficient for R1 of  $k_1(T) = k_{1a}(T) + k_{1b}(T) = 1.56 \times 10^{13} \text{ cm}^3 \text{ s}^{-1} (T/\text{K})^{0.682} \exp(-89.2 \text{ kcal mol}^{-1}/RT) + 4.35 \times 10^{22} \text{ cm}^3 \text{ s}^{-1} (T/\text{K})^{-1.73} \exp(-104.2 \text{ kcal mol}^{-1}/RT)$  between 800 and 2500 K. At 1500 K, these results would predict a thermal lifetime of toluene of  $\sim 3$  ms. The branching ratio  $k_{1a}/k_{1b}$  at high pressure changes from  $\sim 90/10$  at 1000 K to  $\sim 60/40$  at 2000 K [6] and is only weakly pressure-dependent. Therefore, R1a is the dominant unimolecular decomposition channel of toluene at engine-relevant conditions, but R1b becomes increasingly relevant as the temperature increases. The radical products of R1a and R1b can undergo secondary radical-radical and radical-closed shell reactions, which can contribute to the reactive loss of the tracer. Especially under non-diluted conditions in engines, these secondary reactions become increasingly relevant and need to be accounted for in kinetics modeling in order to simulate the fate of the tracer.

In the present work, the fluorescence behavior of toluene before pyrolysis and its pyrolysis products at selected reaction times behind reflected shock waves was investigated using 266 nm laser excitation at various temperatures.

## Approach

Measurements were performed behind reflected shock waves in a stainless-steel shock tube with an inner diameter of 79 mm. The driven section (length: 7.3 m) was separated from the driver section (length: 3.6 m) by an aluminum diaphragm (thickness: 50–90  $\mu\text{m}$ ). The velocity of the incident shock wave was determined using four piezoelectric pressure transducers (603B, Kistler) placed near the end-wall of the tube. Temperature and pressure behind the reflected shock wave were calculated from the measured initial test gas pressure, temperature, mixture composition and incident shock-wave velocity based on ideal one-dimensional shock equations using the CHEMKIN-II package [11]. Mixtures of toluene (for analysis grade, Merck) in argon (purity 5.0, Air Liquide) were prepared manometrically and were allowed to homogenize at least 12 h before use.

The shock tube was equipped with a system for measurement of spectrally-resolved LIF (260–700 nm). The mixture behind the reflected shock wave was excited by a pulsed frequency-quadrupled Nd:YAG laser at 266 nm. The laser beam was introduced through a quartz window in the sidewall of the shock tube 30 mm away from the end flange. The emitted fluorescence was collected perpendicular to the laser beam through a quartz window in the endplate of the shock tube and focused on the entrance slit of a spectrograph coupled to an intensified CCD camera.

A low-pressure mercury discharge lamp was used to calibrate the wavelength axis of the spectrograph. The emission spectra of a deuterium (for  $\lambda < 400$  nm) and a tungsten lamp (for  $\lambda > 350$  nm) with known spectral radiance were used to correct for the wavelength-dependent throughput and camera sensitivity. Laser and camera were synchronized with the shock wave using a delay generator with the signal of the pressure transducer as trigger input. Measurements were taken at various times after the arrival of the reflected shock wave. The slit of the spectrometer was oriented parallel to the laser beam and thus in principle provided one-dimensional spatial resolution. However, since no spatial variation of the signal is expected along the radial coordinate of the shock tube, the fluorescence signal of the recorded image was integrated along the slit direction. A dark image taken before each experiment was subtracted from the measured image.

## Results and discussion

LIF spectra of toluene were measured as a function of temperature between 865 and 1750 K at total pressures near 1.2 and 2.9 bar and using mixtures of 1 and 2% toluene diluted in argon. Figure 1 shows the LIF spectra recorded at 110  $\mu\text{s}$  after the passage of the reflected shock wave as a function of temperature. At 865 K, toluene LIF occurs in the 270–320 nm wavelength range with a peak at around 290 nm. With increasing temperature, the LIF spectrum of toluene shifts to the red ( $\sim 2$  nm per 100 K) and becomes spectrally broader. This behavior has been reported before up to  $\sim 1000$  K [3,4] and the results from our study show that it extends towards higher temperature. As evident from Figure 1, increasing the temperature between 865 and 1225 K leads to a strong decrease of the fluorescence signal. Literature studies restricted to temperatures  $< 950$  K have found a decreasing fluorescence intensity with increasing temperature as a result

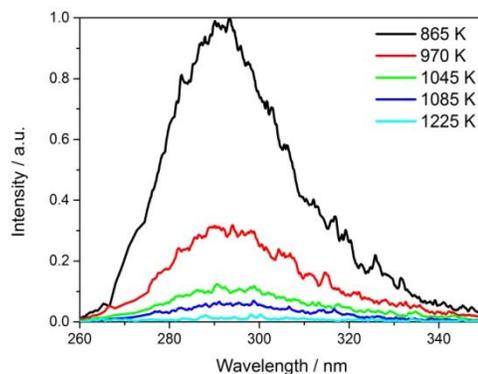


Figure 1: Single-shot LIF emission spectra of 2% toluene in argon after excitation at 266 nm as a function of temperature at a pressure of 1.2 bar, measured at 110  $\mu\text{s}$  after the arrival of the reflected shock wave.

of the decreasing fluorescence quantum yield [3]. Our experimental results are consistent with this observation and suggest that this behavior extends to higher temperature.

