# A SURVEY OF MODEL FUEL MIXTURES SUITABLE FOR EXCIPLEX-SPECTROSCOPY FOR LIQUID/VAPOR VISUALIZATION

# Fredrik Persson, Michael Försth, and Arne Rosén

<u>fredrikp@fy.chalmers.se</u> Department of Experimental Physics Chalmers University of Technology and Göteborg University, Gothenburg, Sweden Phone +46-(0)31-7724546, Fax +46-(0)31-7723496

#### Abstract

This paper presents results of fluorescence measurements of various fuel mixtures. The aim is to assess suitable model fuel mixtures for use in Laser-Induced Exciplex Spectroscopy, LIEF, for liquid/vapor visualization of evaporative sprays. The applicability of LIEF in the study of evaporative sprays under different operating conditions is discussed.

#### Introduction

Not only diesel engines are now equipped with high pressure injectors since it has been shown that directinjected gasoline (GDI) engines use less fuel and emit fewer pollutants. It is thus becoming more and more important to gain a better understanding of spray behaviour in order to further improve fuel consumption and decrease emissions. Visualization and discrimination between the liquid and vapor phases in a spray are in many cases crucial to this understanding. Injection into a cylinder starts with a high-pressure jet. The great pressure is necessary for the jet to break up into a spray, and this occurs mainly because of the turbulence it itself creates. The spray ends up as a cloud of evaporating droplets around the liquid core. Sprays like this contain several individual droplets varying in size from about 2 to about 200  $\mu$ m [1]. The velocity of the spray must be sufficiently high so that the droplets can penetrate and evaporate across the entire combustion chamber in the time available and mix with the air charge before effective combustion occurs. However, knowledge of the break-up of the liquid jet into a spray of droplets, and the subsequent creation of a vapor cloud, is far from complete.

One way to visualize the two phases is by laser-induced exciplex fluorescence, LIEF. In this paper we briefly discuss the mechanism behind LIEF and the choice of model fuel mixture.

# Theory

LIEF is used to obtain a spectral separation of the fluorescence from the liquid fuel and from the vapor fuel. In order to obtain this the fuel is doped with two organic compounds, a monomer, M, and a so-called ground state reaction partner, G. An excited state complex, an exciplex (MG)\*, can be produced from G and an excited monomer, M\*. The monomer excitation occurs by an external radiation source with an accurate wavelength. After photoexcitation the excited monomer, M\*, reacts with a ground state reaction partner, G, to form the exciplex (MG)\*. The fluorescence from the exciplex is red shifted with respect to the fluorescence from the exciplex fluorescence a unique marker of the liquid phase, while the monomer fluorescence can under certain circumstances be a unique marker of the vapor phase. In this section we will try to answer the following questions: 1) Why are the exciplexes produced mainly in the liquid phase? 2) Why and how much is the exciplex fluorescence red shifted?

For reasons of brevity, several important topics will not be discussed, for example solvent effects [2], monomer fluorescence quenching [3] and temperature dependence of the exciplex fluorescence yield [4].

## Why are the exciplexes produced mainly in the liquid phase?

Figure 1a shows the exciplex photochemistry in a spray in a very schematic way. In the gas phase photons with energy hv, from for example a laser, bring the monomers, M, to their excited state, M\*. Because of the relatively low concentrations of G and M in general, and of M\* in particular, the probability of exciplex formation

$$M^* + G \leftrightarrow (MG)^* \tag{1}$$

is low since the production rate of (MG)\* is given by

$$\omega_{(MG)^*} = [M^*][G]k_{forward} \tag{2}$$

where  $k_{forward}$  is the forward rate constant of reaction 1, while [M\*] and [G] are the concentrations of M\* and G, respectively.

In the liquid phase the concentrations are typically a factor of  $\sim 10^3$  greater than in the gas phase. This means that the production of (MG)\* according to expression (2) will be orders of magnitudes greater than in the gas phase. Since the exciplex formation in the gas phase is low, the fluorescence originating from the fuel vapor will come mainly from the reaction M\* $\rightarrow$ M+hv', where hv' is the energy of the M\* fluorescence photons. From a practical point of view it is important that the concentration [G] is high enough that more or less all excited monomers, M\*, are transformed into exciplexes in the liquid. If this is not the case some of the excited monomers will fluoresce with energy hv' before reacting with G into exciplexes. This would be a major problem since this fluorescence energy is supposed to be a marker of vapor fuel only, and not of liquid fuel.

