The potential of on- and off-resonant formaldehyde imaging combined with bootstrapping in diesel sprays

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ABSTRACT

Formaldehyde (CH_2O) is an important intermediate in spray combustion of diesel-like fuels. Experimentally, its spatial distribution is often assessed by means of planar Laser-Induced Fluorescence (PLIF), using a frequency-tripled Nd:YAG laser for excitation and spectrally-filtered fluorescence detection. Especially in soot-laden spray flames, however, considerable spectral interference cannot be avoided, which renders interpretation of the fluorescence distribution challenging. We introduce a more selective strategy, involving dye laser excitation and background subtraction by means of off-resonant excitation in combination with a bootstrap evaluation of sets of individual events. The latter extracts persistent features out of non-simultaneously recorded snapshots of stochastic events, thereby mitigating possible interpretation issues related to the turbulent nature of the process under study. Following this approach, recurrent patterns can be distinguished from random high-intensity events (allegedly due to turbulent fluctuations). We demonstrate our method on the Engine Combustion Network (ECN) "Spray A"-benchmark, with 15 vol-% and 21 vol-% ambient oxygen; we also present spatially well-delimited CH_2O fluorescence distributions, and compare these to simultaneously recorded OH* chemiluminescence intensities.

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1. Introduction

Formaldehyde (CH_2O) is an important intermediate combustion species that indicates the presence of low-temperature reactions, while the hydroxyl radical (OH·) is representative for the high-temperature part of the chemistry. From a diagnostic point of view, unambiguously detecting CH_2O by spectroscopic means is not straightforward. The formaldehyde excitation and emission spectra cover a wide range, which results in crosstalk with other chemical species during excitation and detection. As such, a dedicated excitation strategy must be applied for selective detection of formaldehyde.

For planar Laser-Induced Fluorescence (PLIF) imaging, the third harmonic of a Nd:YAG laser (around 355 nm) can conveniently be used to excite the 4_0^1 transition of CH_2O [1,2]. This approach suffers from two issues: the excitation efficiency is relatively low, and the laser wavelength cannot be altered. The latter precludes the application of a more selective "on-off" approach, in which the signal obtained by on-resonance excitation is corrected for crosstalk by subtraction of an off-resonant contribution: off-resonance tuning of the laser allows correction for broad-band laser-induced signal

not originating from the species of interest. This spectrally-broad background arises partly from high ro-vibrational bands of CH_2O itself [3], and partly from the excitation of other species, of which poly-aromatic hydrocarbons (PAH) are the most notable [4,5]. Such poly-aromatics vary in size and shape, but all poly-aromatics with a carbon number between approximately 14 and 24 emit in the same spectral range as formaldehyde [6]. The selection of a suitable off-resonant wavelength is thus of importance as well.

A detailed study of the spectrum of (thio)formaldehyde was performed by Clouthier and Ramsay [7]. They provided a comprehensive overview of all near-ultraviolet absorption bands in the $\tilde{A}^1A_2 - \tilde{X}^1A_1$ system. Some of the bands that have been utilized for combustion studies are summarized in Table 1, and part of the available literature will be discussed now.

For example, more efficient formaldehyde excitation can be achieved just blue of the third harmonic of a Nd:YAG laser (around 355 nm), but within the same vibronic band (4_0^1). Various research groups [8,9] followed this path using the side-band of a XeF excimer laser. Similar to the work of Böckle et al. [8], the present work aims at improving the excitation efficiency while also allowing for both on- and off-resonant measurements. Burkert et al. [9] did use the tunability of the XeF excimer laser, but the limited tuning range did not allow sufficiently off-resonant measurements. Yet another method was followed by Donkerbroek and co-workers [10]. They applied the third harmonic of a Nd:YAG laser,

Table 1

A selective summary of the available excitation strategies for imaging formaldehyde in combustion systems. Included are the combustion system, fuel, laser and excitation wavelength (λ_{exc}). The notation of the respective bands follows the recommended notation of M_b^a with vibration M and a and b quanta in the upper and lower state, respectively.

	Setup	Fuel	λ_{exc} [nm]	Band
Harrington [5], Böckle [8]	Flame	Methane	353.2	4_0^1
Donkerbroek [10]	CI engine	n-C$_7$	355	4_0^1
	CI engine	Diesel	339.017	$4_0^1 2_0^1$
Bäuerle [13]	SI engine	i-C$_8$/n-C$_7$	353.2	4_0^1
Paul [11]	Flame	Di-methylether	338.1	$4_0^1 2_0^1$
Schießl [12]	SI engine	i-C$_8$/n-C$_7$	339.3	$4_0^1 2_0^1$
Klein-Douwel [14]	Flame	Methane	370	4_1^0
Thering [15]	Flame	Ethylene	355	4_0^1
Paa [21]	Flame	Di-ethylether	342.95	$2_0^0 4_0^3$
Skeen [22], Bruneaux [23]	CVC	diesel surrogates	355	4_0^1
Hubschmid [24]	Flame	Methane	352.5	4_0^1