Figure 2 shows the dependence of the LIF signal a) on temperature between 1225 and 1750 K at a constant reaction time of 260  $\mu\text{s}$  and b) on reaction time at a constant temperature of 1630 K. With increasing temperature, the toluene emission spectrum disappears essentially completely and new spectral features appear far red-shifted compared to the original toluene spectrum as a result of built-up of new species initiated by toluene decomposition. As shown in Figure 2, the LIF emission spectrum at 1630 K and early reaction time is dominated by broadband emission with a peak at 375 nm (420 nm) and a FWHM of 135 nm (140 nm) at 160  $\mu\text{s}$  (260  $\mu\text{s}$ ). This spectral feature exhibits peak intensities comparable to the LIF intensity of toluene at lower temperature, but is orders of magnitude higher in intensity than the expected fluorescence signal of toluene under these conditions. At higher temperature or later reaction time, the emission maximum at  $\sim 400$  nm disappears and the spectrum is instead characterized by a monotonically increasing intensity towards longer wavelength, which resembles that of a black body (i.e., laser-induced incandescence, LII) indicating that soot is formed at least partly.

The change in the spectral features as a function of reaction time suggests a change in the species responsible for the emission signal due to reaction progress. Pyrolysis of toluene forms benzyl and phenyl radicals as primary pyrolysis products via R1a and R1b, respectively [10]. Both these species and products from their consecutive reactions might contribute to the observed spectral features at higher temperature. A realistic modeling of the emission spectra under these conditions requires both a reliable kinetics mechanism for toluene pyrolysis and knowledge of the absorption spectra of intermediates and products at high temperatures. Spectroscopic information of these aromatics at high temperature, however, is sparse and mostly restricted to conditions near room temperature [12], so that we do not attempt a more quantitative interpretation of the emission spectra observed at higher temperature within the scope of the present work.

Sirignano et al. [13] investigated the formation of aromatic species and soot in an atmospheric-pressure counter-flow diffusion flame of ethylene using spectrally- and time-resolved LIF and LII measurements employing 266 nm laser light. They found different types of high-molecular mass aromatic compounds: Highly-packed, sandwich-like structures and more loose aromatic compounds linked together by sigma-bonds, such as the aromatic-aliphatic linked hydrocarbons. The dashed line in Figure 2 illustrates the fitted LIF emission spectra from Ref. [13] near the stagnation plane where benzene and PAHs have their maximum concentrations. The spectrum shows a broad fluorescence emission between 290 and 550 nm which was assigned to both small clusters of PAHs and the formation of higher molecular mass aromatic compounds. For the sake of comparison, fluorescence signals of Sirignano et al. [13] and of this study were normalized to their respective peak values in Figure 2. The good agreement of the spectral shapes might suggest that similar species are present in both studies, although completely different setups (ethylene diffusion flame in Ref. [13] vs. toluene pyrolysis in a shock tube) were used.

## Conclusions

The fluorescence emission spectra of toluene and its decomposition products have been studied behind reflected shock waves over a wide temperature range (865–1755 K) upon 266 nm excitation. The intensity of the toluene-LIF signal decreased with increasing temperature (up to 1200 K) with a red-shift of the peak signal of  $\sim 2$  nm per 100 K. Above 1600 K strong additional spectral features appear that are assigned to originate from pyrolysis products. The spectral shape and hence the pool of generated species changed both with increasing temperature at a given reaction time and with increasing reaction time at constant temperature. In addition, at long residence times and high temperatures the emission spectrum resembles that of a black body (i.e., laser-induced incandescence, LII) indicating that soot is formed at least partly during pyrolysis under the experimental conditions. Under the pyrolytic conditions observed here, strong

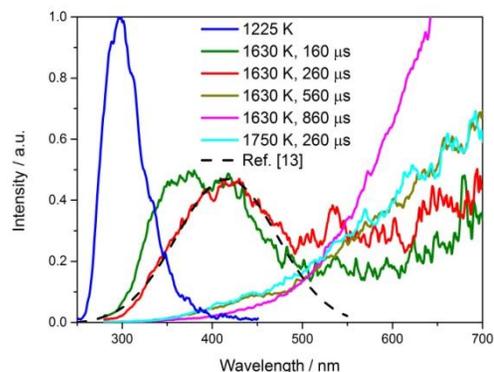


Figure 2: LIF emission spectra of a mixture of 1% toluene in argon at a total pressure of 2.9 bar taken after 266 nm laser excitation at different times and temperatures after the passage of the reflected shock wave. The spectrum at 1225 K represents the LIF spectrum of pure toluene at this temperature (taken at 110  $\mu\text{s}$ ). The substantial change in the spectral shape at the higher two temperatures reflects thermal decomposition of toluene and the emission of products formed from pyrolysis.

fluorescence above 1600 K occurs, which is orders of magnitude stronger than the nascent toluene fluorescence expected in the same temperature range by extrapolation of the temperature-dependent fluorescence cross-section.

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