Furthermore, exciplex formation can be more or less energetically favourable depending on the polarity of the solutions [2]. This effect is much stronger in liquids than in gas due, again, to the much higher density of liquids.

The fluorescence from the de-excitation of the exciplex,  $(MG)^* \rightarrow M+G+hv''$ , is red shifted as compared to the monomer fluorescence, hv'. This means that the exciplex fluorescence can be separately imaged and used as a unique marker of the liquid phase of the fuel. The reason for this red shift is discussed below.

### Why and how much is the exciplex fluorescence red shifted?

Figure 1b shows a schematic potential energy diagram for a combination of M and G molecules and a combination of M\* and G molecules. As seen from the diagram the M\*+G system has a local energy minimum for a certain equilibrium molecular distance. This corresponds to the exciplex (MG)\*. It is also seen that the exciplex fluorescence transition emits less energy, hv'', than in the case of monomer fluorescence, hv'. This means that the exciplex fluorescence is red shifted, has a longer wavelength, than the monomer fluorescence.

The fluorescence from exciplexes at the equilibrium distance can be calculated by assuming that the exciplex is a charge-transfer state. This means that the M molecule acts as an electron donor that has been ionized and the G is an acceptor that has received an electron from M. In other words, we can denote the exciplex (MG)\* as an ion pair ( $M^+G^-$ ). One should also bear in mind the Franck-Condon principle, which states that the transition takes place during such a short time that the molecular distance can be regarded as fixed. This is the same thing as saying that the transitions are vertical, exactly as showed in Fig. 1b. The energy of the photons where the exciplex fluorescence intensity has its maximum can now be written:

$$hv'' = IP_M - EA_G - C \tag{3}$$

where  $IP_M$  is the ionization potential of the monomer,  $EA_G$  is the electron affinity of the ground-state partner and *C* is the coulombic stabilization energy of the ion-pair (M<sup>+</sup>G<sup>-</sup>) as compared to the un-excited atom pair (MG). Solvent effects have been neglected in expression 3 [5].



Figure 1. (a) The principle of LIEF spectroscopy on sprays. (b) Potential energy diagram.

## Experimental

The experiments were carried out in room temperature at ambient pressure in a Cary Eclipse fluorescence spectrophotometer. The instrument consists of two Czerny-Turner monochromators (excitation and emission), a Xenon light source and two photomultiplier tubes as detectors. The Xenon flash lamp gives up to 80 flashes per second with a pulse length of approximately 2 to 3  $\mu$ s and a power of 60-75 kW. The measured fluorescence emission intensity is in arbitrary units. A reference signal was taken before the light entered the sample and was used to improve the signal to noise ratio of the measured intensity.

The liquid sample is placed in a 10 mm x 5 mm x 2 mm quarts glass cuvette for studying the fluorescence emission. The small width of the cuvette is to avoid extinction of the excitation light. The sample was scanned with excitation wavelengths from 190 nm to 550 nm in steps of 5 nm. A fluorescence emissions curve was detected for each step. In future work an Nd:YAG laser with a fundamental wavelength at 1064 nm will be used; for this reason only excitation light from two of the harmonics of the Nd:YAG are discussed in the results (266 and 355 nm). All the chemical mixtures reported here are on a mol percent basis. All chemicals were purchased from Sigma-Aldrich. To validate the instrumentation and techniques used in the room temperature measurement, we have compared fluorescence data from naphthalene, 1-metylnaphthlene, flourobenzene (FBZ) and N, N, N', N' -Tetramethyl-p-phenylenediamine (TMPD) with their respective fluorescence curves in [6].