which was compared to dye laser excitation of transitions in the $4_0^1 2_0^1$ band, using a potentially more effective excitation scheme, which was priorly shown by Paul and Najm [11]. Their goal was to ease interpretation of PLIF images by increasing the formaldehyde-to-background intensity ratio, but the expected improvement was not found in their experiments. For sake of robustness, they still employed a tripled Nd:YAG laser for subsequent PLIF imaging. The $4_0^1 2_0^1$ vibrational band was also used by Schießl et al. [12] to perform semi-quantitative CH$_2$O measurements in the end-gas of a two-stroke spark-ignition (SI) engine. They found their approach suitable to measure absolute number densities, even under the adverse conditions in an engine. In the end gas of a similar SI engine, Bäuerle et al. had shown two-dimensional formaldehyde distributions before, albeit with a different excitation scheme [13].

For quantitative purposes, the temperature dependency of the initial state population is a matter of concern. To alleviate this issue, Klein-Douwel et al. [14] proposed to utilize one of the hot bands of formaldehyde (in particular the 4_1^0 band), of which the absorption strength is low but less sensitive to temperature than that of the 4_0^1 band. For the present work, however, signal yield is considered more important than the reduced temperature sensitivity.

On the detector side the advent of multi-band interference filters enables tuning of the filter to specific emission bands. Angle-tuning of such a multi-band filter also allows for off-band imaging, which could potentially eliminate a significant part of background fluorescence. Thering et al. [15] described the implementation of this method for formaldehyde with 355-nm excitation on a fuel-rich ethylene flame.

Whether poly-aromatic hydrocarbons are formed or not depends on the combustion mode of a specific internal combustion engine. Certain engine types, for example the above mentioned spark-ignition and homogeneous charge compression ignition (HCCI) engines, generally do not form these species during combustion, as a consequence of their premixed combustion mode. This implies that 355-nm LIF can be used for CH$_2$O without too many interpretation issues, as was shown in several publications [16–18].

Conventional compression–ignition (CI) engines with spray-driven combustion, on the other hand, are characterized by high-temperature combustion surrounding a fuel-rich core. Such a combustion regime generally produces considerable amounts of PAH, which also luminesce upon 355-nm excitation. The current understanding of the considered high-pressure sprays is integrated in the Dec model [19]. In the case of CH$_2$O-LIF at compression-ignition conditions, there is a considerable laser-induced background due to other species, notably PAH and soot. The use of a corrective approach to single-out the CH$_2$O contribution from the LIF measurements is thus inevitable.

In this work, a tunable dye laser is used to enable on- and off-resonant excitation (in the 4_0^1 band). The excitation scheme is based on spectroscopic measurements on heated formalin, after which the technique is applied on a diesel spray in engine-like conditions (900 K and 22.8 kg/m^3 in a constant volume combustion (CVC) vessel), following the ECN (Engine Combustion Network) "Spray A" prescriptions [20]. As the on- and off-resonant LIF images could not be recorded simultaneously, because of the availability of only a single 10-Hz system, artificial structure originating from the background subtraction in highly turbulent spray flames becomes inevitable. We introduce a "bootstrap" approach to further improve the interpretation of the results by retrieving persistent features in the LIF images.

2. Methodology

2.1. Experimental apparatus

Engine-like ambient conditions are created in a pre-burn constant-volume combustion vessel. A lean, premixed charge of acetylene, oxygen, nitrogen and argon is burnt to achieve the desired end-gas composition in terms of oxygen concentration. During the relatively slow cool-down period a single diesel-surrogate fuel spray is injected into the target thermodynamic vessel conditions. In-vessel pressure is recorded at a rate of 50 kHz to check whether targets are met. These conditions ("Spray A") resemble a diesel engine at moderate load; it is one of the benchmarks within the scope of the ECN [20]. Several parametric variations have been proposed, and in this work emphasis will be on the baseline case (15 vol-% O$_2$) and the higher oxygen content case (21 vol-%). Formaldehyde PLIF measurements on "Spray A" using 355-nm excitation by means of a frequency-tripled Nd:YAG laser have recently been published [22,25].

2.2. Lasers and detectors

To probe the formaldehyde spectrum around 355 nm, a frequency-doubled Nd:YAG laser is used to pump a frequency-doubled Sirah PrecisionScan dye laser operated on Pyridine 1, effectively resulting in a tuning range of 360 to 335 nm (27,700 to 29,850 cm^{-1}). The dye laser wavelength is monitored with a High-Finesse WS6 wavemeter. For calibration measurements, formaldehyde vapor was created from formalin solution, containing 37% of CH$_2$O by weight.

A Nikkor AF-D 50 mm f/1.4 objective with two filters (WG360 and a short-wave pass with a cut-off wavelength of 500 nm) images the full spray (approximately 90 mm) onto an intensified CCD camera (Roper Scientific PI-MAX 3 with Unigen II intensifier). A