#### **Results and discussion**

The major motivations for this analysis were to find two dopants with minimal fluorescence band overlap between the gas and liquid phase and dopant concentrations at which no or minimal monomer fluorescence occurs in the liquid phase, i.e. the concentration of the ground state reacting partner is sufficiently high so that, after reacting with M\*, there is no or a minimal monomer emission in the liquid phase. To get a picture of the behavior in the gas phase, each dopant was solved solely in the fuel and scanned to find the emission spectrum from different excitation wavelengths. In Table 1 the emission wavelength at maximum fluorescence from the gas phase can be seen together with the boiling point of the individual dopants and fuels. In this research we have examined gas/liquid visualization for both high boiling point fuels such as diesel and low boiling point fuels such as gasoline.

Table 2 shows the wavelength at which maximum fluorescence from the excited monomer,  $M^*$ , and the exciplex occurs for different mixtures. The values in the table are approximate since the emission is relatively broad banded. The reason for putting the molecules together as they are is that their boiling points agree fairly well, and the fact that the given concentrations give low  $M^*$  fluorescence in the liquid phase.

10 % of <b>dopant</b> solved in	Wavelength for max emission (nm)	Boiling point
the fuel	for dopants at	(°C)
the fuel	tor dopants at	$(\mathbf{C})$
	265 nm excitation	( at p=101,3 kPa)
		[7]
Fluorobenzene (FBZ) in Isooctane	290	85
Triethylamine (TEA) in Isooctane	290	89
TMPD in Hexadecane	400	260
N, N-Dibutylaniline in Hexadecane	350	271
1-Cyanonaphthlene in Hexadecane	420	299
1-Methylnaphthlene Hexadecane	350	245
Naphthlene in Hexadecane	340	218
Fuel		
Hexadecane	-	287
Isooctane	-	99
Dodecane	-	216

**Table 1.** Gas phase fluorescence from the different molecules. The emission wavelengths are clearly above the excitation wavelength, so that any problem with Mie scattering should be negligible.

Dopant 1	Dopant 2	Wavelength for max	Wavelength for	Approx.
		emission	(nm)	between M* and
		(nm)	exciplex	exciplex at 265
		M*		nm
				excitation
1%	9%	285	370	85
Fluorobenzene	Triethylamine			
1%	9%	395	480	85
TMPD	1-Methylnaphthlene			
1%	9%	340	380	30
N, N Dibutylaniline	Naphthlene			
2%	8%	330	475	145
1-Cyanonaphthlene	N, N-Dibutylaniline			
1%	9%	340	390	50
N, N-Dibutylaniline	1-Methylnaphthlene			
0.3%	12.75%	390	490	100
TMPD	Naphthlene			
0.3 %	12.75%	330	490	160
TMPD	Naphthlene			

**Table 2.** Fluorescence from different mixtures. The values are approximate since the emission is relatively broad banded. Excitation wavelength 265 nm. The reason for putting the molecules together as they are is that their boiling points agree fairly well. The concentrations chosen give low M\* fluorescence in the liquid phase.

# Low boiling point tracers

Isooctane, FBZ and TEA are the only substances representing fuel and dopants with low boiling points around 90°C, similar to gasoline, used in this study. However, Isooctane has a higher boiling point and a lower volatility as compared with the two dopands, which can cause problems in using these substances as gas and liquid trackers.

Isooctane shows no fluorescence in the excitation and emission scans. Both the dopants FBZ and TEA absorb at 265 nm and have a fluorescence peak around 290 nm, but they do not absorb or fluoresce with an excitation wavelength of 355 nm. An advantage of this red shift in fluorescence, in relationship to the excitation wavelength, is that directly scattered light from 265 nm can easily be removed with a filter so that no Mie scattering disturbs the two-phase visualization in work with the fourth harmonic of a Nd:YAG laser (266 nm) during spray studies. Since both molecules absorb at 265 nm and fluoresce around 290 nm it will be impossible to determine the molecule, FBZ or TEA; from which the fluorescence originates.

#### High boiling point tracers

Hexadecane is used as a high boiling point fuel. Of all the tested combinations it is only Naphthalene together with 1-Methylnaphthalene that do not exhibit exciplex formation. TMPD and naphthalene are perhaps the most famous monomer and ground state reaction partner used in LIEF. What speaks in favour of these dopants is the large band separation between the fluorescence from the two phases and that only TMPD fluoresces in the gas phase when the mixture has been excited with 355 nm, i.e. there is no confusion with one further fluorescing molecule, see Figs. 4 and 5. One problem with this combination of substances is that TMPD is difficult to solve, and small particles may thus remain in the fuel. These particles may obstruct the nozzle when the dopants are used in real spray experiments. A molecular mix with a high boiling point, which shows large fluorescence separation between the excited molecule M\* and exciplex, apart from TMPD and naphthalene, is 3% Cyanonaphthlene and 7% N, N-Dibutylaniline. At this concentration there is sufficiently much G to minimise the monomer fluorescence in the liquid phase. In a gas/liquid study, however, the ground state reacting partner, G, will absorb laser light in the gas phase and have a broad fluorescing band high up in the exciplex fluorescing band. M and G are represented in Fig. 3 by 10% N, N-Dibutylaniline and 10% Cyanonaphthlene in Hexadecane, respectively. One problem with these molecules when they are to be used in spray studies is that they both, as mentioned, absorb at the same wavelength as FBZ and TEA. This can cause laser extinction, for example, when penetrating in the spray.

Both 2% N, N-Dibutylaniline / 8% Cyanonaphthlene in Dodecane and the concentration shift to 2% Cyanonaphthlene / 8% N, N-Dibutylaniline in Dodecane establish an exciplex. The 2% N, N-Dibutylaniline / 8% Cyanonaphthlene peak is red shifted as compared with the 2% Cyanonaphthlene /8% N, N-Dibutylaniline peak, which indicates that the relationship M\*, G must have changed.

In mixtures in which Naphthalene and 1-Methylnaphthalene are used as M or G and an exciplex is formed at 355 nm excitation light, confusion as to where the fluorescence comes from can be avoided, since they do not absorb with 355 nm, which the other molecules used do. 1% TMPD and 9% 1-Methylnaphthlene in Hexadecane establish an exciplex, with a peak location around 480 nm with 355 nm excitation. Gas-phase overlap on the liquid phase complicates the use of these dopants, but proper selection of filters should give information about the two phases on two separate CCD cameras. The combination of N, N-Dibutylaniline and Naphthlene does not form an exciplex at 355 nm excitation wavelength, nor does N, N-Dibutylaniline and 1-Methylnaphthlene.



**Figure 2.** 1% FBZ and 9% TEA in Isooctane. Excitation wavelength 265 nm. The peak to the left of the exciplex is a monomer peak still present in the liquid phase.

**Figure 3**. 3% Cyanonaphthalene and 7% N, N dibutylaniline in Hexadecane. Excitation wavelength 265 nm. Note the large G\* fluorescence overlap into the exciplex fluorescence band.



**Figure 4**. View of excitation and emission transitions of the naphthalene and TMPD exciplex system. With 265 nm excitation wavelength, both Naphthlene and TMPD are absorbing but fluorescing at different wavelengths. An exciplex can accordingly be formed both with Naphthlene and TMPD as a M\*. When 355 nm excitation light is used, however, only TMPD is excited, and hence TMPD is the M\*.



**Figure 5.** Fluorescence from 0.3% TMPD and 12.75% Naphthlene in Hexadecane. The excitation wavelength is 265 nm. Compare with Fig 4.

**Figure 6.** Fluorescence from 0.3% TMPD and 12.75% Naphthlene in Hexadecane. The excitation wavelength is 355 nm. At this excitation wavelength only TMPD will absorb the radiation, see Figs. 4 and 5.

Even at these small concentrations of TMPD there is monomer fluorescence in the liquid phase.

# **Conclusions and outlook**

It has been found that Isooctane, FBZ, and TEA combine to make a suitable mixture for simulating gasoline sprays. This will for example be useful in future GDI studies. If diesel-like sprays are to be studied, the mixture of Dodecane, Cyanonaphtalene, and N, N-Dibutylaniline is a good choice. In the near future these mixtures will be used for applied LIEF studies of sprays in a high temperature/high pressure spray combustion chamber. We will also proceed with more fundamental studies, such as those presented in this report, where the temperature and pressure dependence of various mixtures will be examined.

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